Report.

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LIBERATION OF CHROMIUM AND VANADIUM FROM EAFC SLAG USING FURNACE ROASTING, SMALL SCALE LABORATORY TESTS

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ABSTRACT

The CHROMIC project was funded by Horizon 2020 from 2016 to 2020 to investigate the possibility of extracting critical elements such as chromium (Cr), vanadium (V), molybdenum (Mo) or niobium (Nb) from slag sources containing low amounts of these elements. The complete recovery process was investigated from pretreatment (microwaving and/or crushing), furnace or microwave roasting with an oxidising agent at a high temperature, leaching, extraction of targeted elements from the leachate through different extraction methods and possible utilisation possibilities of remaining material after extraction of targeted elements. The different treatment chains were evaluated based on their environmental imprint and economical feasibility. In this paper, part of the work dealing with the extraction of critical elements such as Cr and V from electric arc furnace carbon slag (EAFC) investigated through modelling and furnace roasting using NaOH as an oxidising agent is presented.

INTRODUCTION

The steel industry strives to achieve a zero waste goal through the utilisation of all materials resulting from the production of steel. Over the years, vast amounts of resources have been put into achieving this goal. In 2018, about 22.6 Mt of steel furnace slag was produced in Europe, of which more than 80% was utilised in various applications (e.g. cement, concrete, road construction, hydraulic engineering, fertiliser, metallurgical use, etc…) [1]. The slag is especially treated by steelworks to achieve desired chemical and physical properties to comply with needs for specific applications.

While the resulting slag is mostly calcium silicate, it contains different trace elements depending on the steel scrap and raw materials used in production as well as the desired steel grade. For example, about 2 wt% of Cr and 0.1 wt% of V can be found in the electric arc furnace slag resulting from carbon steel production (EAFC) [2]. In 2014, both Cr and V were considered critical raw materials by the European Union (EU), as they are mainly imported [3] (in the 2017 version of the critical raw materials list issued by the EU, Cr was removed [4], and in 2020, Cr was also not on the critical raw materials list [5]). In 2016, the H2020 project CHROMIC was started to develop a new process for recovery of valuable metals from sources (which might not currently be utilised) containing low amounts of the desired metals through leaching. The CHROMIC project dealt with complete treatment of different types of slag (from ferrous and ferrochrome production). Physical pretreatment of slag, traditional roasting and microwave roasting were investigated for their release of targeted elements, after which the slag was leached and different extraction methods were investigated to target the extraction of specific elements. The targeted elements were extracted with combinations of selective precipitation, solvent extraction, advanced sorbent materials and further processing to maximise the recovery. The extracted elements/compounds were evaluated for economic value. The leftover material (sludge) was investigated for environmental impact and possible uses to minimise landfilling. The whole process chains (taking into consideration different pretreatment, treatment and recovery technologies) were evaluated for environmental and economic feasibility. This paper presents part of the work that was conducted during the CHROMIC project, focusing on modelling of Cr and laboratory work to recover Cr and V from EAFC slag through furnace roasting of the slag in oxidising conditions. The optimal process was later tried on different slag types and on a larger scale (the results are not presented in this paper).

As the untreated EAFC slag does not leach Cr (due to spinel formation [6,5]) or V, an extensive process had to be elaborated to facilitate the release of these elements from the slag to change the mineralogy. The extraction of Cr and V was conducted through roasting of the slag at high temperatures (600°C–1000°C) with an oxidation additive (e.g. NaOH) to facilitate the leaching of these elements. Optimal roasting conditions were obtained for temperature, reagent type and amount through modelling and laboratory tests to release Cr and V from EAFC slag through leaching.

METHODS

Modelling

Thermodynamic equilibrium calculations were performed with the software FactSage® 5.3 on roasting of three types of chrome-containing slag with Na_2CO_3 (Soda), NaOH and $NaNO_3$ as additives. The aim was to determine which roasting additives and roasting conditions transform the stable chromium compounds into a leachable form. Generally, it is assumed that Na_2CrO_4 ((s) or (liq)) is the most leachable chromium compound.

The following parameters were used for the calculations:

- Amount of slag: 1 t;
- Amount of additive: 200 kg/t (20 wt%); (0 kg/t for comparison at $pO_2=1e^{-01}$ bar)
- Roasting temperature range: 500°C to 1200°C (step: 100 K)
- Oxygen partial pressure: $1e^{-01}$ bar (oxidising conditions, slightly lower than air); $1e^{-04}$ bar (slightly reducing conditions); $1e^{-08}$ bar (reducing conditions; only for soda)

Laboratory experiments

Work described in this paper has been conducted on a mixture of EAFC slag from a slag processor. A muffle furnace was used for the roasting tests. Small scale tests used 100 g of EAF slag per sample (grain size of 2–4 mm or < 1 mm), which were prepared without or with NaOH additive (0%, 1%, 5%, 10%, 20% or 40%) and placed in a cold furnace. NaOH was used due to its low price and better results compared with other partners in the project who used different additives. The furnace was heated up to the defined temperature (600°C, 800°C or 1000°C) for a specific amount of time (0 h, 1 h, 2 h, 3 h, 4 h, 6 h, 8 h, 22 h or 32 h). After the slag was heated up for a specific amount of time, it was taken out of the furnace and cooled inside the crucible (either MgO or Al_2O_3 ceramic crucibles were used). After the slag was cooled, the slag was homogenised and a sub-sample of 90 g was taken for leaching tests.

The chemical composition of Cr and V analysed was determined according to DIN EN 13656.

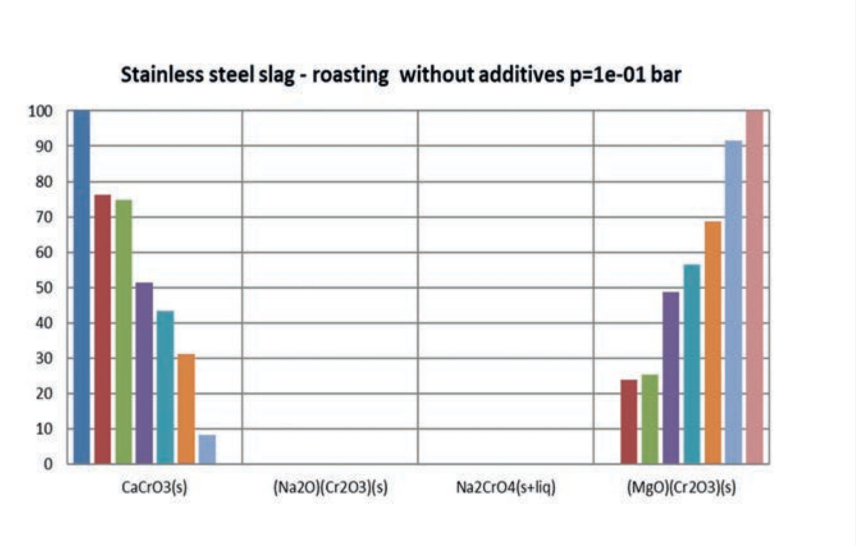

Figure 1: Modelling prediction of Cr distribution without additives in stainless steel slag (pO_2 = $1e^{-01}$ bar)

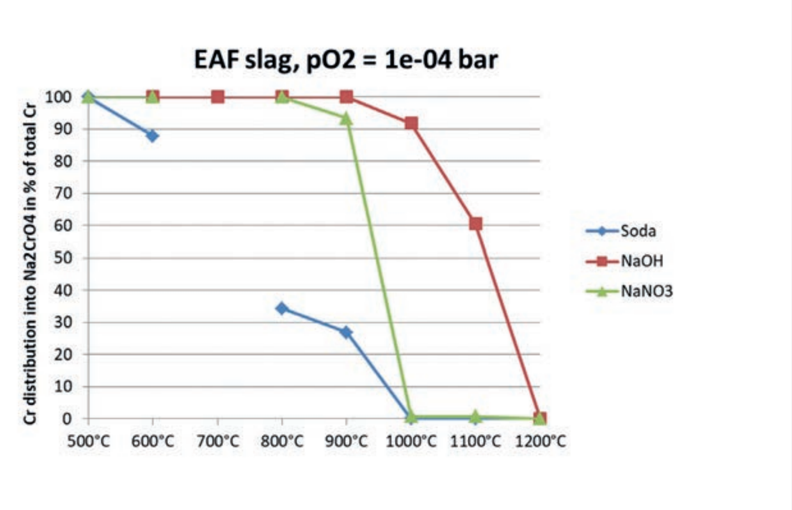

Figure 2: Chromium distribution into the leachable phase Na_2CrO_4 for EAF slag at various roasting temperatures with various additives at pO_2=$1e^{-04}$ bar

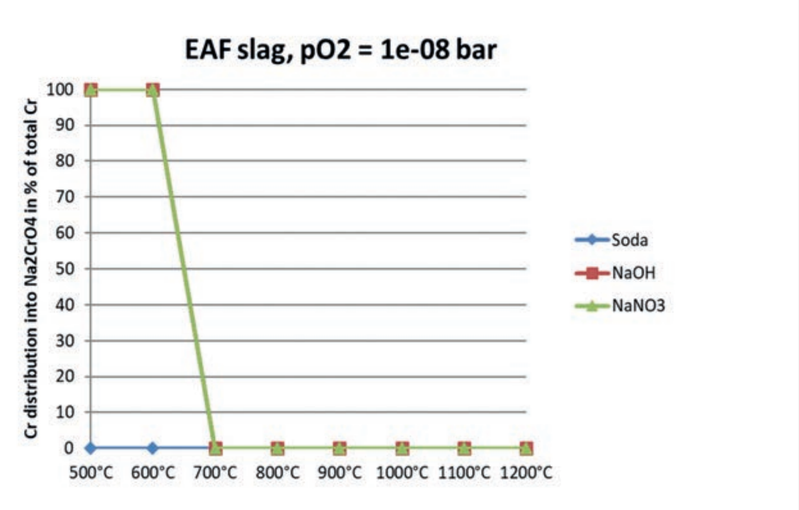

Figure 3: Chromium distribution into the leachable phase Na_2CrO_4 for EAF slag at various roasting temperatures with various additives at pO_2=$1e^{-08}$ bar

The leaching test used in this report is based on EN 12457-4 for a 1:10 slag-to-water ratio. The grain size of slag used was 2–4 mm or < 1 mm. The resulting leachate was analysed with ICP-OES (Varian Vista MPX and Spectro Ciros, with an analytical error of 3%) for Cr and V. After the roasting process with an oxidising agent, it was assumed that the available Cr that can be extracted was in the Cr(VI) form.

All results in this report are presented as a percent of the Cr that leaches out from total possible Cr in the original slag.

MODELING

The BFI has performed thermodynamic modelling of slag to predict at what temperature and with what additives Cr will leach from the slag. Thermodynamic modelling results show that the selected amount of additive in any case is sufficient for complete reaction of Cr in the slag. Without any additives, roasting of the stainless steel slag at oxidising conditions (pO_2=$1e^{-01}$) results in a chromium distribution mainly to $CaCrO_3$ at lower temperatures (100% Cr distribution at 500°C) with a virtually linear transition to the (MgO)($Cr2O_3$)(s) phase (100% Cr distribution at 1200°C) (Figure 1). Both compounds are assumed to be less leachable than Na_2CrO_4.

When using NaOH as an additive for roasting, at oxidising conditions (pO_2=$1e^{-01}$ bar) all the chromium is transferred to easily leachable Na_2CrO_4 at all temperatures. The same behaviour still applies at the lower oxygen partial pressure of $1e^{-04}$ bar (Figure 2). At an oxygen partial pressure of $1e^{-08}$

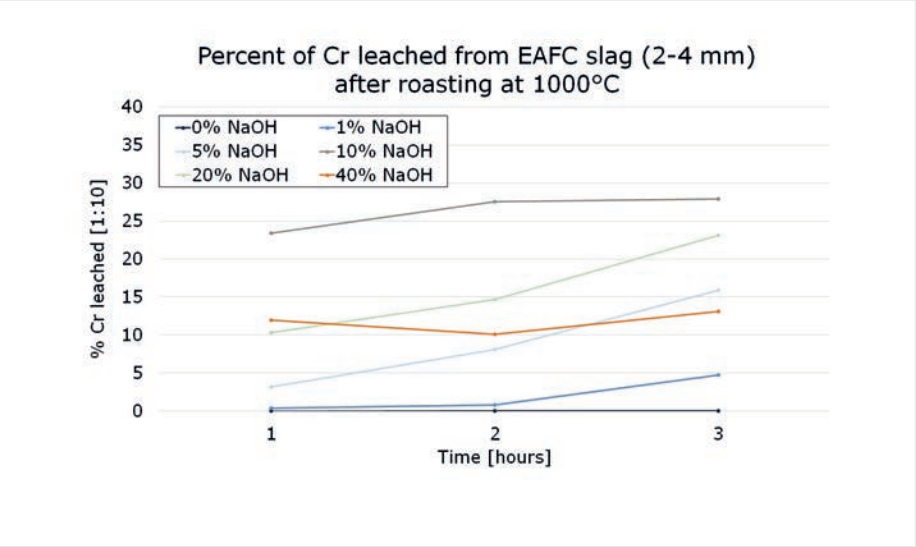

Figure 4: Percent of Cr leached from EAFC after different amounts (0 wt%, 1 wt%, 5 wt%, 10 wt%, 20 wt% and 40 wt%) of oxidising agent (NaOH) were added during roasting

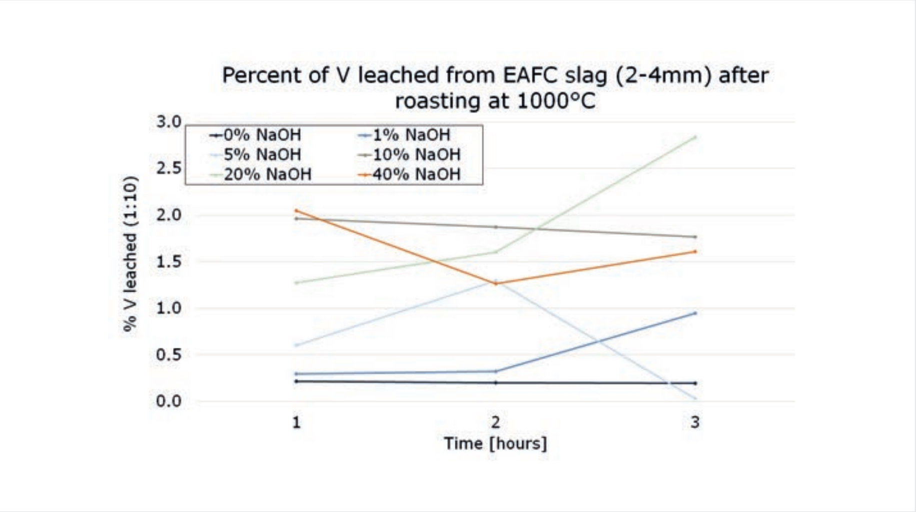

Figure 5: Percent of V leached from EAFC after different amounts (0 wt%, 1 wt%, 5 wt%, 10 wt%, 20 wt% and 40 wt%) of oxidising agent (NaOH) were added during roasting

bar, for NaOH only at low temperatures of 500°C and 600°C is the Cr fully distributed to the (leachable) Na_2CrO_4. At higher temperatures, the Cr is distributed up to 100% to non-leachable Na_2O and Cr_2O_3.

