

Report.

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LEACHING BEHAVIOUR OF FLUORINE FROM ELECTRIC ARC FURNACE SLAGS AND SECONDARY METALLURGICAL SLAGS

Dr. rer. nat. A. Sokol
(FEhS – Building Materials Institute)

INTRODUCTION

Calcium fluoride (CaF_2) is a highly effective flux in the steel-making process, which, in secondary metallurgy in particular, cannot be completely replaced by other fluxes. Secondary metallurgical slags (SEKS) can consequently exhibit increased leaching of fluorine, further complicating their use in addition to the technical limitations due to their tendency to disintegrate. Fluoride can be introduced into the electric arc furnace process through internal material cycles and/or external input materials. Secondary raw materials such as filter dust, separation iron or secondary metallurgical slags containing fluorspar can be reused within the electric arc furnace. Additionally, even steel scrap can also have a notable impact on introducing fluorspar into the process [1]. Consequently, both secondary metallurgical slags and electric arc furnace slags might exhibit elevated fluoride concentrations in the leachate, posing challenges to their application in terms of environmental concerns. As there is limited information available in the literature regard-

ing the behaviour of fluorine in steel slags, the FEhS-Institut für Baustoff-Forschung e.V. undertook an AiF research project (AiF No. 18523) during the period from 1 January 2015 to 31 December 2017 [2, 3]. Due to extensive investigations, the understanding of the leaching behaviour was significantly enhanced. However, the results also raised new questions. Based on the findings from the preliminary project, a further project was therefore launched in 2020 [4]. A key objective of the research project presented here was to expand the state of knowledge about the behaviour of fluorine in secondary metallurgical slags and to extend it to electric furnace slags to be able to make realistic statements about the environmental behaviour of both types of slag. In addition, economically viable measures to reduce fluoride leachability were to be identified.

For the project, six retained samples from the preliminary project (secondary metallurgical slags) as well as new slags were examined. In total, three new secondary metallurgical slags and

five electric arc furnace slags were included. Despite increased concentrations in the eluate, electric arc furnace slags usually have very low fluorine solid contents. These are often too low to make the mineral phases in which the fluorine is present visible and comprehensible using conventional analytical methods (e.g. electron beam microanalysis). For this reason, a fluoride-rich electric arc furnace slag was produced in a steelwork by adding fluorspar to a batch when tapping the liquid slag (Figure 1).

The samples were intensively analysed with regard to their chemical composition, mineralogy and leaching behaviour. Both X-ray diffraction (XRD including Rietveld refinement) and electron beam microanalysis (EBMA) were used to investigate the mineralogical composition. Metallurgical measures were tested in laboratory-scale melting experiments with the aim of investigating the effects of Al_2O_3 or SiO_2 addition on the change in mineralogy in the slags and the subsequent fluorine leaching.



Figure 1: Operational tests for slag conditioning; a: bags with fluorspar, b: tapping of the molten slag, c: pouring the slag into the bed, d: empty slag pot, e: sampling of the bed sample, f: sampling of the rapidly solidified pot rim

MINERAL BINDING OF FLUORINE IN STEEL SLAGS

The primary mineral phases identified by XRD in the examined secondary metallurgical slags (SEKS) include dicalcium silicate (Ca_2SiO_4), bredigite ($\text{Ca}_7\text{Mg}(\text{SiO}_4)_4$) and tricalcium silicate (Ca_3SiO_6). Another common mineral phase found in these slags is mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$). Additionally, fluorine-bearing phases such as fluorspar (CaF_2) and cuspidine ($\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$) have been identified in some cases. Occasionally, jasmundite ($\text{Ca}_{11}(\text{SiO}_4)_4\text{O}_2\text{S}$) is also present.

The main mineral phases of the investigated electric furnace slags are wuestite ($(\text{Fe,Mn,Mg})\text{O}$) and calcium silicates. Calcium silicates refer to calcium-rich silicates from the olivine group with the general composition $(\text{Ca,Mg,Fe,Mn})\text{SiO}_4$. This group includes phases such as larnite ($\beta\text{-Ca}_2\text{SiO}_4$), kirschsteinite (CaFeSiO_4), bredigite ($\text{Ca}_{14}\text{Mg}_2(\text{SiO}_4)_8$), monticellite (CaMgSiO_4) or calcio-olivines ($\gamma\text{-Ca}_2\text{SiO}_4$). The sample enriched with fluorspar in the plant contains 3.2 mol% fluorspar (CaF_2), which may indicate incomplete dissolution of the added fluorspar. Cuspidine ($\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$) has also been identified in this sample.

Within the scope of the EMSA investigations, backscattered electron images (BSE) and elemental distribution

maps (area scans) were generated to visualise the association of fluorine with specific elements and to identify mineral phases containing fluorine. Additionally, individual mineral phases were quantitatively analysed for their chemical composition using wavelength-dispersive X-ray microanalysis (WDX).

All mineral phases that were detected by X-ray were also identified with the microprobe. Wuestite can be recognised in the backscattered electron image as brightly reflecting roundish or branched surfaces (Figure 2). Spinel can be recognised by its isometric, triangular or octahedral cut surfaces and is zoned (Figure 2). Its composition varies but can be recognised in all samples by the clear signals for chromium. Zoning is evident through edges that are richer in aluminium and magnesium. Phases with lower iron content, such as olivine and melilite, appear dark in the BSE image.

The chemical composition of the mineral phases and contents of individual parameters were measured using spot WDX analyses. In secondary metallurgical slags, the fluorine-bearing mineral phases are fluorspar, cuspidine, fluoromayenite and dicalcium silicate, which is consistent with the results from the preliminary project.