Generally, roasting at oxidising reaction conditions (oxygen partial pressure of 1e^{-01} bar) with sodium containing additives (soda, NaOH or NaNO3) promotes the desired formation of leachable chromium compound Na_2CrO_4. At lower oxygen partial pressures up to 1e^{-08} bar, soda as an additive performs comparatively worse, whereas NaOH and NaNO3 still deliver acceptable results at low roasting temperatures of < 700°C (Figure 3). A lower temperature from a thermodynamic point of view generally promotes Cr distribution into Na_2CrO_4. But here, also, kinetics play an important role, so that an optimum temperature for roasting can only be defined in roasting trials.

The calculations indicate that the contained chromium within the slag can more easily be transferred into a leachable form with the investigated additives for the ferrochrome slag and the stainless steel slag rather than the carbon steel EAF slag.

LABORATORY EXPERIMENTS

After the modelling and literature review, small scale laboratory experiments were conducted to find the optimal roasting procedure to release Cr and V from the EAFC slag [8]. The factors considered were the amount of NaOH added (which was chosen as the oxidising agent), time of roasting, temperature during roasting and slag grain size. From the untreated EAFC slag, less than 0.001% of the available Cr and 0.334% of the available V leached out in 1:10 leaching tests. After roasting of the slag at 1000°C for 1 h, 2 h or 3 h without an oxidising agent, the leaching of Cr and V was the same as in the untreated EAFC slag (Figure 1). This is due to the stable minerals these elements form in the slag.

The chemical composition of the slag is an average used in this report to calculate the efficiency of the process of liberating Cr and V. However, due to inhomogeneity of the slag, the exact values can vary [2].

Amount of NaOH added during roasting (1 wt% to 40 wt%)

Sodium hydroxide (1 wt%, 5 wt%, 10 wt%, 20 wt% or 40 wt%) was

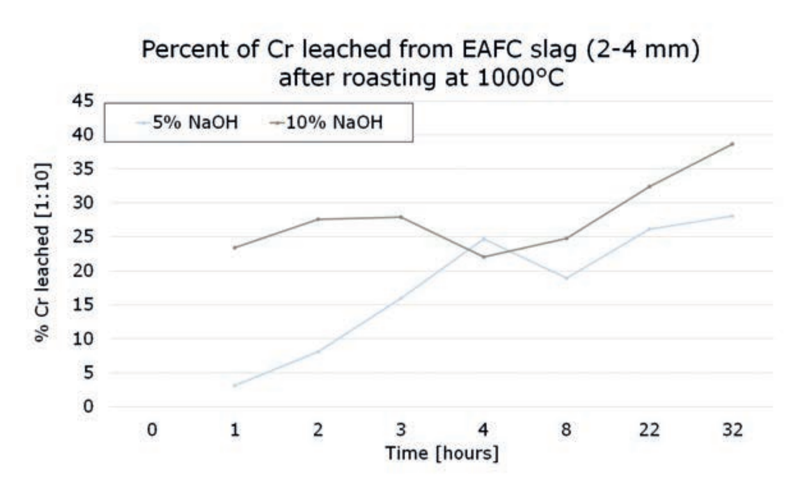

Figure 6: Percent of Cr leached from EAFC after roasting for 1 to 32 hours

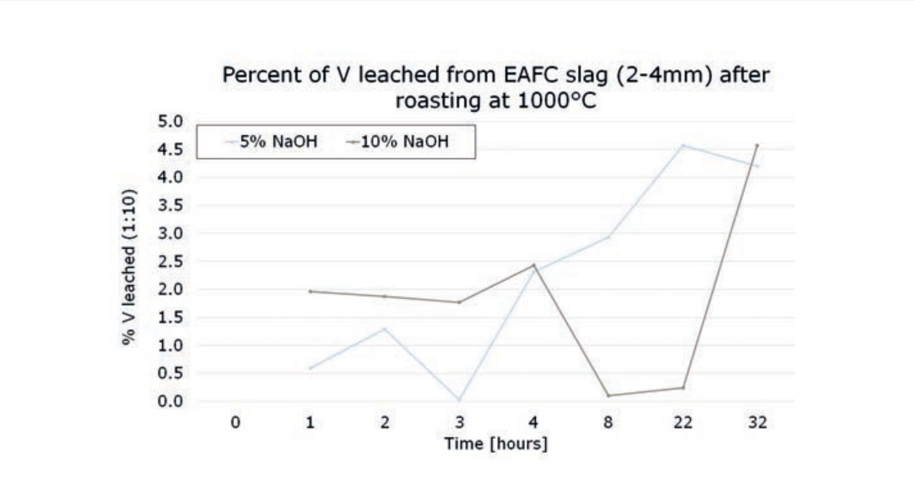

Figure 7: Percent of V leached from EAFC after roasting for 1 to 32 hours

added to the slag before roasting to create oxidising conditions and to facilitate the release of Cr and V during leaching. The additive was chosen based on its price and lack of interference in the metal extraction process after leaching. From modelling, it was estimated that with the addition of 40 wt% of NaOH, 100% of Cr can be released. However smaller values would be more practical.

With different amounts of additive, the results were not very straightforward (Figure 4). During a short roasting time of 1 to 3 hours, 10 wt% NaOH addition released the most Cr from the slag during leaching. 40 wt% NaOH addition showed a lower release rate than with 10 wt% or 20 wt% NaOH addition. This could be due to the high amount of additive blocking oxygen that is needed for the reaction between slag and NaOH to take place. The results are more difficult to interpret for V leaching, which could be due to the low percent of V to leach out (Figure 5).

Duration of roasting (1 to 32 hours)

The duration of roasting increases leaching of Cr slightly (Figure 6) and does not significantly increase leaching of V (Figure 7). For Cr, a higher addition of NaOH plays a more significant role than increasing the roasting time by 10% (increase of 15% Cr leaching from 1 h to 32 h of roasting). For a lower NaOH addition, such as 5 wt% NaOH, the time plays a more significant role (about 26% increase in Cr leaching from 1 h to 32 h of roasting). However, already after 4 h of roasting the leaching of Cr is about 25% of the total Cr in the slag and the longer roasting time (up to 32 h) increases the leaching by about 3%.

Due to the low percent of V leaching, while with an additional roasting time more V is leached out, the amount is insignificant to justify the increase of time.

Roasting temperature (600°C to 1000°C) and grain size of the slag (2–4 mm or <1 mm)

Three different temperatures were investigated, 600°C, 800°C and 1000°C, for the roasting of the slag. The temperature had a significant influence on the release of Cr and V from the slag. The maximum obtained release of Cr at 600°C was less than 15%, at 800°C was less than 35% and only at 1000°C was all of the Cr leached out (see Figure 8). Even though it is calculated that ~100%

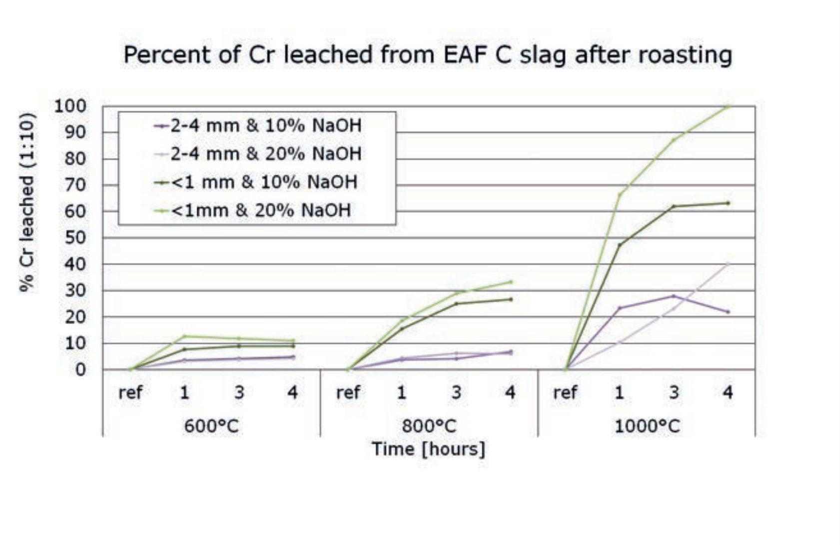

Figure 8: Percent of Cr leached after roasting tests (1:10 slag to water leaching)

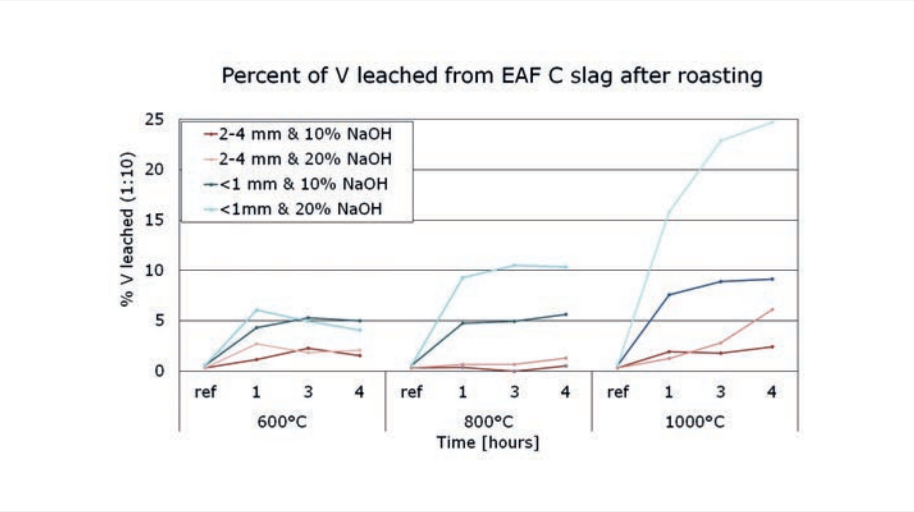

Figure 9: Percent of V leached after roasting tests (1:10 slag to water leaching)

of Cr is extracted, possibly not all Cr is extracted from the slag due to the inhomogeneous composition of the slag, and the resulting slag material after roasting and leaching can still contain small amounts of Cr that might require further treatment.

The maximum obtained release of V at 600°C was less than 7%, at 800°C was less than 15% and at 1000°C was less than 25% (see Figure 9).

The grain size of the slag had a significant effect on the release of Cr and V at a higher temperature, especially at 1000°C (Figures 5 and 6). After roasting at 1000°C with 20 wt% NaOH addition to slag <1 mm, 100% of Cr was released in the leachate.

Chemical composition of the slag before and after roasting

Slag after leaching was analysed with XRF for total composition and compared with untreated slag (Table 1). The slag was not "washed" after the leaching test to remove any excess elements that might have stayed on the slag as residue. The analysis was done to approximate how much Cr and V was removed from the slag; however, as slag is not homogenous this is an estimate. The heterogeneity of the slag and analysis was discussed in Horckmans et al. 2019 [2]. The recovery rate of Cr is different when looking at the total composition compared with only leaching amounts. The recovery rate of Cr based on the leaching of EAFC slag (<1 mm) with 20% NaOH and 4 hours of roasting was 100%, while the recovery rate from the total composition was 70%. For V, the recovery rate by looking at leaching or chemical composition is very similar (~25% and 33%, respectively).

SUMMARY

The extraction of Cr and V from EAFC slag is possible with roasting at high temperatures with an oxidising agent. The optimal conditions were determined for Cr but not for V.

The amount of NaOH added during roasting plays a significant role in changing the slag chemistry to release Cr during leaching. However, in the small-scale batch test, the addition of higher amounts of NaOH (40 wt%) hindered the release of Cr most likely because it covered the surface of the slag and prevented access to oxygen, which is necessary for the reaction to take place. The duration of roasting of the slag played a more significant role at a higher temperature (1000°C) and with a smaller grain size (<1 mm). The duration of the roasting also played a

Roasting temperature	Additive	Time	Grain size	Cr	Percent of total	Recovered amount	V	Percent of total	Recovered amount
°C	%	Hours	mm	wt%	%	g/kg of slag	wt%	%	g/kg of slag
0	0	0	–	2.23*	–	–	0.092*	–	–
1000	20	4	< 1	0.67	70	15.6	0.062	33	0,30

** analysis conducted with ICP*

Table 1: Total composition

role, but 4 hours was deemed sufficient to achieve the release of Cr. This might be reduced when other parameters are adjusted and/or better contact with air is assured so there is enough oxygen for the reaction to take place faster.

To extract Cr from the EAFC slag, the temperature should be 1000°C, the grain size of the slag should be <1 mm with the addition of 20 wt% NaOH, and roasting should be done for 4 hours. However, depending on the requirements, these parameters can be readjusted.

Further studies with different types of slag and larger amounts were also performed during the CHROMIC project (results not presented in this paper). After the roasting process, the slag was leached and further processes to extract Cr and V from the leachate were also developed in the CHROMIC project [9, 10].

ACKNOWLEDGEMENT

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VANADIUM IN ELECTRIC ARC FURNACE SLAG AND MEASURES TO MINIMISE ITS RELEASE INTO THE ENVIRONMENT

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INTRODUCTION

Electric arc furnace (EAF) slag from carbon steel production is a by-product of melting steel scrap in an electric arc furnace. The slag is generated by the addition of fluxes, such as limestone and/or dolomite. The liquid slag, which has tapping temperatures of around 1600°C, is air cooled in slag pits, forming crystalline slag.

EAF slag is mainly used as a building material in road construction and earthworks [1], which makes it an important substitute for natural resources, leading to significant minimisation of natural resource utilisation. For its use as a construction and building material, EAF slag must fulfill stringent technical and environmental requirements. For the assessment of environmental compatibility, leaching tests are used. Currently, in Germany, a batch leaching test with a liquid-to-solid ratio of 10 (L/S = 10) [2] is used for the assessment of the environmental compatibility of construction materials. In August 2023, a new nationwide regulation will enter into force (Ersatzbaustoffverordnung [3]), specifying the requirements for secondary construction materials. In this regulation, more testing parameters will be of interest and new leaching tests will be introduced (a percolation test, DIN 19528 [4] and a batch test, DIN 19529 [5]) with a liquid-to-solid ratio of 2 (L/S = 2) instead of 10. Based on the concentration levels in the eluates of the new leaching tests, quality classes for different applications have been defined. Vanadium is one of the new parameters that must be determined nationwide as soon as the new regulation comes into force. Based on the existing data, numerous types of EAF slag from German electric steelworks would not meet the requirements of the best quality class SWS-1 due to vanadium leaching. This may lead to restrictions so that these types of slag could no longer be used in sensitive areas, such as open, unbound road construction, without technical safety measures [6].

The release of heavy metals, such as vanadium, during weathering is known to be strongly dependent on the mineralogy of the slag. Various studies are available on the interactions between mineralogical composition and leaching [e.g., 7, 8, 9]. However, the exact mechanisms controlling the leaching of vanadium from electric arc furnace slag are still largely unknown.

The FEhS-Institute therefore launched a research project [10] that is presented here and where the influence of the mineral bonding of vanadium in electric furnace slag on the leaching behaviour was investigated in detail. Another aim of the project was also to use the newly acquired knowledge to find options for modifying the mineralogy of slag to increase the mineralogical binding of vanadium and thus to reduce its leaching. The metallurgical measures that were tested are additions of different additives to the liquid state of the slag as well as different cooling rates.

In total, eight different types of EAF slag were investigated concerning their chemical composition, mineralogy and leaching behaviour. For the mineralogical composition, both X-ray diffraction (XRD) and electron microprobe analysis (EMPA) were used. For the experiments to test possible metallurgical measures, one type of EAF slag was selected that shows particularly high vanadium concentrations in the eluate. With this slag, melting experiments were carried out on a laboratory scale.

CHEMICAL AND MINERALOGICAL CHARACTERISTICS OF EAF SLAG

The chemical composition determined by total microwave digestion of the selected EAF slag is presented in Table 1. Table 2 presents semi-quantitative data on the mineralogical composition of the EAF sample determined by XRD in its original state and after modification in a melting test. The main mineral phases in the original EAF slag sample are wuestite ((Fe, Mn,Mg)O) and larnite (β-Ca_2SiO_4). Further phases are spinel, brownmillerite ($Ca_2(Al,Fe)_2O_5$) and melilite (åkermanite-gehlenite series with the following composition: $Ca_2(Mg, Al, Fe)Si_2O_7$)). Larnite is a calcium silicate similar to minerals of the olivine group with the general composition $(Ca,Mg,Fe,Mn)_2SiO_4$. In EAF slag, other members of this mineral group can also occur, like kirschsteinite (CaFe SiO_4), bredigite ($Ca_7Mg(SiO_4)_4$) or calcio-olivine (γ-Ca_2SiO_4). In the analysed sample, only larnite was detected, which was also confirmed by the microprobe measurements. After modification of the slag in the molten state, however, other phases of this group were formed (see discussion below).

Using an electron microprobe, backscattered electron (BSE) images (Figure 1) and quantitative element analyses of the various mineral phases by wavelength dispersive spectrometry (WDS) were carried out. The mean vanadium contents of the individual mineral phases are listed in Table 3. In the original sample, spinel contained the highest content of vanadium (0.46 wt%). Also, in the remaining seven types of EAF slag in this project as well as in different previous studies (e.g. [11, 12]), spinel was found to be the main carrier phase for vanadium. However, the phases from the olivine group (larnite, bredigite, kirschsteinite) as well as melilite and brownmillerite are also able to incorporate vanadium in significant amounts.

FeO	wt%	31
CaO	wt%	27
SiO_2	wt%	14
MgO	wt%	8.6
MnO	wt%	6.2
Al_2O_3	wt%	6.0
CO_2	wt%	1.8
Cr_2O_3	wt%	1.7
TiO_2	wt%	0.54
P_2O_5	wt%	0.36
V_2O_5	wt%	0.22
BaO	wt%	0.13
SO_4	wt%	0.20
F	wt%	0.02

Table 1: Bulk chemical composition of the EAF sample

From the results of the semi-quantitative mineral composition (XRD) and the quantitative microprobe mineral analyses, the relative distribution of the total vanadium among the individual mineral phases can be calculated. The corresponding calculated values are given in Table 4. Spinel does not bind the main part of the total vanadium in the sample, although it has the highest vanadium content. About 40% of the total vanadium is bound in larnite, 29% is present in wuestite, while spinel contains only about 20% of the total vanadium.

Leaching tests were performed using one stage batch tests at a liquid-to-solid ratio of 2 l/kg (L/S = 2) [5] as well as 10 l/kg (L/S = 10) [2]. Two different grain sizes were used for the leaching tests: 0–32 mm and 1–4 mm. Table 5 contains concentrations of selected parameters in the obtained eluates. In the batch tests at L/S=2, significantly higher vanadium concent-

	Name	Formula	EAF	EAF modified			
			Original	Fast cooling	Slow cooling		
					No additives	Al_2O_3 addition	SiO_2 addition
	Wuestite	$(Fe_{1-x-y},Mg_x,Mn_y)O_z$	37	38	28	27	22
	Spinel	$(Fe,Mg,Mn)(Al,Cr)_2O_4$	10	2	16	22	15
Olivine A_2SiO_4*	Larnite	β - Ca_2SiO_4	35	13	26	21	-
	Bredigite	$Ca_{14}Mg_2(SiO4)_8$	-	32	-	-	-
	kirschsteinite	$CaFeSiO_4$	-	-	-	-	57
	Melilite	$Ca_2(Mg,Al,Fe)Si_2O_7$	8	7	29	28	5
	brownmillerite	$Ca_2(Al,Fe)_2O_5$	10	6	2	2	-

* A = Ca^{2+}, Fe^{2+}, Mg^{2+}

Table 2: Bulk mineralogical composition (wt%) of the EAF slag before and after treatment

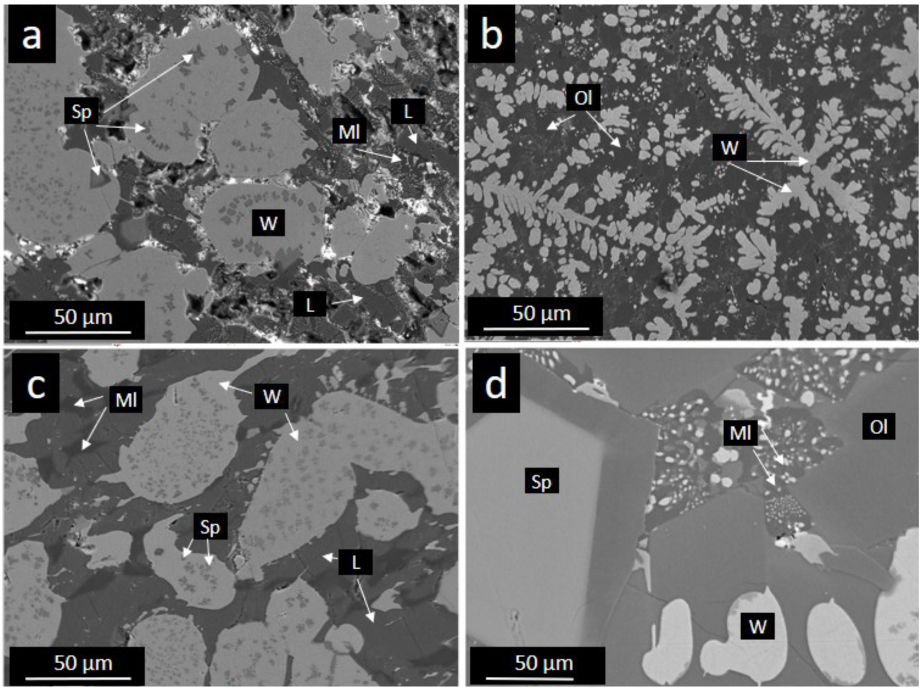

Figure 1: Backscattered electron (BSE) images of the EAF slag in original state (a) and modified by fast (b) und slow (c) cooling rate as well as by the addition of Al_2O_3 resulting in the formation of large spinel phases (d); W: wuestite, L = larnite, Ol = olivine, Sp = spinel, Ml = melilite

	Original	Fast cooling	Slow cooling	Al_2O_3 addition*	SiO_2 addition*
Spinel	0.47	0.27	0.29	0.30	0.47
Wuestite	0.19	0.10	0.08	0.17	0.10
Larnite	0.27	0.33	0.37	0.19	-
Bredigite	-	0.37	-	-	-
kirschsteinite	-	-	-	-	0.29
Melilite	0.15	0.36	0.31	0.36	0.31
Brownmillerite	0.16	0.20	0.36	0.18	-

** Slow cooling*

Table 3: V_2O_5-contents in the mineral phases of the investigated EAF slag before and after treatment

	Original	Fast cooling	Slow cooling	Al_2O_3 addition*	SiO_2 addition*
Spinel	20	2	18	26	27
Wuestite	29	16	9	18	8
Larnite	40	18	38	15	-
Olivine	-	50	-	-	59
Melilite	5	10	31	40	6
Brownmillerite	6	4	3	1	-

** Slow cooling*

Table 4: Percentage distribution of vanadium among the different mineral phases

rations are measured than in the test at L/S = 10. The SWS 1 limit value of the upcoming new Regulation (Ersatzbaustoffverordnung [3]) (180 µg/l) is clearly exceeded in the L/S= 2 leaching test for the 0–32 mm grain size, and using the 1–4 mm grain size, even the SWS 2 limit value of 450 µg/l is reached. With the L/S=10 test, the concentrations are lower, but the limit values of the still valid current regulation (TL Gestein-StB [13]) are still exceeded (SWS 1: 50 µg/l; SWS 2: 100 µg/l).

MELTING EXPERIMENTS ON A LABORATORY SCALE

For the melting experiments, the sample was crushed to a grain size of 1–4 mm. This narrow grain range was intended to ensure good comparability of the results by excluding effects due to different fine grain contents. In a first step, the impact of the cooling rate on the vanadium release was investigated. The sample was filled in a MgO-crucible with low porosity to prevent interaction with the slag, placed in the Tammann furnace, and heated up to 1600°C. The remelted sample was cooled with two different cooling rates. Fast cooling is achieved by pouring the liquid slag on a steel plate, which ensures rapid heat dissipation (100°C/min [14]). Slow cooling (20°C/min) takes place when the sample is left in the crucible inside the switched-off furnace.