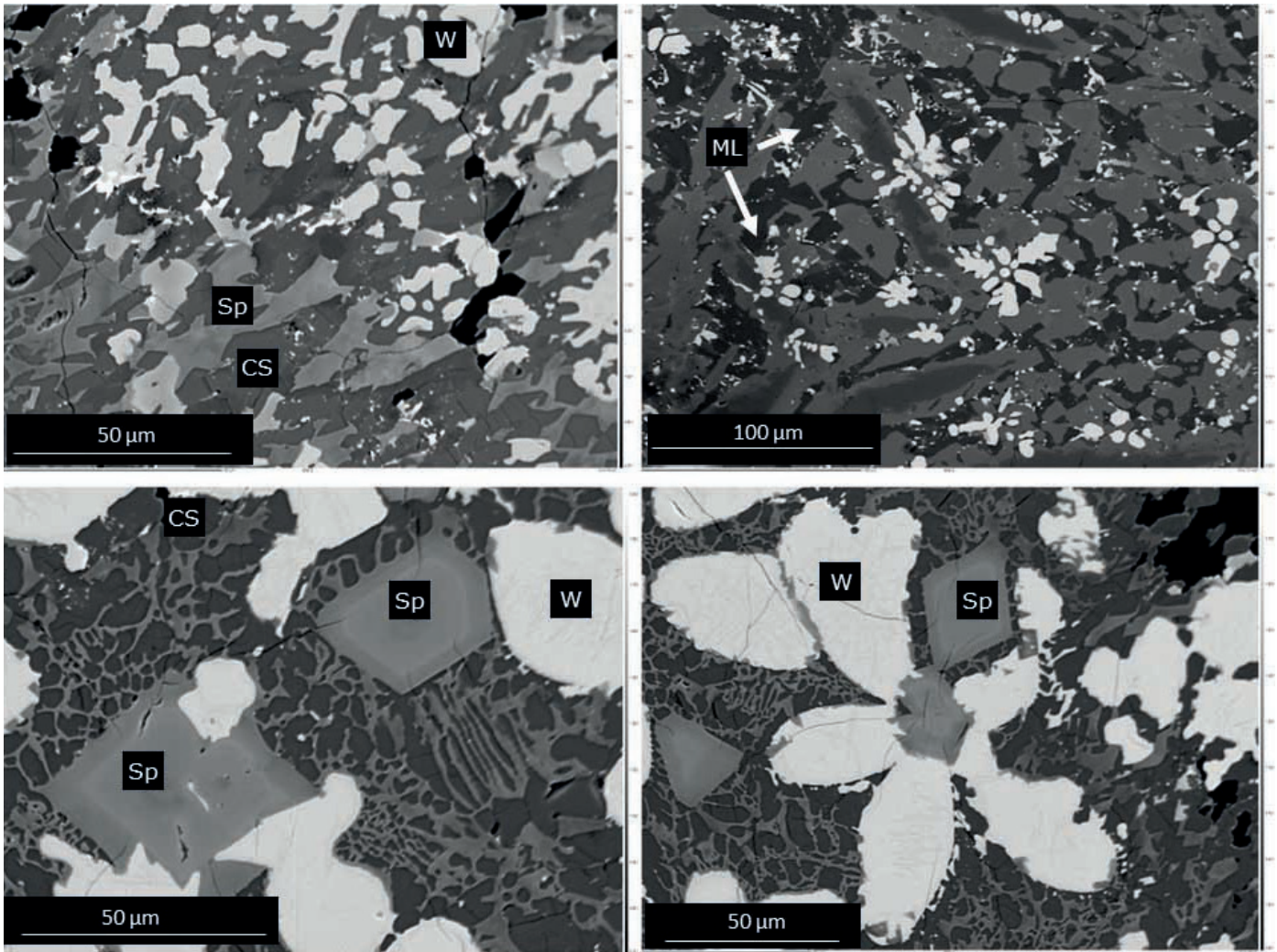


Figure 2: Backscattered electron images (BSE) of the electric furnace slags. W = wuestite, Sp = spinel, CS = calcium silicate, ML = melilite

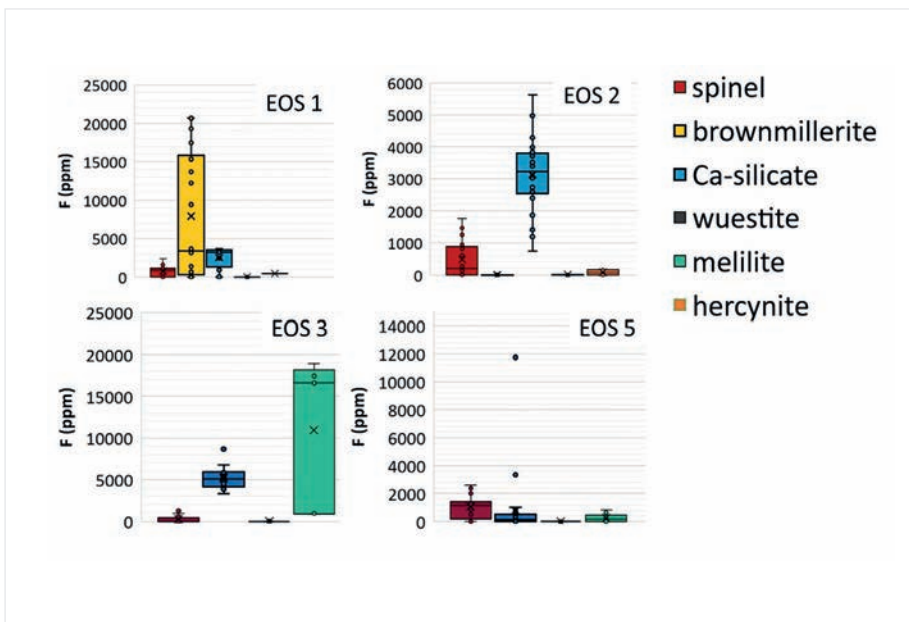


Figure 3: Fluorine content in individual mineral phases of the examined electric furnace slags

In Figure 3, the fluorine contents in individual mineral phases of the examined electric furnace slags are graphically represented. It is evident that fluorine is distributed across various mineral phases. In some samples, it is associated with aluminium in aluminium-bearing mineral phases (brownmillerite, melilite), while in other samples, it is associated with calcium silicate, which contains the highest fluorine content. The sometimes significant levels of fluorine in the spinels of the electric furnace slags are noteworthy. From the literature, it is known that fluorine, due to its ion radius (1.33 Å), slightly smaller than that

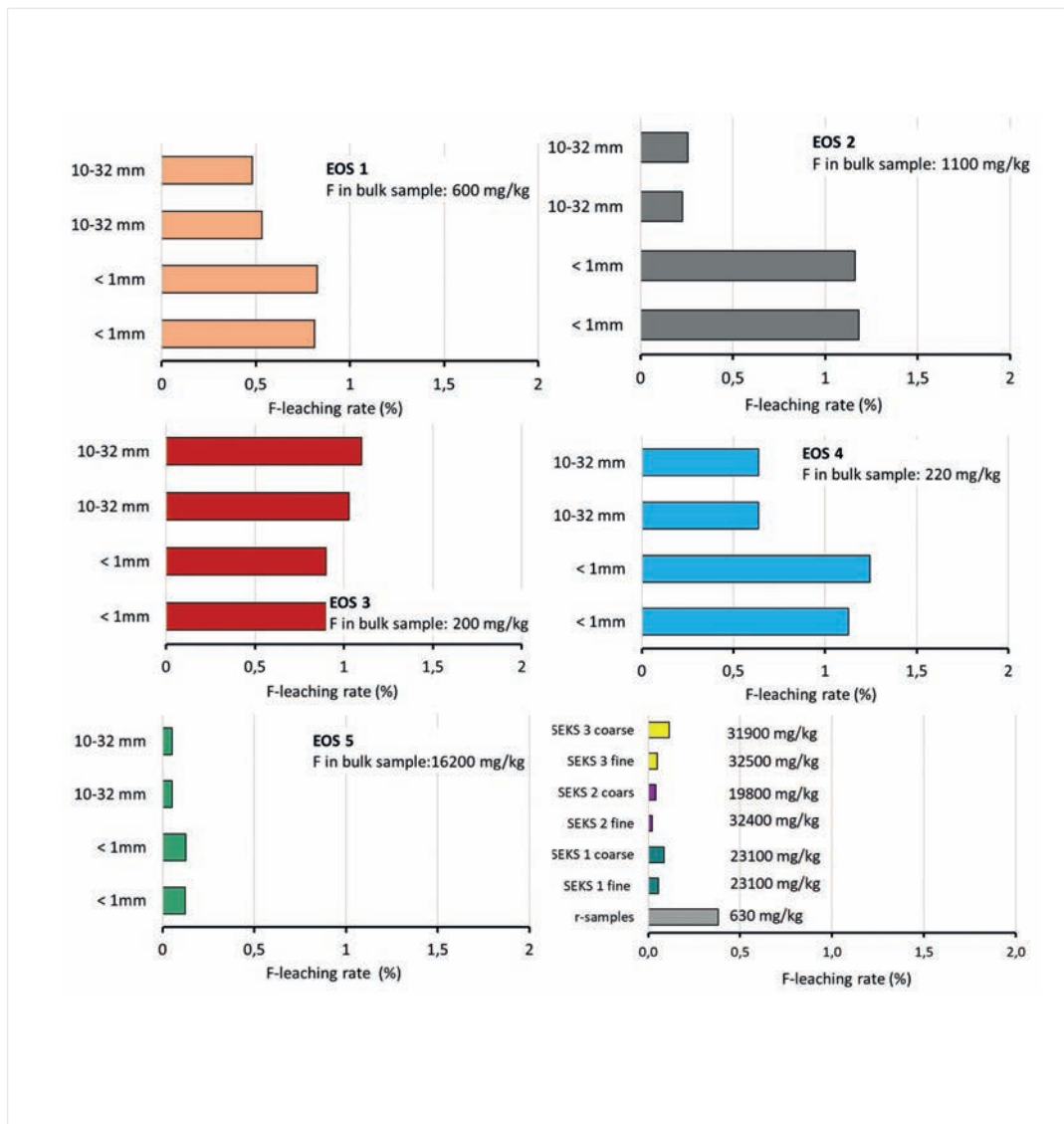


Figure 4: Percentage fluorine leaching rates for the investigated electric arc furnace slags and secondary metallurgical slag in the 2:1 batch test (DIN 19529) in various grain sizes (r samples = reserve samples from preliminary project, SEKS fine = 0/1mm, SEKS coarse = 5/32mm). The solids content for fluorine in mg/kg is also shown.

of oxygen O^{2-} (1.40 Å), can replace oxygen in various mineral phases [5]. In natural rocks, fluorine is measured in micas, olivines, pyroxenes, amphiboles and apatites [6, 7]. However, fluorine has also been detected in spinel and magnetite [6].