In a second step, conditioning agents were added. Since spinel has been shown to be the main carrier of vanadium and since it is considered stable and insoluble in water, it was investigated whether the addition of Al_2O_3 (3 wt% in the form of bauxite) could increase

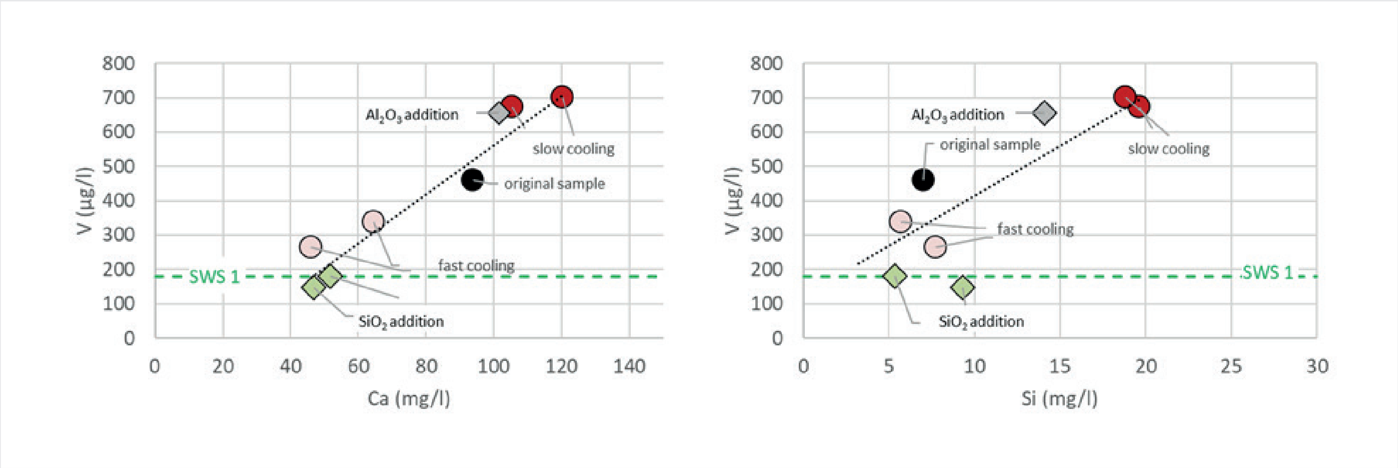

Figure 2: Correlation between vanadium (V) and calcium (Ca) as well as vanadium (V) and silicium (Si) in eluates of the EAF sample in the original slag and after treatments

		Batch test L/S=2:1		Batch test L/S=10:1	
Grain size		0–32 mm	1–4 mm	0–32 mm	1–4 mm
pH-value		11.0	11.6	11.4	11.4
Al	µg/l	6384	5516	2697	2621
Cr	µg/l	4.8	6.0	3.1	2.1
Fe	µg/l	15	2.9	47	4.0
K	µg/l	1164	1278	263	289
Mg	µg/l	134	132	401	353
Mo	µg/l	33	57	6.5	14
Ca	mg/l	77	92	40	50
Si	mg/l	8.4	7.3	12	12
V	µg/l	364	456	210	285

Table 5: Results from the leaching tests with the investigated EAF slag

vanadium-containing spinel formation and thus reduce vanadium leaching. Additional tests were carried out with the addition of SiO_2 (10 wt% in the form of quartz sand). The mixtures of slag and additive were melted in MgO crucibles and then cooled slowly, assuming that slow cooling simulates most closely the cooling conditions in pits in steel works. The resulting solidified samples were characterised chemically and mineralogically and the leaching behaviour was determined using a batch test at L/S = 2 [5].

The mineralogical compositions of the modified and solidified types of slag are listed in Table 2, the measured V_2O_5 contents of the individual mineral phases are given in Table 3, and the relative distribution of vanadium among the mineral phases can be found in Table 4.

Obviously, the cooling rate as well as the addition of agents resulted in changes to the bulk mineralogy of the sample. The relative amounts of the different phases vary, which influences the leaching properties of the sample. The results of the leaching tests are shown in Figure 2, where the Ca or Si concentrations measured in the eluates are plotted against the vanadium concentrations. Both, the slow cooling as well as the addition of Al_2O_3 led to an increase in vanadium release compared with the original sample. Despite the observed increase of spinel formation, vanadium release could not be reduced. In contrast, the fast cooling clearly resulted in lower vanadium concentrations in the eluate. The addition of SiO_2 was even more effective; the concentrations are below the limit value of SWS-1 (Figure 2).

Regarding the mineralogy, it can be observed that in the two samples with successful reduction of vanadium leaching, the mineral phase larnite was partially or completely replaced by other phases from the olivine group (Table 2). In the original sample the larnite content is 35%. In the fast cooled sample, only about 13% was detected, but an additional phase, bredigite, was formed (32%). In the sample that was treated with SiO_2, the crystallisation of larnite seemed to be totally suppressed, instead 57% of the phase kirschsteinite was formed. Table 4 shows that the vanadium content of these additional olivine phases is approx. 50% (bredigite) and 59% (kirschsteinite). The lower vanadium release in these treated samples can be explained by assuming a greater stability and lower solubility of these newly formed phases compared with larnite.

LEACHING MECHANISMS OF VANADIUM

As described above, in the original EAF slag sample, about 40% of the total vanadium was incorporated in larnite. The remaining 60% was distributed among other mineral phases, with spinel and wuestite hosting 20% and 29%, respectively. Compared with larnite, spinel and wuestite have been proven to be stable in other studies (e.g. [11]). Thus, it can be concluded that the vanadium concentration in eluates is primarily controlled by the dissolution of the larnite. The results of the melting experiments support this thesis, because the changes to the EAF slag resulted in lower crystallisation of larnite in favour of other less soluble calcium silicates, which led to significantly lower vanadium concentrations in the eluate. Also, the vanadium concentration in eluates of the modified sample (Figure 2) correlates with the Ca and Si concentrations. This observation represents further evidence that mainly larnite is responsible for the release of vanadium, as calcium and silicon are released simultaneously.

In summary, it can be concluded that calcium silicates in EAF slag are mainly responsible for the release of vanadium during leaching. The vanadium concentration of an eluate therefore depends on the actual distribution of vanadium among the different minerals and especially on the amount of the easily soluble larnite (Ca_2SiO_4). By adding SiO_2 (quartz) to the molten slag and thereby lowering the CaO/SiO_2 ratio, the mineralogy of the slag can be modified in such way that larnite formation is supressed in favour of more stable phases of the olivine group (such as bredigite or kirschsteinite). Such a transformation results in a significant reduction of vanadium release.

SUMMARY

The treatment of the EAF slag sample through the addition of SiO_2 (quartz) has proven to be effective in increasing the chemical bonding of vanadium. The efficiency of the treatment was experimentally demonstrated. However, the results described above so far refer to a single electric arc furnace slag sample. For verification reasons of the identified mechanisms, investigations of further types of electric furnace slag are necessary.

ACKNOWLEDGEMENTS

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CALCIUM SILICATE MASONRY UNITS MADE WITH METALLURGICAL SLAGS

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INTRODUCTION

From 01/09/2018 to 28/02/2021, the research association Kalk-Sand e.V. and FEhS-Institute successfully worked on the research project AiF 20268 „Utilization of metallurgical slags for the production of calcium silicate masonry units for increasing the constructional noise abatement"[1]. The project objective was to substitute natural heavy aggregates, such as basalt split, with different types of steel and other metallurgical slag (copper and ferronickel slag) and rutile sand for the production of calcium silicate masonry units with a higher apparent density and thus with higher noise abatement. The research association Kalk-Sand e.V. was mainly involved in the brick tests both on a semi-technical and a technical scale and with testing typical brick properties. The FEhS-Institute was mainly involved in slag characterisation, the evaluation of the environmental compatibility of the bricks and the materials (leaching), and the evaluation of the condensates resulting from the autoclaving process regarding their environmental properties and their corrosion potential.

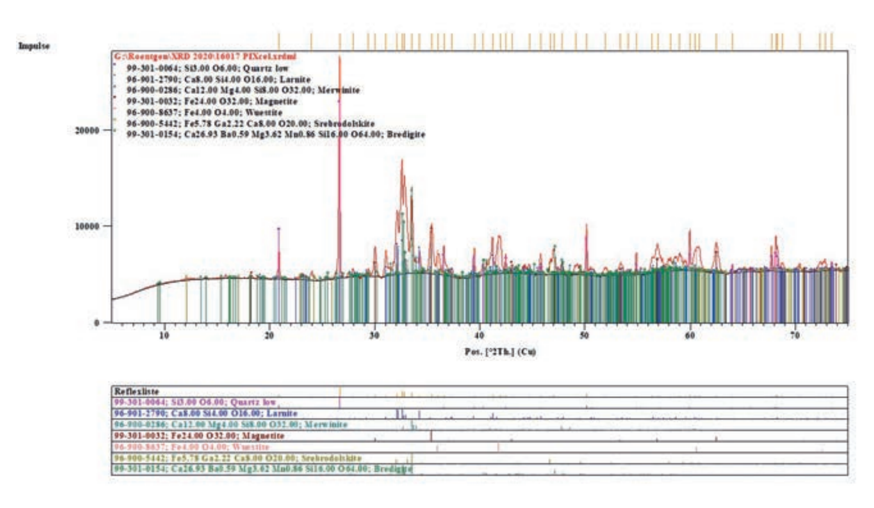

Figure 1: XRD diagram for BOF-1 (Technical scale test No. 2)

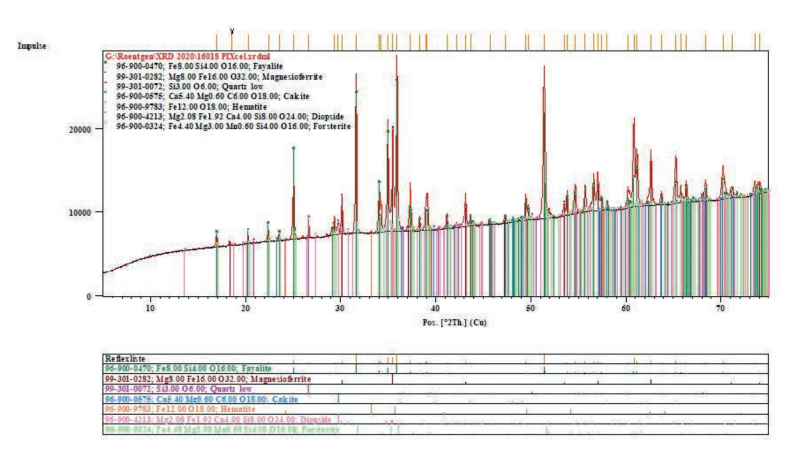

Figure 2: XRD diagram for COS-2 (Semi-technical scale tests)

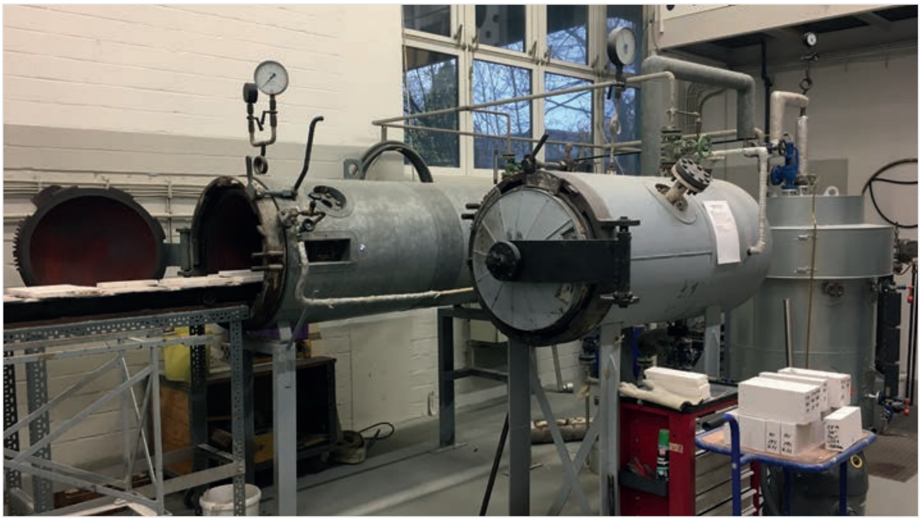

Figure 3: Semi-technical scale test facility of the research association Kalk-Sand e.V. in Hannover

Table 1 gives an overview on the chemical composition of the materials used in the project. According to the different metallurgical processes, the types of slag were very different regarding their chemical and mineralogical properties. Figure 1 and Figure 2 show two x-ray diffraction diagrams as examples.

For the selection of the two types of BOF slag, it was ensured that their free lime content was different. The EAF and BOF slag, copper slag No. 2 and the ferronickel slag were crushed, sieved (0–5 mm) and dried, whereas copper slag No. 1 and rutile sand were fine (< 0.2 mm) and moist due to their production processes (flotation). Both semi-technical and technical tests with EAF and BOF slag of 0–5 mm were not successful. Therefore, some additional tests were carried out on a semi-technical scale with coarse ground EAF and BOF slag ($d_{50} \approx 1$ mm).

TESTS ON A SEMI-TECHNICAL SCALE

Figure 3 shows the semi-technical test facility of the research association Kalk-Sand e.V.. According to earlier experiences, there is a good transferability of the results from the semi-technical scale tests to practice regarding the technical properties of the calcium silicate masonry units. 34 test series were carried out on a semi-technical scale, varying the type of aggregate, its share (0–40 wt%), in some cases its fineness, and the pressure during the forming process (12 and 14 N/mm²). The burnt lime content was regularly and uniformly 7 wt% and the pressing moisture was 5 wt%.

Application	EAF-1		EAF-2	BOF-1		BOF-2	COS-1	COS-2	FeNi S	Rutile sd.
	Semi	Practice	Semi	Semi	Practice	Semi	Semi	Semi	Semi	Semi
SiO_2	9.46	9.72	12.8	23.5	30.0	12.7	27.0	30.2	37.0	17.7
Al_2O_3	5.97	5.73	4.98	1.39	1.93	1.62	3.98	3.45	5.71	0.72
CaO	26.9	23.6	26.1	45.5	40.5	43.4	3.05	2.32	5.34	0.35
CaO_{free}	0.33	-	0.23	0.35	0.51	2.90	< 0.20	< 0.20	< 0.20	< 0.20
MgO	7.14	7.24	9.37	1.64	1.69	2.12	1.09	1.11	7.76	0.07
P_2O_5	0.35	0.33	0.34	1.61	1.48	1.33	0.07	0.12	0.02	< 0.02
TiO_2	0.36	0.36	0.77	0.78	0.73	0.60	0.37	0.26	0.25	78.8
Fe_{total}	26.7	29.3	28.1	15.2	14.4	21.8	41.4	40.1	27.6	0.08
Fe_{total}*	27.3	29.6	29.0	15.6	14.2	23.0	38.6	39.5	26.2	0.11
FeO*	17.0	22.0	28.7	10.9	9.16	7.62	37.4	42.2	33.0	n.b.
Fe_2O_3*	18.9	16.4	8.05	7.90	8.02	21.2	13.4	9.23	0.18	0.00
$Fe_{met.}$ *	0.90	1.00	1.02	1.58	1.50	2.26	0.11	0.22	0.44	n.b.
Mn_{total}	4.72	4.62	2.16	1.73	1.42	2.15	0.05	0.11	0.22	0.04
Cr_2O_3	2.41	2.73	1.27	0.24	0.19	0.61	0.03	0.08	2.77	0.15
Cr-VI [mg/kg]	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Na_2O	< 0.02	< 0.02	< 0.02	< 0.02	0.75	< 0.02	0.37	0.40	0.08	< 0.02
K_2O	< 0.02	< 0.02	< 0.02	< 0.02	0.20	< 0.02	1.04	0.85	0.59	< 0.02
S_{total}	0.21	0.16	0.10	0.05	0.05	0.11	0.08	0.20	0.14	0.02
Bound H_2O	0.99	0.50	0.05	0.08	0.47	1.39	< 0.03	< 0.03	< 0.03	< 0.03
Bound CO_2	0.97	0.58	0.18	0.42	0.48	0.79	0.04	0.07	0.16	0.85

** separate Fe analyses*

Table 1: Chemical composition of the slags for tests on a semi-technical and technical scale in wt%

Beside the apparent density of the aggregate itself, the pressure and the pressing moisture, it is the packing density of the aggregates that is an essential parameter for producing bricks with an increased apparent density [2]. Thus, in a first step, the packing density $\Phi_{Comb.}$ of the different raw mixtures was calculated. This was the basis for a first estimation of whether the different combinations might result in bricks with an increased apparent density. The packing densities Φ_{own} of quartz sand 0–2 mm and basalt split 2–5 mm (56.8 vol% and 59.9 vol%, respectively) were typical for natural aggregates used for calcium silicate masonry unit production. From all industrial aggregates, the fine rutile sand had the maximum and a very high packing density. But for the metallurgical slag also, relatively high values between 57.1 vol% and 62.3 vol% were calculated. Differences in the packing density ≤ 2 vol% are not presumed to be significant, whereas differences ≥ 5 vol% are considered to be significant.

By combining the different industrial and natural aggregates, relatively high maximum packing densities $\Phi_{Comb.}$ were theoretically calculated between 64.9 vol% (COS-1, COS-2, ferronickel slag) and 84.0 vol% (rutile sand). Thus, at least from a theoretical point of view, the basis was provided to achieve high apparent densities of the bricks with improved noise abatement.

Figure 4 shows an example of the result of the packing density calculations by using BOF-1 (0–5 mm). It can be seen that by substituting natural aggregates with 60 wt% BOF-1 and based on a ratio of 90 wt% sand 0–2 mm to 10 wt% split 2–5 mm, a maximum packing density of 65.2 vol% might be possible. This value corresponds more or less with the maximum resulting from using only natural sand and

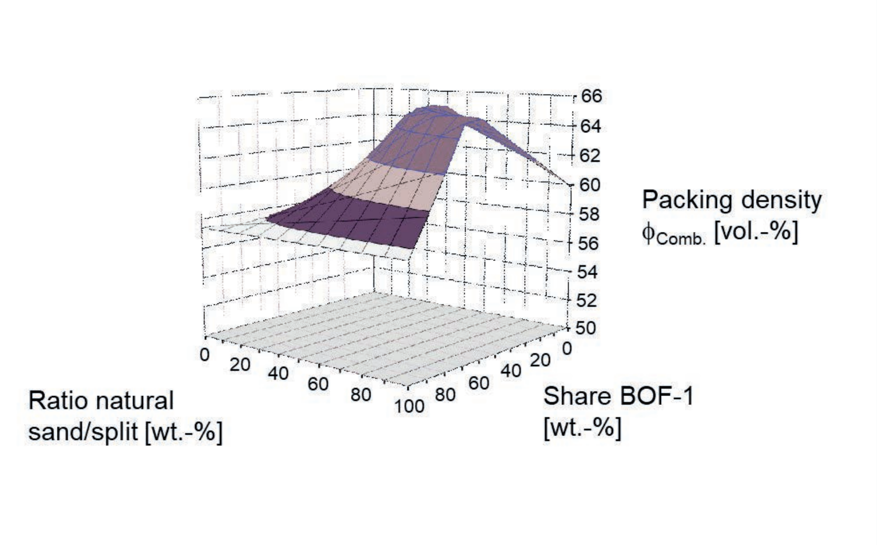

Figure 4: Result of the packing density calculations for mixtures of BOF-1 (0–5 mm), sand (0–2 mm) and basalt split (2–5 mm)

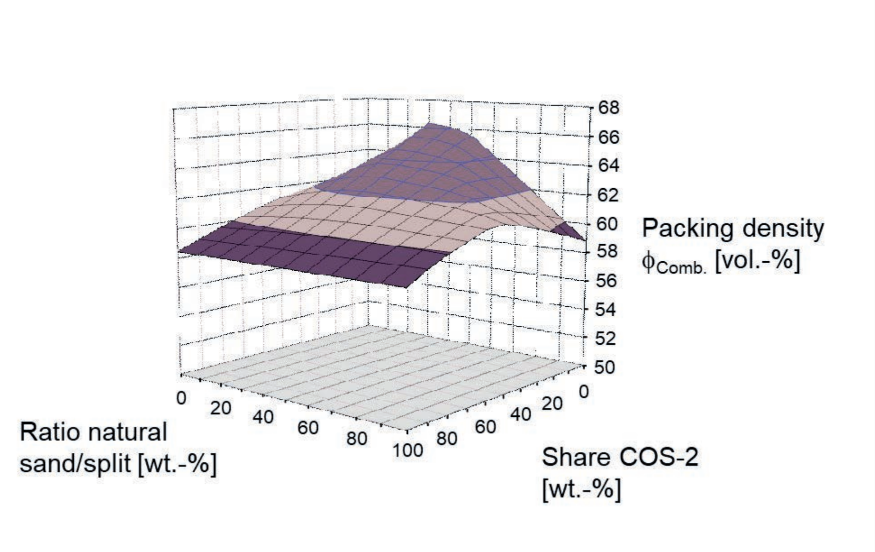

Figure 5: Result of the packing density calculations for mixtures of COS-2 (0–5 mm), sand (0–2 mm) and basalt split (2–5 mm)

split (64.9 vol% for a sand/split ratio of 40/60). The minimum packing density using 10 wt% BOF-1 would be 56.9 vol%.

In addition, Figure 5 shows the result of the calculations using COS-2 (0–5 mm). It can be seen that by substitution of the natural aggregates with 40 wt% COS-2 (which was later realized on a semi-technical scale) and based on a sand/split ratio of 75/25, a maximum packing density of 61.0 vol% is theoretically possible. This corresponds more or less with the value resulting from the exclusive use of natural aggregates (62.0 vol% for a sand/split ratio of 75/25).

To produce calcium silicate masonry units with increased apparent density, it is not sufficient to achieve a maximum packing density. Moreover, considering the production process, it is necessary to consider the mixing, compacting and venting behaviour of the aggregate mixtures. Regarding the aggregates themselves, a high apparent density of the bricks requires a maximised content of industrial aggregates. For that reason, it was not possible to adjust a combination that results in the maximum theoretical packing density Φ_{Comb} for every test.

For the tests on a semi-technical scale, the share of basalt split (20 wt%) and in some cases also the share of sand (80 wt%) was substituted step-by-step with industrial aggregates in different dosages (10 / 15 / 20 / 30 / 35 / 40 wt%). In doing so, the substitution rate was chosen in such a way that the industrial aggregate was used as much as possible, that a sufficient mixing behaviour of the lime-sand-aggregate mix was secured and that stable bricks were produced with a sufficient green strength. Thus, for each aggregate, the addition had to be adjusted individually according to the practical workability of the mixtures. By using the coarser slag, it was possible to substitute not only the whole split but also a part of the sand (e.g. with COS-2), whereas with the finer industrial aggregates, it was only possible to substitute maximum 10 wt% of the split (e.g. with COS-1, rutile sand or coarse ground BOF/EAF slag). With increasing amounts of fine aggregates, it was increasingly difficult to ensure sufficient venting of the lime-sand-aggregate mix during the brick forming process.

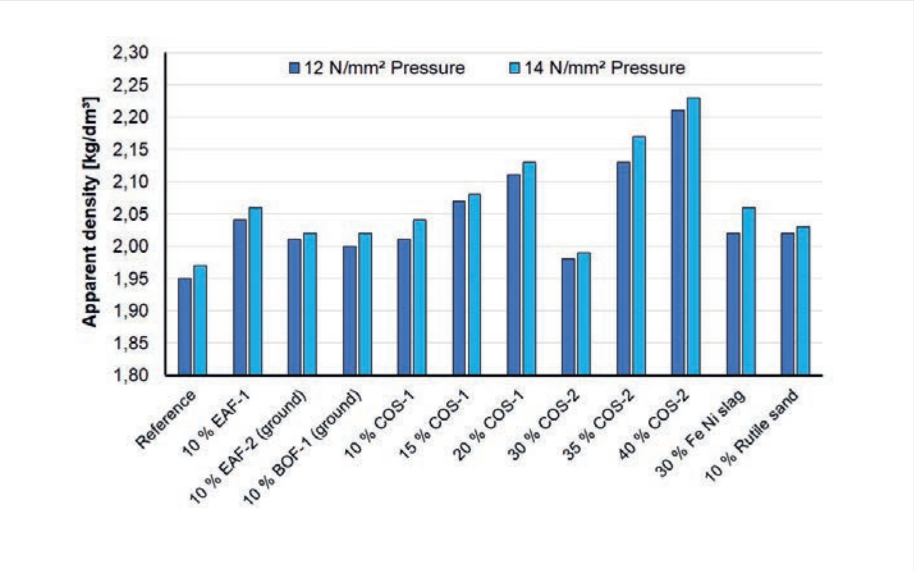

Figure 6: Apparent densities of the calcium silicate masonry units depending on type and share of the industrial aggregates and the pressure

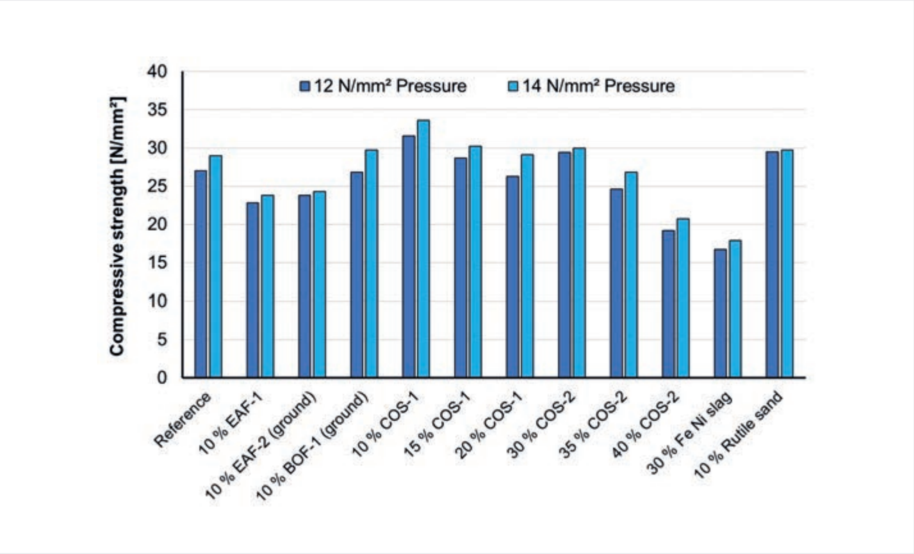

Figure 7: Compressive strength of the calcium silicate masonry units depending on type and share of the industrial aggregates and the pressure

Different physical parameters have been tested using the calcium silicate masonry units produced on a semi-technical scale and with the dimension „KS-DF" (24 cm x 11.5 cm x 5.2 cm). However, at this point, only the apparent density and the compressive strength of the bricks will be discussed. They are the most relevant quality parameters and are used for classification [3].

Figure 6 and Figure 7 show the values of the apparent densities and the compressive strength of the bricks depending on the type and share of the used aggregates and the pressure during the forming process. The burnt lime content CL90 (i.e. for the production of calcium silicate masonry units: CaO + MgO ≥ 90 wt% and MgO ≤ 1.5 wt%) was consistently 7.0 wt% for all mixtures.