LEACHING BEHAVIOUR OF FLUORIDE DEPENDING ON SOLIDS CONTENT AND MINERALOGY

The fluorine solid contents of the samples examined here exhibit a wide range. In the secondary metallurgical slags, solid content varies between 1.98 mol% and 3.38 mol%, while in the electric furnace slags, they range from 0.02 mol% to 1.62 mol%. The high value of 1.62 mol% is not typical in electric arc furnace slags (EOS). As described earlier, fluorspar was intentionally added to a sample in a steelwork to generate EOS with elevated fluoride content. As depicted

in Figure 4, the percentage leaching rates, relative to fluorine solid content, in the 2:1 batch test (according to DIN 19529 [8]) are generally quite low (maximum 0.38% for secondary metallurgical slags and maximum 1.3% for electric arc furnace slags, Figure 4).

Secondary metallurgical slags tend to disintegrate, with not the entire slag mass typically breaking down, resulting in finely disintegrated alongside coarse, non-disintegrated grain fractions. To identify potential differences in fluorine content between the disintegrated and non-disintegrated portions of the slag, these fractions were separately examined and are indicated in Figure 4 (SEKS fine = disintegrated portion, 0/1mm; SEKS coarse = non-disintegrated portion). For electric arc furnace slags, the fine grain size

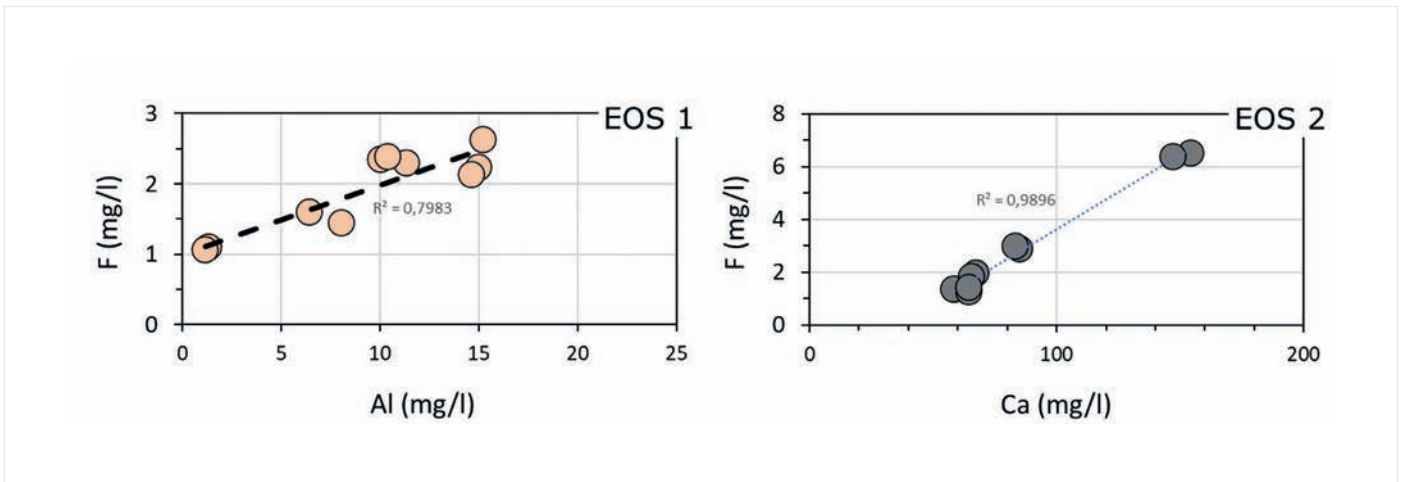


Figure 5: Comparison of the concentrations of fluorine and aluminium or calcium in the 2:1 batch test

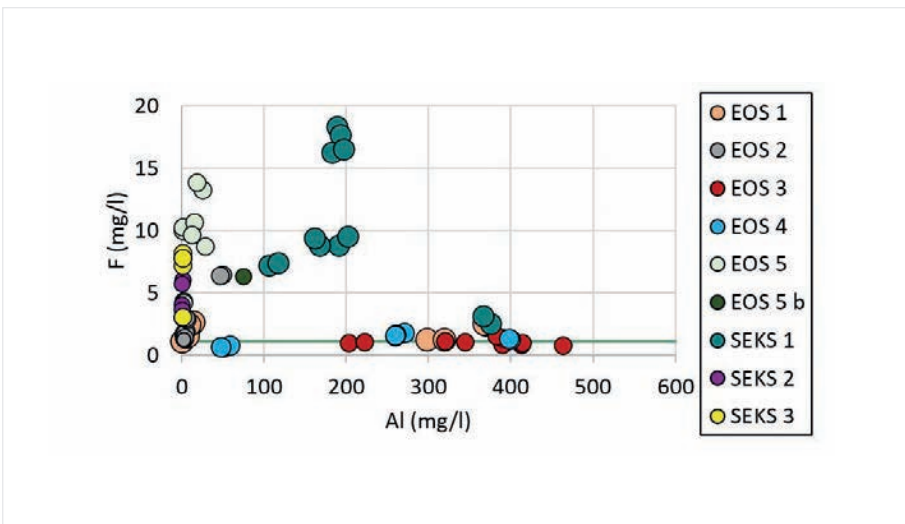


Figure 6: Relationship between the concentrations of aluminium and fluoride in the eluates (shaking batch test, $L/S=2:1$, DIN 19529) of the investigated EOS and SEKS. All tests with all individual grain sizes are shown. The green line corresponds to the EBV material class SWS-1 [11].

for the leaching tests was produced by crushing. Solid content is based on the average sample.

As leaching behaviour is known to be controlled by mineralogy, no general correlations between solids content and concentration are expected. Depending on which mineral phase fluorine is bound to, it is released to a greater or lesser extent based on the solubility behaviour of the mineral phase. In the examined electric arc furnace slags, a linear relationship between aluminium and fluorine or calcium and fluorine is observed in the eluates, depending on which mineral phase serves as the host for fluorine. In the case of sample EOS 1, for instance, it is brownmillerite that exhibits the highest fluoride content (up to approximately 2.2 mol%, Figure 3). Brownmillerite is an aluminium-bearing phase, which is why a simulta-

neous increase in the concentrations of fluorine and aluminium is observed (Figure 5). In the case of sample EOS 2, it is calcium silicate that exhibits the highest fluoride content (up to approximately 0.6 mol%, Figure 3). Accordingly, a positive correlation between Ca and F is evident during elution (Figure 5).

Processes within the eluate itself can also influence the concentration actually measured. In the present study, as well as in the preliminary project, a correlation between the concentrations of aluminium and fluoride was observed. Above an aluminium concentration in the range above 300 mg/l, only small fluoride concentrations are consistently measured (Figure 6). A plausible explanation for this relationship could be precipitation reactions in the eluate. Depending

| | | SEKS 1 | | SEKS 2 | |
|--------------------------------|------|-----------|----------------------------------|-----------|----------------------------------|
| | | reference | + Al ₂ O ₃ | reference | + Al ₂ O ₃ |
| Batch test, L/S = 2:1 | | | | | |
| Al ₂ O ₃ | wt.% | 4.04 | 8.29 | 16.1 | 21.7 |
| F | wt.% | 3.1 | 3.35 | 2.7 | 2.7 |
| Al | mg/l | 177 | 299 | 328 | 487 |
| F | mg/l | 2.11 | 15.3 | 4.5 | 0.5 |

Table 1: Solids content and eluate concentration (DIN 19528) of selected parameters in the tested slags SEKS 1 and SEKS 2 in the original state (reference) and after treatment in the molten state by adding 3 wt.% alumina (+Al₂O₃).

on the SiO₂ or Al₂O₃ content of the samples, precipitation of various hydration products such as calcium silicate hydrate (C-S-H gel), calcium aluminium hydrate (C-A-H phase), and calcium aluminium silicate hydrate (C-A-S-H gel) can occur in the eluate [9]. These hydration phases are capable of immobilising fluoride from the solution through coprecipitation. The immobilisation capacity of the C-A-H phases is the greatest compared to the other two hydrate phases [10]. In filter residues, hydration phases such as katoite, strängite or hydrocalumite were indeed detected in the context of the research project. It is likely that these phases also remove fluoride from the solution.

FLUORIDE IMMOBILISATION

The laboratory-scale melting experiments aimed to permanently reduce the leachability of fluoride, enabling an environmentally friendly use of the slags. The treatment in the molten state aimed to change the mineral binding of fluoride in a way that it becomes firmly bound and cannot leach in environmentally significant amounts. The findings from the preliminary project [2, 3] were used in this project step. The preliminary project involved laboratory-scale melting experiments with

secondary metallurgical slags. These experiments demonstrated that rapid (100 °C/min, 50 °C/min) and moderate cooling (20 °C/min) results in significantly higher fluoride leaching compared to the original sample. With a slow furnace cooling rate of 5 °C/min, the fluoride leaching rate is in the same order of magnitude as that of the original sample. A correlation was observed between the presence or absence of aluminium-bearing mineral phases, especially mayenite and fluorine-mayenite, and fluoride concentrations in the eluate. The addition of P₂O₅ prevented the disintegration of the slags to a large extent. However, the change in chemistry also resulted in the suppression of mayenite or fluorine-mayenite formation even during slow cooling at 5 °C/min, leading to high fluoride concentrations in the eluate. Even in the presence of fluorapatites, considered stable, fluoride leaching was usually higher than in the original sample. A significant reduction in fluoride leaching could not be achieved in the melting experiments. However, it was observed that the presence or absence of readily soluble aluminium phases (mayenite) can apparently influence fluoride concentrations in eluates. As described above, the aluminium introduced into the

eluate forms calcium aluminium hydrate phases that can coprecipitate fluoride. Building on these findings, the present project tested the addition of Al₂O₃ to investigate whether more stable aluminium-bearing phases might form, which could also incorporate fluoride and release less fluoride due to the stability of these phases. Alternatively, increasing Al₂O₃ content could lead to enhanced aluminium release. In the eluate, the high aluminium concentration might reduce fluoride concentration by causing aluminium hydrate phases to precipitate and extract fluoride from the solution.

In the melting experiments with secondary metallurgical slags, the addition of Al₂O₃ (3 wt.% alumina) led, as expected, to a change in mineralogy. In one sample (SEKS 2), which already had a relatively high Al₂O₃ content (approximately 16 mol%) in its original state, it was observed that the treatment slightly increased the aluminium concentration in the eluate (from 338 mg/l to 487 mg/l) and significantly decreased the fluoride concentration (from 9.0 mg/l to 0.5 mg/l) (Table 1). The reduction in fluoride concentration could be explained by the formation of fluorite (CaF₂) in addition to cuspidine in the treated sample, resulting in

less fluoride being incorporated into calcium silicates. According to some studies, fluorite is significantly less soluble than fluoride-bearing calcium silicates [12]. Another reason could be the higher aluminium concentration in the eluate, leading to the precipitation of aluminium hydrate phases.

In another sample (SEKS 1), significantly lower Al_2O_3 content (approx. 4 wt.%) was measured in the original state. The addition of Al_2O_3 also led to a change in the mineralogy. In the eluate, the aluminium concentration increased only slightly (from 55 mg/l to 77 mg/l). However, the fluorine concentration rose sharply (from 3.19 mg/l to 15 mg/l). This result is difficult to understand, as cuspidine was formed in significant quantities in the treated sample. Cuspidine is fluorine-bearing and is considered less soluble than fluorspar, for example [13]. In this case, the aluminium concentrations are too low to allow the precipitation of aluminium hydrate phases.

In the melting experiments with electric arc furnace slag, the addition of Al_2O_3 resulted in the formation of larger amounts of spinel. Although mineralogical studies indicated that spinel can incorporate fluoride, in this case no reduction in fluoride release was achieved. However, the addition of SiO_2 significantly reduced the concentration of fluoride in the eluate. A probable reason is that in the SiO_2 -treated sample, larnite was completely replaced by kirschsteinite. As observed in previous experiments [14], kirschsteinite is more stable against an attack by water, resulting in less fluoride release overall.

SUMMARY AND OUTLOOK

An essential goal of the research project was to expand the knowledge based on insights from the preliminary project [2, 3] regarding the behaviour of fluorine in secondary metallurgical slags and electric arc furnace slags and to identify mechanisms leading to fluoride release. Furthermore, economically viable measures for reducing fluoride leachability were to be outlined.

The investigations conducted have led to a range of new insights, particularly regarding the behaviour of fluoride in electric arc furnace slags, mineral formation, interactions between chemistry and mineralogy, and release mechanisms. After evaluating the results from the laboratory melting experiments, it can be concluded that due to the variable distribution of the parameter fluoride among different mineral phases, an effective treatment method for secondary metallurgical slags and electric arc furnace slags cannot be specified.

The addition of Al_2O_3 can lead to a reduction in fluoride release in one slag, while in another slag, this treatment may have the opposite effect. Similarly, treating the slags with SiO_2 addition can reduce fluoride release, but likely only in slags where calcium silicate serves as a host phase for fluoride. Therefore, treatment measures can only be developed individually based on the specific slag chemistry. The most effective and secure measure to avoid fluoride leaching is to minimise fluoride input to the maximum extent. As identified in the aforementioned research project [1], steel scrap was deter-

mined to be a significant source of fluoride input. Steel scrap thus has a significant impact on slag composition. To avoid contamination, attention should be focused on scrap management.

ACKNOWLEDGMENT

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YIELD RESULTS FROM THE SLUDGE2P PROJECT POT TRIAL – ENERGY SELF-SUFFICIENT PHOSPHATE RECOVERY FROM SEWAGE SLUDGE

Dr. sc. agr. H.-P. König
Dr. rer. nat. L. Gronen
(FEhS – Building Materials Institute)

INTRODUCTION

The Sludge2P project aims at developing and testing the entire utilisation of sewage sludge. Various process steps are combined in such a way that the required energy can be completely covered by the energy content of the processed dry sewage sludge. Ideally, an additional energy surplus is also achieved for other applications. The phosphate-enriched ash is to be thermochemically processed so that it can be used as a phosphate fertiliser.

First, the dried sewage sludge is converted into an H₂-rich synthesis gas and a pyrolysis coke in the gasification compartment of the IPV process used. In the combustion part of the system the coke is incinerated in a fluidised bed reactor to sewage sludge ash (SSA). Hence, the energy content of the pyrolysis coke and the synthesis gas serve as the energy supply for the subsequent process. In the second step, the generated SSA is thermochemically treated with Ca-Si carriers to bind the phosphate present in the SSA into plant-available mineral phases [1]. Preliminary tests have shown that

a mixture of Ca-rich secondary metallurgical slags (SEKS) and pure quicklime gave the best results in terms of P availability [2]. To test P availability in pot trials, three smelt products (mixtures of SSA, quicklime and SEKS) were selected and compared with pure SSA, one unfertilised control and triple superphosphate as reference fertiliser. P fertilisation levels were staggered into two dosing levels (fertilisation level 1 corresponding to half the phosphate requirement (150 mg P/pot) and fertilisation level 2 corresponding to the full phosphate requirement (300 mg P/pot).