The apparent densities were partially improved clearly by the substitution of natural aggregates with metallurgical slag. The apparent density classes 2.0 and 2.2, defined in DIN EN 771-2 [3] (= oven-dry density 1810-2000 kg/m³ and 2010-2200 kg/m³, respectively), were correctly achieved. In a particular case (40 wt% COS-2), even the highest apparent density class 2.4 (> 2200 kg/m³) was fulfilled. Thus, the primary research task of the project – the increase of the apparent density of the bricks without any technical disadvantages – was achieved.

The increase of the pressure from 12 N/mm² to 14 N/mm² resulted only in a slight increase in the density values.

The compressive strengths of the bricks were in the range of typical calcium silicate masonry units of the classes 12, 16, 20 and in a single case 28 (= normalised compressive strength in N/mm² [3]). In practice, the classes 12 und 20 are the most relevant ones [4]. In most cases, at lower substitution rates with metallurgical slag, the strength requirements were fulfilled or exceeded compared with the reference. With higher substitution rates, reduced strengths have also been measured. Nevertheless, the compressive strength values were still at such a level that they were able to correctly fulfil the strength classes 12 to 20.

With the increase of the pressure from 12 N/mm² to 14 N/mm², only slightly higher compressive strengths have been achieved.

The ratio of flexural strength to compressive strength was about

Figure 8: Damage-free calcium silicate masonry units from tests on a semi-technical scale with COS-1 (10 wt%), COS-2 (35 wt%), rutile sand (10 wt%) and coarse ground BOF-1 (10 wt%); from top left to bottom right

1:10 to 1:12, which is within the typical range for calcium silicate masonry units.

Figure 8 shows some of the bricks with promising properties produced on a semi-technical scale. This means that at least comparable, although in most cases higher, apparent densities were achieved and the strengths were not impaired and no scaling occurred on the brick surfaces.

TESTS ON A TECHNICAL SCALE

During the project, three tests on a technical scale were carried out in two plants with different industrial aggregates. Due to a project delay resulting from the pandemic situation and required repair work for the semi-technical facility, a lot of tests were carried out later than they were originally planned. Thus, the first two tests on a technical scale had already been carried out in 2020 with steel slag before the results of the semi-technical scale tests were available. EAF-1 and BOF-1 were applied in staged shares substituting both the basalt split and a part of the sand. Regarding their chemical and mineralogical properties, the material batches used for these tests corresponded with the batches for the tests on a semi-technical scale (see Table 1). The brick production was without any difficulties and both the dimensional accuracy and the green strength fulfilled the requirements. However, after the autoclaving process (≈ 19 h, max. 194°C, 13 bar and ≈ 7 h, max. 203°C, 16 bar, respectively), a lot of scaling occurred on the surfaces of the bricks (Figure 9). On closer inspection, slag grains were identified consistently at the center of the scaling (Figure 10). The mode of failure was the same for EAF-1 and BOF-1 (Figure 11) despite the significant differences of the chemical and mineralogical slag properties. The concrete cause of damage still could not be identified. A reaction of free lime with $Ca(OH)_2$ might be possible to rule out due to the low free lime content (see Table 1). Moreover, before the brick forming process, the raw material mix is stored together with the burnt lime and water in a reactor for about 1.5 hours. Thus, free oxides would have time to react. No periklase was identified by XRD for EAF-1 nor for BOF-1. However, XRD of the white powder taken from the

Figure 9: Calcium silicate masonry units made with BOF-1 before (left) and after (right) the autoclaving process in the technical scale test No. 2

Figure 10: Damaged spot of a calcium silicate masonry unit made with 43 wt% BOF-1 after the technical scale test No. 2

Figure 11: Calcium silicate masonry units made with EAF-1 after the technical scale test No. 1

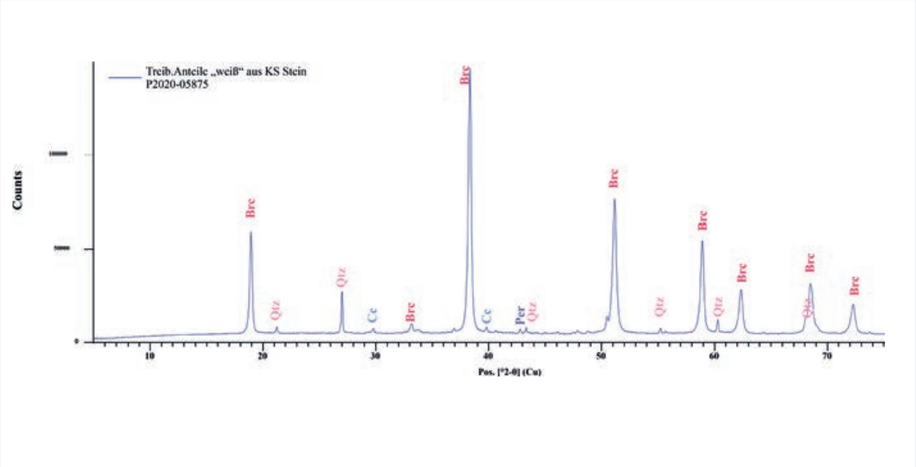

Figure 12: XRD of white powder taken from damaged spots of calcium silicate masonry units made with 43 wt% BOF-1 after the technical scale test No. 2

damaged spots of the bricks made with BOF-1 clearly identified $Mg(OH)_2$ (brucite), Figure 12. Beside free oxides, a different thermal expansion behaviour of the steel slag compared with the CSH matrix of the bricks might also be a potential cause of damage. However, initial trials to measure the thermal expansion coefficient with drill cores from coarse steel slag failed due to the failure of the samples (Figure 13). The very low content of residual metal may also play a role, which is concentrated in a few

Figure 13: Damaged 5 cm drill core made from BOF-1 after the thermal expansion test

Figure 14: Magnetic BOF-1 grain from a damaged calcium silicate masonry unit made on a semi-technical scale

Figure 15: Damaged calcium silicate masonry units with 10 wt% BOF-2 made on a semi-technical scale

Figure 16: Damage-free calcium silicate masonry units made with COS-2 in technical scale test No. 3 with different substitution rates of the natural aggregates

slag grains. During tests on a semi-technical scale, it was observed that BOF-1 grains in the center of damaged spots were magnetic (Figure 14).

The semi-technical scale tests generally confirmed the negative experiences of the technical scale tests with steel slag (Figure 15). However, it was shown that after grinding the slag to a low fineness (about 55 wt% < 1 mm), calcium silicate masonry units could be produced without scaling (Figure 8, lower right). Unfortunately, during the project period, it was not possible to verify this positive result in a technical scale test.

Based on very positive results in semi-technical scale tests, two additional tests on a technical scale with COS-2 and rutile sand are planned for 2021. However, it was impossible to carry out a test with rutile sand because it was not possible to dose the material due to its very high moisture content of about 20–25 wt%. It is perhaps possible to consider whether drying of the material might be an option. On the other hand, with COS-2, the test on a technical scale was carried out without difficulty. The natural aggregate consisting of sand 0–2 mm and basalt split 2–5 mm (= 100 wt%) was substituted in different shares up to a maximum 45 wt%. The bricks with the format KS-R(P) 20 – 2.0 6DF (175) were formed and compacted without any problems. After the autoclaving process, they did not show scaling and they possessed good technical properties. For example, with the maximum content of 45 wt% COS-2, the apparent density of the bricks increased from 1.81 kg/dm³ to 2.08 kg/dm³ and their compressive strength increased from 32.7 N/mm² to 36.8 N/mm². At the same time, the burnt lime content could be reduced by 13%. This is positive not only due to cost reasons but it reduces also the CO_2 footprint of the calcium silicate masonry units dominated by the upstream chain of the burnt lime. A darker colouration of the bricks was visible only on a very limited scale despite the utilisation of the dark copper slag (Figure 16).

ENVIRONMENTAL COMPATIBILITY

The environmental compatibility of the calcium silicate masonry units made with matallurgical slag has mainly been evaluated on the basis of the chemical constituents leached under defined conditions (tank test acc. to DIN CEN/TS 16637-2 for 64 days). Due to the high temperature processes from which the slag results, organic constituents are not of interest but released heavy metals are. The test results have been compared for compliance with the requirements defined in the ABuG [5], which are valid in Germany for concretes made with industrial aggregates and in contact with water. Compared with bricks made with natural aggregates, the use of the different industrial aggregates did not result in a systematic increase of the heavy metals content of the leachates. For the bricks with natural aggregates and as a rule also for the bricks with industrial aggregates, the measured release rates in mg/m² were in magnitude order below the limits of the ABuG. Only for a single brick was there an exceeding of the vanadium limiting value, which is still currently specified in the ABuG. Only after the utilisation of 10 wt% of the fine COS-1 – which is not produced in Germany – were 3 limiting values exceeded. However, the leachates of bricks made with 30 wt% or 40 wt% COS-2 from Germany clearly underrun all limiting values.

Moreover, for COS-2, the leachate concentrations were significantly lower with a substitution rate of 40 wt% instead of 30 wt%. This corresponds with a higher packing density of the raw material mix (64.7% instead of 61.3%). The limited lower capillary porosity of bricks (15.7 vol% instead of 16.5 vol%) seems to be of less importance. The comparison of the leachates for bricks containing 10 wt% and 20 wt%, respectively, COS-1, shows that the release also decreased with the higher dosage. This corresponds again with the higher calculated packing density (66.7% instead of 62.0%) whereas the capillary porosity was more or less constant (17.1 vol% instead of 16.8 vol%).

Based on the positive technical results for bricks made with coarse ground EAF-2, these bricks were also leached. The grinding did not cause a systematic increase in the heavy metals release compared with bricks made with unground EAF-2. The use of 20 wt% coarse ground BOF-1 instead of 10 wt%

Figure 17: Some of the bricks made on a semi-technical scale for the tank leaching tests and corresponding condensates from the autoclaving process

also changed the leaching behaviour only on a limited scale.

In addition to the leaching tests with bricks, the industrial aggregates themselves (crushed material < 10 mm) were also leached according to the batch test defined in DIN EN 12457-4 (w/s = 10:1, 24 h). For the evaluation of the results, the limiting values can again be used alternatively and are defined in the ABuG for different industrial aggregates [5]. No systematic exceeding of the limiting values was observed for any of the industrial aggregates.

CORROSION BEHAVIOUR

Because it was known from the former utilisation of granulated blast furnace slag for the production of calcium silicate masonry units [6, 7] that intensified corrosion of the autoclaving facilities might occur, the condensates generated during the autoclaving process were collected (Figure 17). These condensates were analysed both for their corrosive impact on steel and concrete structures and their environmental compatibility (heavy metals content). In summary, it can be concluded that using metallurgical slag instead of natural aggregates (basalt split and sand) results in no increase in the corrosion potential. The heavy metals content of the condensates clearly underrun all limiting values defined in different German regulations for the discharge of waste water, e.g. in [8, 9].

SUMMARY

Extensive investigations of calcium silicate masonry units produced both on a semi-technical and technical scale could show that it is possible to substitute natural heavy aggregates, e.g. basalt, with industrial aggregates with a higher apparent density, e.g. copper or ferronickel slag, without impairing the physical properties of the bricks. Depending on the type and share of the aggregate, the apparent density and the compressive strength of the bricks are increased. Moreover, in some cases a reduction of the cost and CO$_2$ intensive burnt lime dosage was possible.

Both in semi-technical and in technical scale tests during the autoclaving process, BOF and EAF slag of 0–5 mm caused scaling on the brick surfaces independent of their content of free oxides. However, the structural conditions of the bricks and therefore also their strength were not impaired. After a coarse grinding of the steel slag (d$_{50}$ ≈ 1 mm), calcium silicate masonry units could be produced free from defects, at least on a semi-technical scale.

The utilization of fine grained and at the same time very moist aggregate < 0.2 mm (one of the types of copper slag and rutile sand) was indeed possible on a semi-technical scale. But problems arose in practice, e.g. regarding dosage and storage. At this point, pre-conditioning of these aggregates is necessary (drying and de-agglomeration, where necessary) in order to technically make use of their advantageous properties.

The analyses of the leachates of bricks made with industrial aggregates confirm that the environmental compatibility of the calcium silicate masonry units is ensured. This is also the case for the condensates generated during the autoclaving process. No corrosive impact of these condensates is detectable.

The project results open up a new market for different types of metallurgical slag, in particular for copper and ferronickel slag. For the producers of calcium silicate masonry units with an increased constructional noise abatement, some alternatives could be identified for the use of natural aggregates as could some cost reduction potentials.

Open questions remain to be answered regarding the cause of damage after the use of unground steel slag (popouts) and the technical potential after a coarse grinding of these types of slag. Moreover, the question should be pursued as to whether the utilisation of industrial aggregates might also enhance other, e.g. thermal, properties of the bricks besides the brick properties already characterised in the finished project.