MATERIALS AND METHODS

The integrated pyrolysis and incineration plant is operated by employees of Siegen University at the Entsorgungsbetrieb Siegen (sewage treatment plant of the municipality of Siegen), where the main process steps are simulated and evaluated using measurement technology. To develop the optimum formulations to produce the fertiliser, the precursors sewage sludge ash (SSA), secondary metallurgical slag (SEKS) and quicklime (CaO) were tested in the FEhS

smelting facility on laboratory scale. The produced fertilisers were further tested for their amount of extractable P using various solvents such as water, neutral ammonium citrate, citric acid and formic acid. The most satisfying fertiliser recipes were used in a top-blown rotary converter (TBRC) at the Institute of Nonferrous Metallurgy at the University of Leoben for upscaling trials (S2P-1 consisting of 70% SSA and 30% CaO, S2P-4 consisting of 40% SSA + 60% SEKS, and S2P-5 consisting of 50% SSA + 40% SEKS + 10% CaO). The TBRC was equipped with a 40-litre sample vessel, which has been lined with MgO refractory for the experiments. The TBRC is fired by a central CH₄-O₂ burner. Two batches of 30kg material of each mixture were fed into the furnace at a temperature of 1450°C. Each batch was treated in the furnace for about 30 - 45 minutes until the temperature of 1450°C was reached again and no more pellets were visible in the furnace. The tapping was carried out into a ZrO₂-coated slag pot.

In each case, the smelt products cooled in the pot overnight and

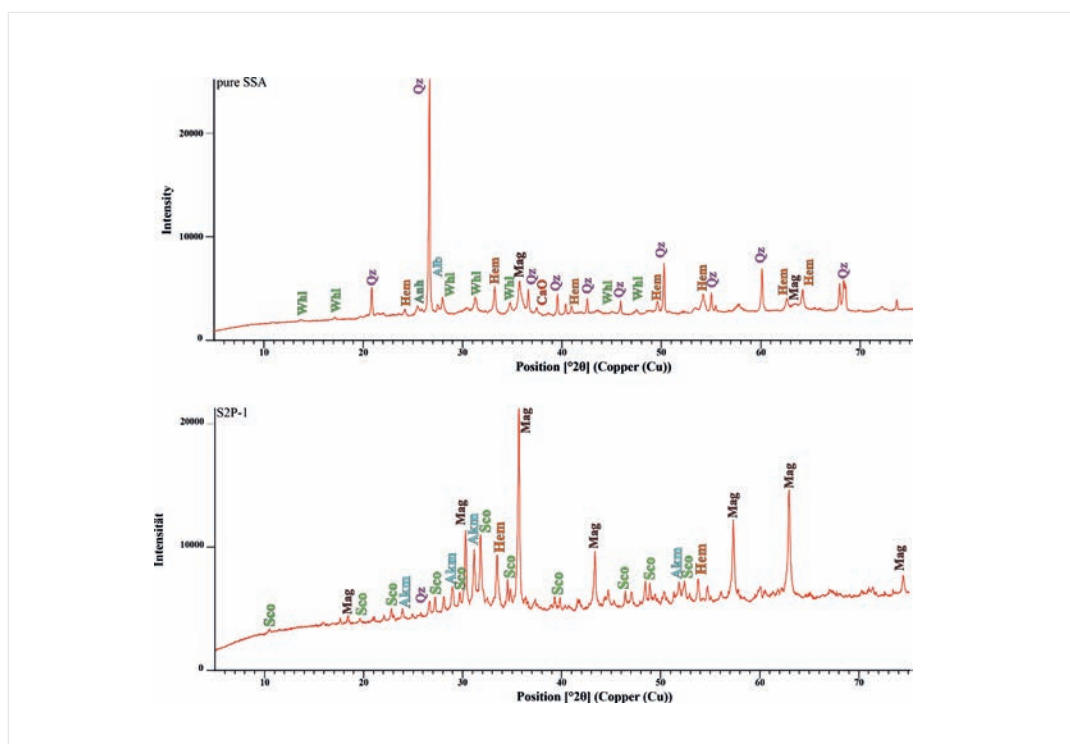


Figure 1: Mineralogical composition of the untreated SSA (top) and the S2P-1 TBRC product

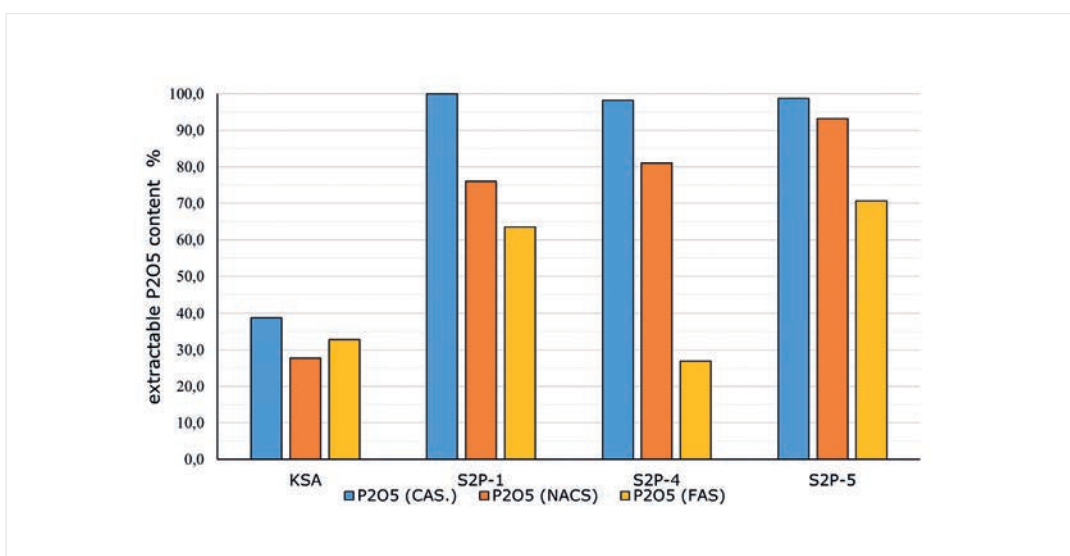


Figure 2: Extractable P_2O_5 contents for the extractants citric acid (CAS), neutral ammonium citrate (NACS) and formic acid (FAS)

were manually crushed the following morning. Representative sub-quantities were prepared for further investigations and the planned pot trials.

Two pot trials (one each with canola and corn) were used to compare the efficiency of the recycled fertilizer produced. Fertilisation levels were staggered into two dosing levels (fertilisation level 1 corresponded to half the phosphate requirement (150 mg P/pot) and fertilisation level 2 corresponded to the full phosphate requirement (300 mg P/pot). Corn and canola were selected for the pot trials because of their different P absorption capacities [3]. The seeds were sown in the

pots filled with a synthetic soil substrate (HGoTECH Substrate Type P0). Treatments were established in four replicates. The aboveground biomass was harvested at crop flowering, i.e. eight weeks after trial planting for canola and nine weeks after trial planting for corn.

RESULTS AND DISCUSSION

Figure 1 plots the mineralogical compositions of the untreated SSA (top) and the S2P-1 TBRC product (bottom) as determined by XRD. The untreated SSA is mainly composed of the minerals quartz (Qtz), hematite (Hem), magnetite (Mag) and albite (Alb).