ACKNOWLEDGEMENT

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INCLUSION OF FERROUS SLAG IN THE NEW EUROPEAN FERTILISER PRODUCT REGULATION – AN INTRODUCTION TO THE NEW LEGISLATION AND AN OVERVIEW ON THE CURRENT STATE OF IMPLEMENTATION

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The new European Fertiliser Product Regulation (FPR, Regulation EU No. 2019/1009) is laying down rules on making fertilising products available to the internal market. Although this regulation has been in force since 2019, it will become applicable from 17th July 2022. Compared with the present regulation EC No. 2003/2003, which focuses on mineral fertiliser and some liming products, the FPR was designed to promote a circular economy by improving the marketability of recycled nutrients and thus reduce dependency on imports of limited raw materials such as rock phosphate. To achieve this goal, organic fertilisers and organo-mineral fertilisers have been included in this regulation as well as liming materials, soil improvers, substrates, bio-stimulants and inhibitors. This broad range of fertilising products requires comprehensive rules to cover all aspects of quality, efficacy, and transparency as well as new harmonised standards to ensure a safe and environmentally-friendly use of the products. Most of these requirements have been fixed in the annexes while the more general provisions and obligations for manufactures and economic operaters are layed down in the regulation itself. Meanwhile, the harmonised standards are to be drawn up by CEN.

First of all, Annex I defines the seven so-called Product Function Categories determining the application of the product (PFC 1. fertiliser, PFC 2. liming material, PFC 3. soil improver, PFC 4. growing media, PFC 5. inhibitors, PFC 6. plant biostimulants, and PFC 7. fertilising product blends) as well as minimum nutrient contents for each sub-category. In addition, each PFC sets up the respective limits for contaminants in the final product.

Annex II describes the criteria for the input-material's origin, i.e. annex II relates the FPR to other regulations and directives (e.g. waste directive) and refers to criteria from these regulations and directives. So far, ten so-called Component Material Categories (CMC) are in force; four additional are in the elaboration process. Most of the fertilising materials that had been marketed according to regulation 2003/2003 now fall under CMC 1 "virgin material substances and mixtures" except for by-products in the sense of the waste directive (Directive 2008/98/EC). The four new CMCs are to define criteria for by-products such as ferrous slag from steel production (CMC 11), precipitated phosphate salts and derivates such as struvite (CMC 12), thermal oxidation materials and derivates such as ashes (CMC 13), and pyrolysis and gasification materials such as biochar (CMC 14). While most of the new CMCs are to be adopted soon, the work for CMC 11 on by-products is to be finished soon.

The Commission authorised the JRC (Joint Research Center of the EU Commission) to develop a list of substances that fall within the scope of CMC 11 by-products, as well as criteria for component safety and agronomic efficiency. On 14th June 2021, the JRC submitted its "By-Product Interim Report" on the preparation of CMC 11. The interim report proposes to split off high-purity materials such as ammonium sulphate from caprolactam production into a separate CMC and to apply CMC 11 only to by-products of lower purity. The remaining materials are grouped according to their origin. In addition to those limits for contaminants established in the Product Function Categories, group-specific environmental safety parameters are proposed. For the group of ferrous slag, these are limits for the total content of the elements chromium (400 mg/kg DM), vanadium (600 mg/kg DM), and thallium (2 mg/kg DM). The report points out that higher concentrations of these elements might lead to an accumulation in the soil and thus potentially pose a hazard to humans and the environment through formation of hexavalent chromium.

These limits for chromium and vanadium are based on "worst-case assumptions" derived from laboratory studies, tests with slag unsuitable for fertilisation and studies on the environmental behavior of soluble chromium compounds. Data, analysis, and experiences from agricultural field trials as well as from real fertiliser slag provided by the FEhS-Institute have not been taken into consideration. An actual risk assessment for humans and the environment based on the behaviour of fertiliser slag applied to arable soils or grassland has not been carried out. The FEhS-Institute therefore rejects the proposed limit values and has submitted technical comments on the report via EUROSLAG. In autumn 2021, the JRC will use the input received on the "By-Product Interim Report" to prepare a 3rd draft for the regulation of by-products, based on which the EU Commission will then prepare the final text to supplement the FPR. However, it can be assumed that the JRC won't make fundamental changes to its proposals anymore.

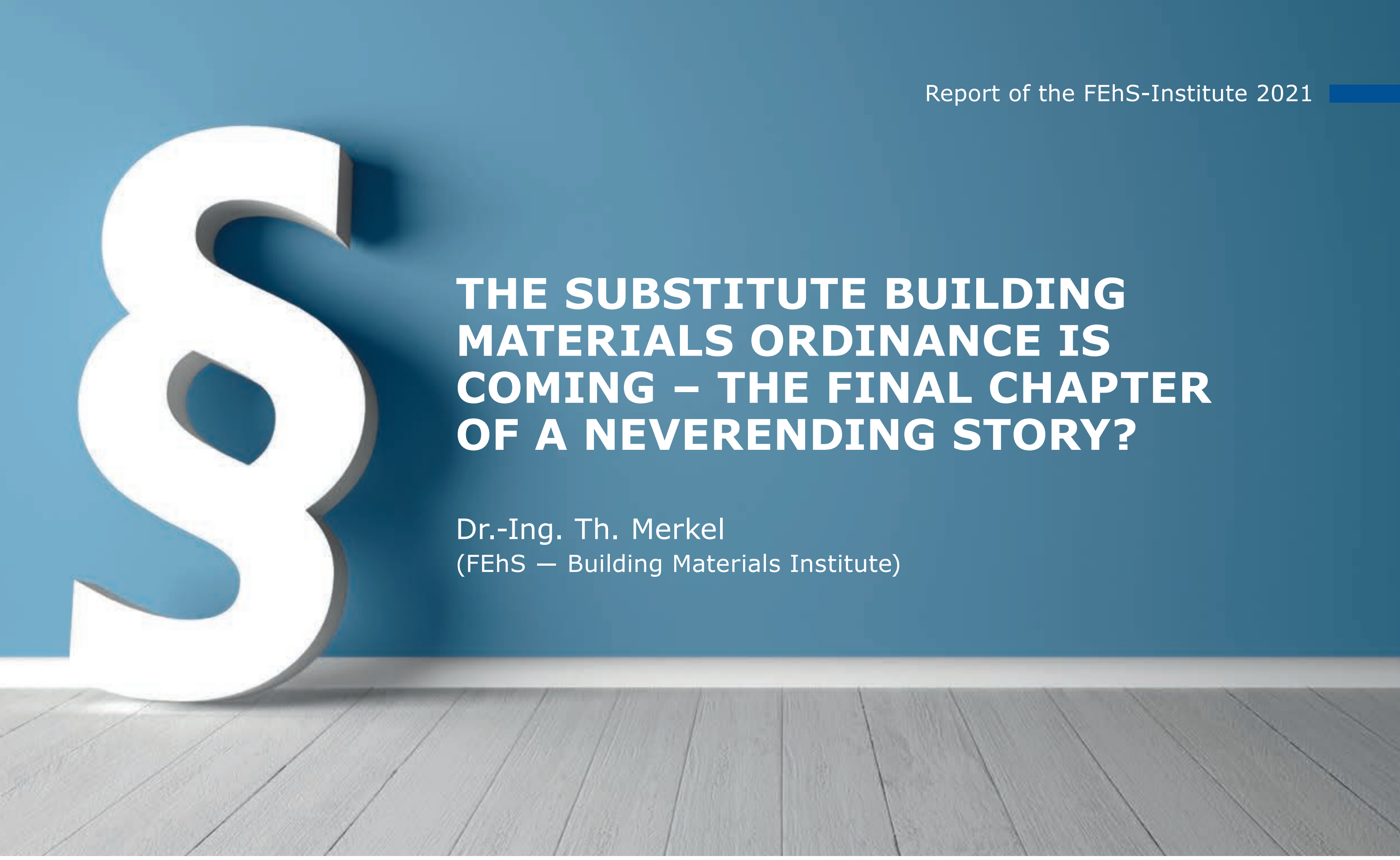
The labelling requirements of Annex III regulate the markings that must be affixed to packaging or provided to the user by attaching accompanying documents. Here, the changes compared with the old regulation become very obvious. The familiar type designation has been replaced by long PFC descriptions and labelling of the ingredients. Completely new are the instruction for intended use, including application rates, timings, and frequencies, as well as target crops. Besides, recommendations for storage and handling CE markings are required as well. All this together will significantly increase the space required on the packaging material and accompanying documents, and together with the many language versions, will present manufacturers with considerable technical problems.

Another challenge for manufacturers will be the new tolerance rules. Tolerances are allowed deviations from declared nutrient content. These tolerances are to cover deviations due to variations in the production processes, sampling and analysis. In regulation 2003/2003, only negative tolerances were applied. This means tolerances were applied in the case of a measured nutrient content being below the declared nutrient content. If the measured value was in the range of the tolerance, the product was still marketable, if not, the case was punished by the respective authorities. But this rarely happened since most manufactures just declared nutrient contents that were certainly met. If the actual content significantly exceeded the marked value, this had no consequences. The FPR now additionally applies positive tolerances in case of exceeding the declared nutrient content. This makes the steering of the production much more challenging to the manufacturer. Especially products derived from natural materials vary in their nutrient content and the manufacturer must ensure to stay in the permitted range by not falling below the lower tolerance limit and also not exceeding the upper tolerance limit.

Finally, Annex IV of the FPR introduces conformity assessment procedures and the CE marking of fertilising products. In all cases, manufacturers have to establish technical documentation on the production process including a product analysis and a risk assessment. Within Part I of Annex IV, rules are layed down to assign the CMCs to the relevant module, e.g. in case of a product consisting solely of CMC 11 material (ferrous slag), module A will be applicable. While conformity assessment module A consists of an internal production control with the product responsibility remaining solely with the manufacturer, the other modules are dependent on supervised product testing or on examinations by external notified bodies. So far, no notified bodies have been established and the interest of suitable institutions is very low. Only a few member states have reported interest of institutions to become a notified body. Besides, for many of the products covered by the FPR, no harmonised standards exist that are prerequisite to estimate the business model.

As already mentioned, the FPR will be applicable from 17th July 2022. From the present point of view, the work on the regulation won't be finished by then. Especially the elaboration of harmonised standards will exceed the date of applicability and hinder the use of this new regulation. Presently, the Commission hopes that at least the required standards are developed by then, even if harmonisation is still pending. But so far, the contract to fund CEN's work has not been signed.

The FEhS Institute and EUROSLAG in cooperation with EUROFER will proceed to defend the interests of the steel industry and to make ferrous slag-based fertilizers an essential part of the European circular economy. Therefore, communication with the EU Commission, the members of the European Parliament and the national representatives in the EU Council working groups will continue to work towards the removal of the very strict limit values. Until then, the status quo, i.e. the possibility to place ferrous slag-based fertilisers on the market in accordance with national legislation and by mutual recognition, will remain in place. <<<



THE SUBSTITUTE BUILDING MATERIALS ORDINANCE IS COMING – THE FINAL CHAPTER OF A NEVERENDING STORY?

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In Germany, around 260 million tonnes of industrial by-products and mineral construction waste are generated annually, on the one hand by industrial processes such as the production and processing of metals, or power generation, and on the other hand by construction activities. The use of these building materials in road construction has been established and proven effective over the course of many years. It is essential to take into account all the requirements that arise from structural engineering considerations, but also in relation to environmental compatibility. Using these construction materials then contributes significantly to the conservation of natural rock raw materials and avoids placing a further burden on already limited landfill capacity.

In this context, however, a conflict of interests arises between the goals of pollution prevention on the one hand and resource protection on the other. To achieve the latter, the circular economy concept demands the fullest possible utilisation of usable materials, thus avoiding or at least minimising waste. Soil and water protection, on the other hand, aims primarily to avoid any negative impact on soil and (ground-) water, and requires strict assessment standards. Excessive requirements in soil and water protection, without holistic balancing of the consequences for all resources, ultimately have a negative impact on the circular economy.

The Federal Ministry for the Environment (BMU) is trying to resolve this conflict of goals. As early as 2005, the Federal State Working Group on Waste (LAGA) had asked the BMU to take over this task, after previous unsuccessful attempts to harmonise regulations for assessing the environmental impact of mineral waste throughout Germany. It is after all agreed that potential pollution of groundwater and soil is unaffected by the federal borders within Germany, and that variations in assessment across federal borders make no sense in terms of environmental protection.

As a result of these efforts, a framework regulation known as the 'Mantelverordnung' (MantelV) has now been published in the Federal Law Gazette dated 16 July 2021 [1]. This essentially introduces the new regulation on requirements for the installation of mineral substitute building materials in technical structures (Substitute Building Materials Ordinance – 'ErsatzbaustoffV', abbreviated EBV) and revises the Federal Soil Protection and Contaminated Sites Ordinance [2]. The scope of the EBV also covers small revisions of the Landfill Ordinance [3] and the Commercial Waste Ordinance [4]. After a transitional period of 2 years, the regulation will enter into force on 1 August 2023. A development spanning many years is thus nearing its conclusion. The EBV replaces the different regulations in the individual federal states, which should simplify using the construction materials covered by the ordinance. In addition, the ordinance, which applies throughout Germany, offers improved legal certainty and clarity, which should also benefit the use of secondary construction materials.

CONCEPT

The EBV regulations are based on a scientific concept [5, 6], which was developed on the basis of a broad-based collaborative research project regarding seepage prognosis [7]. Threshold values for groundwater [8] or background values in groundwater [9] are assumed and, based on this, model calculations are used to derive which concentrations of certain constituents may permissibly be contained in leachate leaving a layer or a structure. Taking into account the movement of the leachate (together with its constituents) to the groundwater and the accumulation of the constituents due to deposits in the soil, material-specific limit values ("material values") and possible applications were derived. The fact that assumptions have to be made, categorisations performed and simplifications permitted for the development of a nationwide ordinance is fundamentally understandable and ultimately inevitable.

A whole range of materials was considered. From the iron and steel industry, air-cooled blast furnace slag (ABS), granulated blast furnace slag (GBS) and steel furnace slag (SFS) are covered by the ordinance. The definition of different "quality classes" (based on different leachability) enables targeted use depending on the construction method on the one hand and the sensitivity of the ground (soil, groundwater) on the other.

If the mineral secondary construction materials in technical structures are exposed to weathering effects such as precipitation and temperature fluctuations, there is always the possibility that substances will be dissolved from the building material and released through contact with precipitation or seepage water. The release process depends on a variety of boundary conditions. Decisive factors in determining the release potential are e. g. mineralogical and chemical bonding, integration into the surrounding matrix, degree of crystallinity, grain size, and acid or base neutralisation capacity. Numerous studies show that for most substances there is no correlation between their total contents in solids and solubility, meaning that the release potential cannot be estimated on the basis of solid contents [10]. As a result, even the currently applicable federal state regulations generally use leachability in the evaluation of secondary building materials for use in technical structures. Only organic parameters that may be contained in soils or recycled building materials are required to be analysed in the solid.

QUALITY ASSURANCE

Up to now, an agitation method with a liquid/solid ratio (L/S) of 10:1 based on a European standard [11] has been used as the standard test method in the field of road construction. This principle is also utilised by the EBV. However, based on the scientific studies cited above [5, 6], it utilises new leaching processes with a L/S of 2:1 [12, 13] instead of the 10:1 ratio conventionally used previously. A conversion of the results is not possible, meaning that the material values specified in the ordinance are not comparable with the conventional requirement values used previously.

A basic element of the EBV is that it is no longer necessary to obtain a permit under water legislation for the combinations of construction material, construction method and location of the building project specified in the ordinance - as such, adverse changes in the groundwater quality or harmful soil changes need not be feared.

An important prerequisite for this is quality control of the construction materials, consisting of suitability testing, factory production control and third-party control.

In this context, however, a difference to previous practice becomes apparent: Whereas previously the construction materials have been sampled and inspected 2 or 4 times a year by a third-party inspection body, the inspection frequency will now be increased, in some cases significantly, depending on the quantity produced. In addition, future inspections will also have to be carried out as part of the production control process. Although there are simplifications for members of a recognised quality assurance association, the overall effort will clearly be increasing.

APPLICATION REQUIREMENTS AND POSSIBILITIES

Based on the results of the suitability testing, the secondary building materials are classified in order to be able to determine their installation options. The ordinance shows in table format where use of the respective construction material is possible. The decision takes into account the method of installation (e. g. asphalt surface, aggregate base course or road embankment) as well as the properties of the groundwater cover and, where applicable, the location within a water protection area. The basic principle of these tables was adopted from the 'Reclamation Decrees' of the federal state of North Rhine-Westphalia, where this principle has proven effective since 1991 [14].

With regard to installation, it is not only the aforementioned permitted installation methods that need be taken into account. Minimum installation quantities have been specified for a number of secondary construction materials, in order to prevent the distribution of these construction materials over many small-scale construction measures. However, this will also eliminate established sales channels. Bound construction methods, for example, are significantly affected by the regulations regarding minimum installation quantities.

Documentation requirements will also increase: For a whole range of secondary construction materials, the planned use must be indicated four weeks before the start of installation, and a further notification must be submitted after completion of the construction work, stating the quantities and material classes actually installed. The (as yet undefined) responsible authority will then finally document the use of notifiable secondary building materials in a register - expressly separate from the register of suspected contaminated sites ("contaminated site register"), since the regulations of the EBV are explicitly intended to prevent the risk of harmful soil changes.

In summary, it is concluded that eliminating the need for a permit under water legislation has been replaced by a whole range of additional requirements. It remains to be seen whether, overall, the best possible use of by-products and the recovery of mineral waste within the meaning of Section 6 of the Circular Economy Act (KrWG) [15] envisaged by the Federal Ministry for the Environment (BMU) can actually be achieved. The MantelV already contains the obligation to monitor this and, if necessary, take corrective action. Accordingly, it is intended to review the impact on material flows two years after entry into force and to adjust the Ordinance if necessary. Furthermore, the ecological and economic effects of the Ordinance shall be evaluated – independently of or in addition to any short-term review and readjustment that may become necessary – and submitted to the German Parliament four years after its entry into force as documentation of scientifically supported monitoring.

PRODUCT CLASSIFICATION

From the outset, the EBV was not aimed solely at mineral waste, but was also intended to regulate the use of by-products, as well as substances that have reached the end-of-waste status. The term "substitute building material" was therefore created at the time as a common name. For some years, the drafts also contained explicit provisions on which substitute building materials could be recognised as by-products or end-of-waste materials. These provisions ultimately did not meet with consensus, and so were removed again. The general regulations of the Circular Economy Act (KrWG) [15] thus continue to apply to the construction materials dealt with in the EBV, i. e. they have not been supplemented or superseded by a special regulation.

The KrWG defines four criteria for by-products (section 4) and for the end-of-waste status (section 5), which form the prerequisite for recognition as a product. The first three criteria are generally not controversial. Only the wording in the fourth criterion "... and overall does not lead to harmful effects on humans and the environment" is repeatedly the subject of controversy.

Section 1 of the EBV "Scope of application" focuses precisely on that wording when stating: "The provisions of this Ordinance shall regulate, with regard to mineral substitute building materials within the meaning of section 2 number 1, the ... conditions under which the use of these mineral substitute building materials overall does not lead to harmful effects on humans and the environment within the meaning of section 4(1) number 4 last sub-clause of the Circular Economy Act or section 5(1) number 4 of the Circular Economy Act".

The Ordinance thus clarifies that – provided that the fulfilment of the other criteria of sections 4, 5 KrWG is ensured – secondary construction materials that comply with the rules of the EBV with regard to their quality and quality assurance and which are intended to be also used in accordance with the rules of the Ordinance are not regarded as waste, but as by-products or as substances that have reached the end-of-waste status.

CONCLUSIONS

In the assessment of mineral construction waste and industrial by-products, a balance is needed between the justified requirements for soil and water protection on the one hand and the promotion of the circular economy and resource conservation on the other, i. e. a proportionate definition of requirements that ensures the protection of soil and groundwater but does not exceed this goal. This is the only way to enable and responsibly maximise the use of industrial by-products and recycled materials. Finding this balance was the aim of the German Federal Ministry for the Environment (BMU) in developing the Substitute Building Materials Ordinance (EBV).

The development of the EBV over many years has recently led to increasing uncertainties about the extent to which the previous federal state regulations are still up to date. In this respect, it is very welcome that this process has now reached its conclusion - at least for the time being. How the anticipated shifts in material flows will play out in practice, and in particular as relates to landfill capacities, will require observation. <<<

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PRODUCTION AND USE OF FERROUS SLAG IN 2020

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Ferrous slag (blast furnace slag and steel furnace slag) is a by-product of steel production and has been marketed successfully for decades as a construction material or as fertilizer. The ratio of use exceeds 90% and the use of slag is an excellent example of the conservation of natural resources.

GERMANY

Data concerning production and use in Germany in 2020 are shown in Table 1 (blast funace slag) and Table 2 (steel furnace slag). For comparison, the data for 2019 are also shown.

Production	2020	2019
Granulated BFS	**5.80**	6.48
Air-cooled BFS	**0.61**	0.82
Sum	**6.41**	7.30
From interim stock	**0.91**	0.74
Total	**7.32**	8.04

Use	2020	2019
ABS for aggregates	**0.27**	0.13
ABS for aggregate mixtures	**0.48**	0.51
GBS for cement production	**6.42**	7.15
GBS for other purposes	**0.08**	0.11
Intra-industry consumption	**0.07**	0.14
Total	**7.32**	8.04

Table 1: Production and use of blast furnace slag in Germany 2020/2019 (in million tonnes)

Production	2020	2019
Slag from oxygen steel making	**2.53**	3.02
Slag from electric arc steel making	**1.46**	1.47
Others (SecMS etc.)	**0.46**	0.52
Sum	**4.45**	5.01
From interim stock	**0.01**	
Total	**4.46**	5.01

Use	2020	2019
Metallurgical use	**0.61**	0.56
Fertilizer	**0.43**	0.40
Construction material	**2.66**	2.12
Others	**0.21**	0.27
Sum	**3.91**	3.35
Final deposit	**0.55**	0.66
To interim stock		0.97
Total	**4.46**	5.01

Table 2: Production and use of steel furnace slag in Germany 2020/2019 (in million tonnes)

In 2020, total crude steel production in Germany was about 35.7 million tonnes [1]. This was 10% lower than in the previous year (39.7 million tonnes) particularly because of the pandemic situation. The production of by-products also declined corresponding to this decrease. In 2020, 10.9 million tonnes of ferrous slag were produced in Germany, corresponding to 90% of the previous year's production (12.3 million tonnes).

This shortage led to the reduction of interim stock. In 2020, the stock was reduced by 0.9 million tonnes while in 2019 an increase of 0.3 million tonnes took place. In total, 11.2 million tonnes of ferrous slag were used as construction materials or fertilizer (2019: 11.4 million tonnes).

Looking at the data in detail, in the case of blast furnace slag (BFS), the proportion of granulated BFS is about 90% of the total quantity. Consequently, the marketing of granulated BFS into the cement industry remains the most important field of use, even though the absolute value has declined considering the reduced production volume (6.4 million tonnes, 2019: 7.2 million tonnes). The production of CEM II and CEM III cements is the most important application of BFS, which also makes an important contribution to CO_2 reduction in the cement industry. The high value use of air-cooled BFS for manufacturing asphalt or concrete increased (0.3 million tonnes, 2019: 0.1 million tonnes), while the traditional use for aggregate mixtures remained at approx. 0.5 million tonnes.

Looking at the production of steel furnace slag (SFS), the decrease in production (4.5 million tonnes, 2019: 5.0 million tonnes) was obviously due to the integrated steel plants, while in steel shops with electric arc furnaces, approximately the same amount of slag was produced as in 2019.

Comparing the use in the different application areas reveals an increase of approx. 10% in metallurgical applications (0.6 million tonnes) and in use as a lime fertilizer (0.4 million tonnes). A slight decrease is apparent in the use as a simple bulk material or similar applications without a formal quality control system (0.2 million tonnes, 2019: 0.3 million tonnes). This is certainly to be seen in connection with a significant increase in the construction materials market (2.7 million tonnes, 2019: 2.1 million tonnes).

In total, more slag products could be sold (11.2 million tonnes) than were even produced (10.9 million tonnes) in Germany in 2020.

EUROPE

The European slag association, EUROSLAG, provides European slag data on a yearly basis. Preliminary figures for 2020 are given in Table 3 (blast furnace slag) and Table 4 (steel furnace slag). However, these figures must be certified as it has not yet been possible to obtain a satisfactory number of responses.

Based on the hot metal and crude steel production provided by Worldsteel [1], a rough estimation of BFS production and SFS production can be made. This leads to about 22 million tons of BFS and 17 million tons of SFS produced in the EU-28 countries in 2020. The reported data provided in tables 3 and 4 represent about 73% of the BFS and 67% of the SFS figures. These are roughly the percentages obtained for the year 2019, so a comparison between the years 2020 and 2019 is possible, even if the reporting countries are not exactly the same.

Comparing the production figures shows a decrease in production by 10% as reported above for Germany. A difference seems to arise in SFS production, as in other European countries obviously not only integrated steel plants are concerned.

Comparing the percentages for BFS with those reported from Germany reveals that the figures are quite close together: About 90% of the blast furnace slag is granulated and subsequently 90% of it is used for cement production. The second largest amount is used for road construction. Only a very small part is used for other purposes such as fertilising and glass production.

About 70% of the SFS produced is used for construction purposes; for roads, dams or hydraulic structures for example. About 10% is used for metallurgical purposes, 6% as fertilizer and another 5% for other uses. 9% of the SFS produced was finally deposited.

In total, the (reported) use exceeds the (reported) production not only in Germany but also in Europe. The particular effect of the pandemic situation is surely one reason, among others. But it is also ultimately the result of the ongoing efforts of both slag producers and processors to provide exactly those qualities the market is asking for. <<<

Production	**2020**	2019
Granulated BFS	**14.3**	17.5
Air-cooled BFS	**1.9**	2.4
Sum	**16.2**	19.9
From interim stock	**1.7**	0.9
Total	**17.9**	20.8

Use	**2020**	2019
Cement production and concrete additives	**14.6**	17.7
Road construction	**2.8**	2.5
Others	**0.3**	0.4
Final deposit	**0.2**	0.2
Total	**17.9**	20.8

Table 3: Production and use of blast furnace slag in Europe 2020/2019 (in million tonnes)

Production	**2020**	2019
Slag from oxygen steel making	**6.0**	7.3
Slag from electric arc steel making	**3.9**	4.8
Others (SecMS etc.)	**1.4**	1.0
Total	**11.3**	13.9

Use	**2020**	2019
Metallurgical use	**1.1**	1.3
Fertilizer	**0.6**	0.6
Construction material	**8.0**	7.7
Others	**0.6**	0.9
Sum	**10.3**	10.5
Final deposit	**1.0**	1.5
To interim stock	**< 0.1**	1.9
Total	**11.3**	13.9

Table 4: Production and use of steel furnace slag in Europe 2020/2019 (in million tonnes)

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