| Analyt | Unit | SSA 2022 | SEKS | S2P-1 TBRC | S2P-4 TBRC | S2P-5 TBRC |
|--|-------|----------|-------|------------|------------|------------|
| As | mg/kg | 27.4 | 0.6 | 10.0 | 6.8 | 7.6 |
| Pb | mg/kg | 373.0 | 2.1 | 85.0 | 64.0 | 71.8 |
| B | mg/kg | 140.0 | 38.6 | 41.2 | 42.5 | 44.9 |
| Cd | mg/kg | 9.9 | 0.1 | 0.7 | 0.5 | 0.6 |
| Cr ^{VI} | mg/kg | < 1 | < 1 | < 1 | < 1 | < 1 |
| Cr | mg/kg | 833.0 | 527.0 | 152.0 | 101.0 | 97.1 |
| Co | mg/kg | 38.1 | 2.5 | 15.7 | 18.1 | 14.6 |
| Fe | mg/kg | n.a. | n.a. | n.a. | n.a. | n.a. |
| Cu | mg/kg | 1955.0 | 4.2 | 14.7 | 554.0 | 596.0 |
| Mn | mg/kg | n.a. | n.a. | n.a. | n.a. | n.a. |
| Mo | mg/kg | 39.1 | 5.3 | 146.0 | 9.4 | 11.2 |
| Na | mg/kg | 6580.0 | 309.0 | 3168.0 | 2702.0 | 3063.0 |
| Ni | mg/kg | 530.0 | 15.2 | 146.0 | 52.3 | 68.1 |
| Hg | mg/kg | 0.4 | < 0.1 | 0.1 | < 0.1 | 0.1 |
| Tl | mg/kg | 0.8 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| V | mg/kg | 187.0 | 305.0 | 58.9 | 163.0 | 141.0 |
| Zn | mg/kg | 5530.0 | 28.0 | 1640.0 | 732.0 | 1010.0 |
| P ₂ O ₅ | %-wt. | 12.6 | 0.4 | 6.6 | 5.4 | 6.8 |
| P ₂ O ₅ (CAS) | %-wt. | 7.1 | 0.4 | 6.9 | 5.1 | 2.3 |
| P ₂ O ₅ (NACS) | %-wt. | 5.1 | 0.4 | 6.4 | 3.3 | 3.5 |
| P ₂ O ₅ (H ₂ O) | %-wt. | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| P ₂ O ₅ (FAS) | %-wt. | 5.1 | 0.2 | 3.9 | 4.1 | 5.0 |

Table 1: Results of trace element determination after aqua regia digestion and P₂O₅ extraction with citric acid (CAS), neutral ammonium citrate (NACS), water (H₂O) and formic acid (FAS) of the starting materials and products from the TBRC

Whitlockite is the only phosphate mineral detected. After smelt treatment with Ca carriers in the TBRC, the expected change in phosphate mineralogy towards Ca-Si phosphates like silicocarnotite (Sco) can be observed, see Figure 1 (below). Furthermore, magnetite shows up next to hematite as Fe phases and åkermanite (Akm). For the products S2P-4 and S2P-5 the formation of nagelschmidite next to apatite was shown. This can be attributed to the increased formation of åkermanite, which binds more Si from the SSA due to the increased Al content of the SEKS used. The Si content is therefore no longer available for the formation of the above-mentioned Ca-Si-P phases and apatite is formed when the smelt cools.

The smelt treatment at the pilot plant scale reproduces the results obtained in the laboratory experiment in terms of modification of phosphate mineralogy towards phases showing improvement of P availability in laboratory analysis and in plant trials.

Table 1 shows the chemical trace element compositions (aqua regia) of the starting materials and the products generated in the TBRC. For elements of environmental relevance such as Cd, Tl, Hg and Cr^{VI}, only very low concentrations were detected, most of which were below the detection limit of the analytical method used (ICP-MS). For Ni, however, the S2P-1 recipe shows a concentration above the limit for fertilisers of 80 ppm [4]. From the data collected from the parent compounds, it appears that the high Ni contents are inherited from the SSA. This is also evident for the relatively high content of Zn. The contents of V originate both from the sewage sludge and from the SEKS slag used and show particularly elevated contents in the products S2P-4 and S2P-5, which have high proportions of SEKS.

Figure 2 shows the phosphate extractable with citric acid, neutral ammonium citrate and formic acid from sewage sludge ash and the smelt products S2P-1,

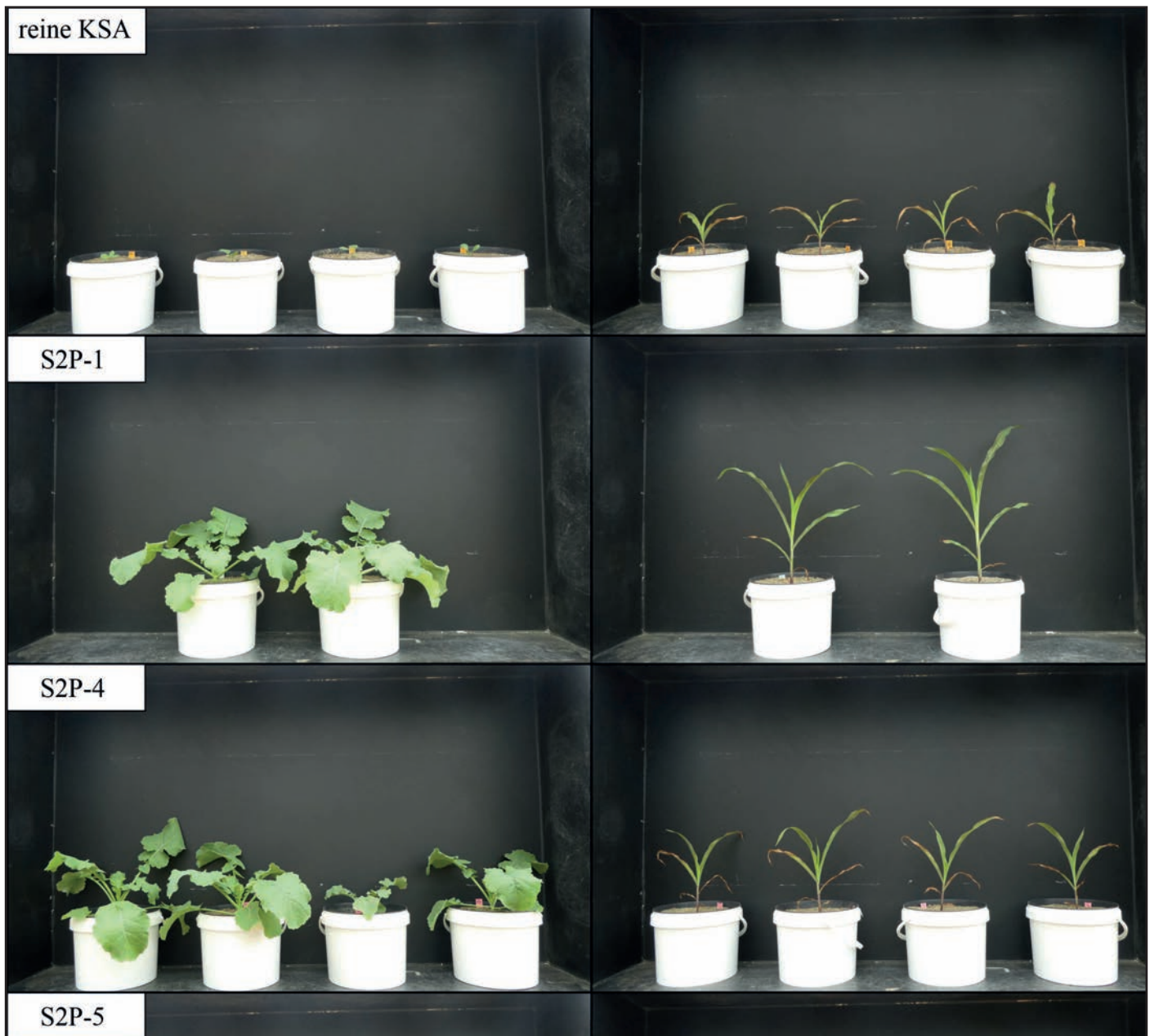


Figure 3: Results of the pot trials of fertiliser level 2 for the three tested smelt products as well as pure sewage sludge ash (canola on the left and corn on the right)

S2P-4 and S2P-5. Compared to the untreated SSA, the thermochemical treatment significantly improved the extractability of phosphate with citric acid and neutral ammonium citrate from the products S2P-1 and S2P-4. From S2P-1 in particular, the entire phosphate content could be extracted with citric acid and with an efficiency of 90% with neutral ammonium citrate. This result sug-

gests good plant availability of the latter products.

As expected, the plants fertilised with triple superphosphate (Figure 4 and 5) developed best, due to the high phosphate solubility of this fertiliser, followed by the plants of S2P-1. The plants of the other two products developed slightly worse than those fertilised with S2P-1. The plants fertilised

with pure SSA had the worst growth by far. These plants were retarded even compared to the unfertilised control (Figure 3). However, the difference between canola and corn is significant. Whereas rapeseed has a very good assimilation capacity for phosphate and responded well to the smelt products in terms of yield, corn showed significantly poorer yield developments with the smelt pro-

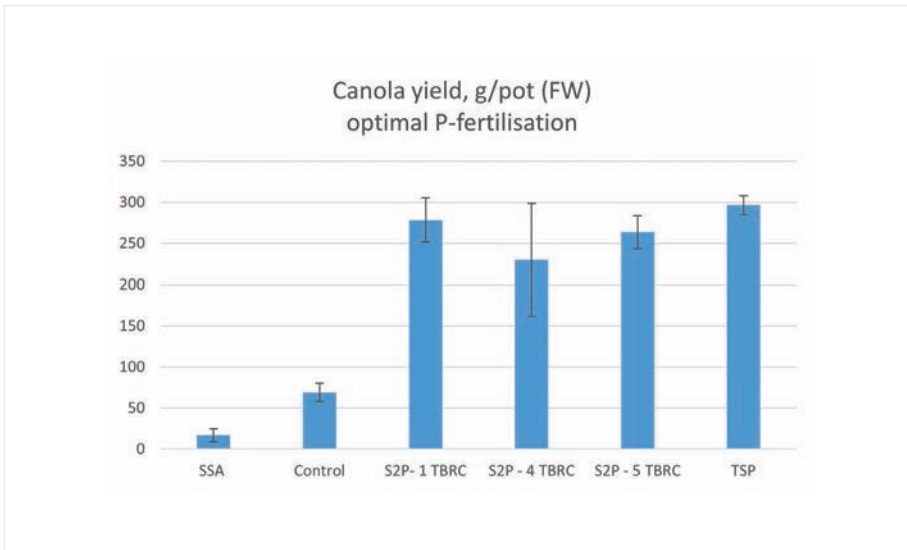


Figure 4: Fresh biomass yield of canola at optimum P supply. Comparison of the produced experimental fertilisers with the pure SSA, the unfertilised control and plant-available mineral fertiliser (triple superphosphate, TSP)

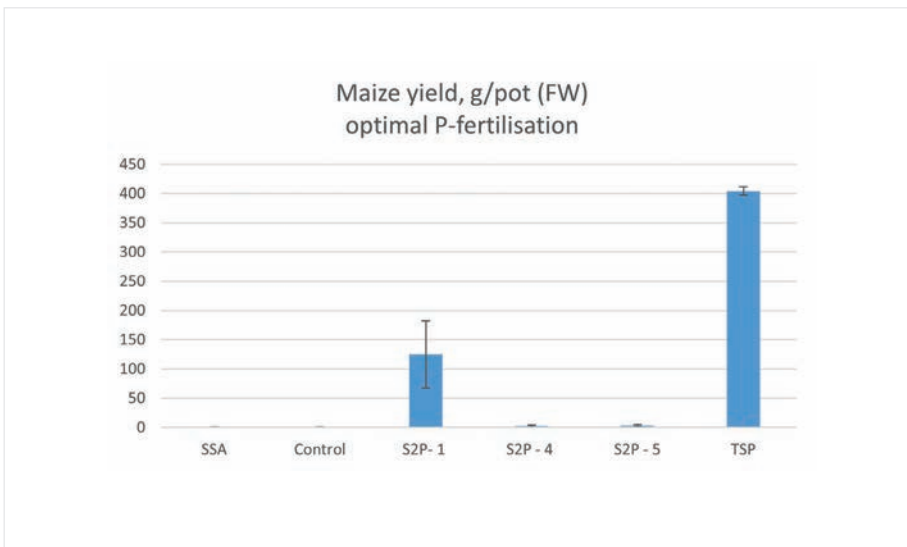


Figure 5: Fresh biomass yield of corn at optimum P supply. Comparison of the produced experimental fertilisers with the pure SSA, the unfertilised control and plant available mineral fertiliser (triple superphosphate, TSP)

ducts S2P-4 and S2P-5. This yield result for corn roughly reflects the neutral ammonium citrate solubility of phosphate, which was slightly better than that of SSA but significantly worse than that of S2P-1 for S2P-4 and S2P-5 (Figure 2). The results illustrate that good P solubility of the fertilisers used is particularly important for plants with

lower P assimilation capacity. Overall, a first positive conclusion can already be drawn. Phosphate availability could be significantly improved by thermal treatment compared to pure SSA, which was confirmed both by the corresponding phosphate extraction methods for fertilisers and in the pot trials. However, the smelt products

are not equivalent, so the choice of the appropriate target crop is also important when using such products.

SUMMARY

The recovery of phosphate from sewage sludge is possible in various ways. The integrated pyrolysis and incineration with subsequent thermochemical treatment considered in this paper is characterised by energy self-sufficiency. In the investigations presented here, selective mixing of sewage sludge ash, quicklime and secondary metallurgical slags produced smelt products that were significantly improved in their phosphate solubility compared to pure sewage sludge ash. This was also evident from the biomass yields in two pot trials. However, the crops differed in their response to the experimental fertilisers. Canola, which has a good P assimilation capacity, was able to convert the phosphate of the melting products into yield significantly better than corn. To ensure efficient use of these recycled products, the use of such products should be matched to the crop species.

ACKNOWLEDGEMENTS

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KONDEOS PROJECT – CONDITIONING OF ELECTRIC ARC FURNACE SLAG FOR THE PRODUCTION OF AN EBV-COMPLIANT PRODUCT

D. Algermissen, M. Sc.; D. Ebert, M. Sc.
(FEhS - Building Materials Institute)

Dr.-Ing. M. Foppe; Dr. rer. nat. M. Cancarevic;
M. Kassenbrock, M. Sc.
(Georgsmarienhütte GmbH, Georgsmarienhütte)

Dipl.-Oec. H.-J. Rauen; Dipl.-Ing. H. Tabani
(Hermann Rauen GmbH & Co. formerly Steinhandel Rauen, Mülheim)

Professor Dr.-Ing. R. Deike; M. Großarth, M. Sc.;
J. Kuschewski, M. Sc.
(University of Duisburg-Essen, ITM)

The steel industry is facing new challenges in road construction due to altered leaching processes and the new requirements of the Substitute Building Materials Ordinance (Ersatzbaustoffverordnung, EBV), which came into effect in August 2023. To continue meeting the high standards of material classes SWS 1 and SWS 2, additional measures are required from steel producers and slag processors. In the research project „KONDEOS“, measures such as metallurgical conditioning of electric arc furnace slag, specific cooling and processing were tested at the Georgsmarienhütte electric steel plant. Georgsmarienhütte collaborated with slag processor Hermann Rauen, DK Recycling and Roheisen GmbH, the University of Duisburg-Essen and the FEhS-Institut during this research project.

SLAGS FROM THE STEEL INDUSTRY

Production and utilisation

The German iron and steel industry produces approximately 12.5 million tonnes of slag per year, constituting the largest mass flow of by-products in that sector [1]. These slags are mainly classified into two categories: blast furnace slag (63%) and steel furnace slag (37%). Blast furnace slags are fully uti-

lised, primarily as granulated blast furnace slag in the cement industry. Steel furnace slags, including electric arc furnace slags, have more diverse applications. However, road construction is the primary field of application, with approximately two-thirds of the utilised slags being marketed in this sector in the year 2022.

The German Substitute Building Materials Ordinance

Until 2005, the Joint Federal/State Waste Management Working Group (LAGA) made unsuccessful attempts to establish a nationally uniform regulation for assessing the environmental compatibility of mineral by-products and waste. Consequently, the Federal Ministry for the Environment, Nature Conservation, Nuclear Safety and Consumer Protection (BMUV) was asked by LAGA to take the lead in this matter. Over a period of 16 years, the so-called „Mantelverordnung“ was developed, which includes, among other things, the Substitute Building Materials Ordinance (EBV). On 16 July 2021, this regulation was published in the Federal Law Gazette and finally came into effect on 1 August 2023, following a two-year transitional period [2, 3].

Until then, the environmental parameter limits determining the possible uses of electric arc furnace slag had been set by individual federal states, often referring to the Technical Delivery Conditions for Aggregates in Road Construction (TL Gestein-StB) [4]. With the introduction of the EBV, two leaching procedures with a water/solid ratio of 2:1 were implemented, accompanied by an adjustment of the limits and the addition of molybdenum as a new parameter. Examinations of electric arc furnace slag (EAFS) from FEhS member plants suggested that the new procedures and assessment criteria would often lead to the inability to meet the required limits of material classes SWS 1 and SWS 2. This posed a potential threat to the usability in the primary application area of road construction.

The Research Project „KONDEOS“

The research project KONDEOS, supported from 2019 to 2023 as part of the funding initiative „r+Impuls – Innovative Technologies for Resource Efficiency – Impulses for Industrial Resource Efficiency“ by the Federal Ministry of Education and Research, was based on extensive preliminary investigations. These aimed to develop metallurgical processes to condition electric arc furnace slags in such a way that their environmental compatibility concerning the EBV leaching processes and prescribed limits is improved.

Led by Georgsmarienhütte GmbH and in close collaboration with Rauen GmbH & Co. formerly Steinhandel Rauen, DK Recycling and Roheisen GmbH, the Chair of Metallurgy and Forming Technology

at the University of Duisburg-Essen and the FEhS Institut für Baustoff-Forschung e.V., the insights gained from extensive laboratory and operational trials were successfully integrated into the steelworks' production process.

CONDITIONING OF THE ELECTRIC ARC FURNACE SLAG

Initial position

Until the EBV came into effect, electric arc furnace slags typically met the demanding criteria of material class Z1.1 or SWS 1. This fact, combined with their positive building physics properties, made them sought-after construction materials in road construction. However, regulatory changes have led to situations in some electric steel plants where the EAFS no longer meets the requirements of even material class SWS 2 according to the EBV, resulting in the loss of usability in the primary application area of road construction. The consequence is the disposal of EAFS in landfills. Internal investigations revealed that, in many cases, there is insufficient landfill space, leading to a potentially existential threat for an electric steel plant.

Throughout various preliminary investigations, laboratory procedures were developed to enhance environmental compatibility according to the EBV, enabling the fulfilment of material class SWS 1 requirements [5-7]. The focus was on the leaching of molybdenum, a new parameter in the EBV for steel furnace slags. The results showed that a reduction in basicity fundamentally has a positive impact on environmental compatibility. In conjunction with rapid cooling in particular, the leaching of moly-

bdenum can be significantly reduced without adversely affecting other parameters.

Experimental injection system

In the context of industrial production scales, transferring such laboratory experiments proves to be extremely challenging and risky. This is due to the instability of operational conditions and the necessity to reliably implement the procedure even with varying chemical compositions of EAF slags. Conditioning in the liquid state is particularly challenging, as it must occur without a dedicated treatment station for logistical and economic reasons. Simultaneously, decoupling this treatment from the actual electric arc furnace process requires a thoughtful approach to avoid adversely affecting the metallurgical slag work required for the steel production process.

In the KONDEOS research project, an experimental injection system was therefore installed directly under the electric arc furnace, in close proximity to the slag pot. This system allows conditioning agents to be introduced into the slag pot during the slag tapping process. This approach utilises the heat energy of the slag and the kinetics in the slag pot to introduce and dissolve conditioning agents into the melt without additional energy expenditure. Figure 1 illustrates the flow of molten electric arc furnace slag from above into the slag pot. The introduction of conditioning agents is carried out using a lance above the slag pot.

Over 150 experiments were conducted in the electric steel plant as part of this project, with appro-



Figure 1: Slag pot positioned under the electric arc furnace

ximately 15–20 tonnes of electric arc furnace slag conditioned in each experiment. For this purpose, the originally constructed experimental injection system had to be significantly modified to increase the delivery capacity significantly and keep the delivery rate as constant as possible. Only in this way could sufficient, defined quantities of conditioning agents be introduced.

The required performance enhancement of the experimental injection system in the operational process was gradually achieved by selectively varying the following parameters:

- the throttle at the outlet (adjustment of the outlet cross-section from the sending vessel)
- the camber pressure
- the amount of conveying gas
- the fluidisation degree of the conditioning agent (loosening).

Through the fine-tuning of the injection parameters, the average injection rate for conditioning mixture 1 was increased by 19%, while the variation in the average injection rate compared to the initial state was reduced by 15%.

For quartz sand, the injection rate was increased by 61%, and the variation in the average injection rate was reduced by 57% through optimal throttle opening sizing combined with optimised plant parameters.

In parallel with the improvement of the treatment plant, difficulties in injection, such as blockages,

were effectively minimised and largely eliminated. Thanks to the increased average injection rate for both conditioning mixture 1 and quartz sand, it was ensured that sufficient conditioning takes place during the tapping of the furnace slag from the electric arc furnace. The successful alignment of the average injection rate from batch to batch enables nearly uniform conditioning of successive batches, which is crucial for integration into the operational workflow. Due to continuous delivery, only small amounts of undissolved conditioning agents occurred, which could be detected by X-ray analysis. However, thorough further optimisation of the injection rate based on the amount of slag, this was avoided in the later stages of the project. This is particularly important when injecting quartz sand for occupational and health protection reasons.

Cooling of the slag

Due to the predetermined tapping intervals of slag from the electric arc furnace, as well as internal steelworks and slag pot logistics, it was necessary to significantly reduce the cooling times of the slag in the slag pot and the initiation of the separation of metal droplets – a process whereby metal droplets are separated from the slag – from the 24 hours originally planned in the project. This adjustment proved crucial, especially for conditioning mixture 1, to provide sufficient time for effective segregation of the produced reduction metal, facilitating the later separation of metal and slag. The adaptation of the timelines was successfully integrated into the regular steelworks logistics, reducing the slag pot cooling time to approximately 1 hour. This ensured a reliable

| Molybdenum | SWS-1 | SWS-2 | > SWS-2 |
|------------------------|-------|-------|---------|
| Conditioning mixture 1 | 65% | 35% | 0% |
| Quartz | 29% | 69% | 2% |

Table 1: Percentage classification of treated EOS (8–11mm) into EBV material classes based on Mo leaching from shaking procedure 2:1, separated by reducing and non-reducing treatment

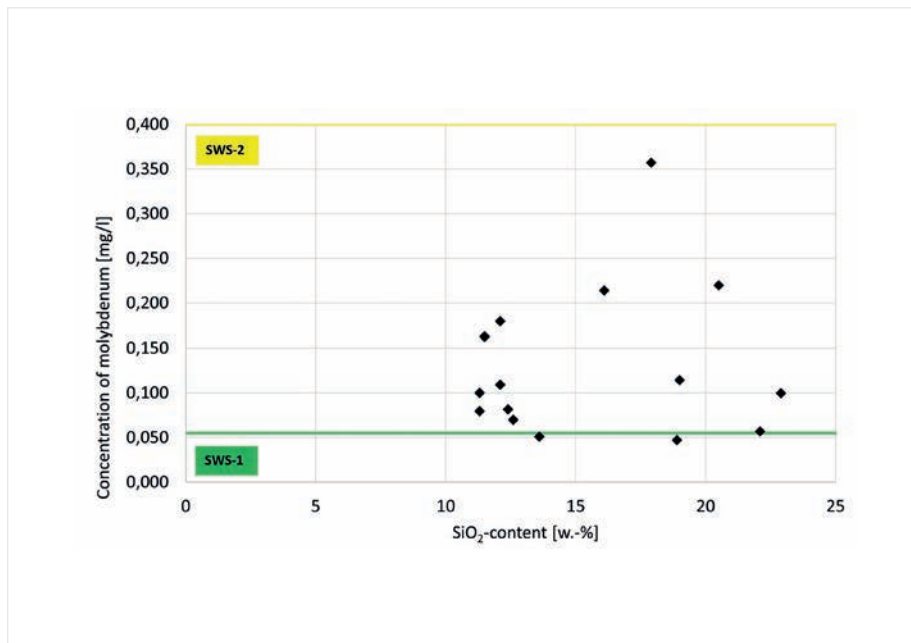


Figure 2: Relationship between Mo concentration and SiO₂ content of EOS during slow cooling without reduction; with limits according to the Substitute Building Materials Ordinance (EBV)

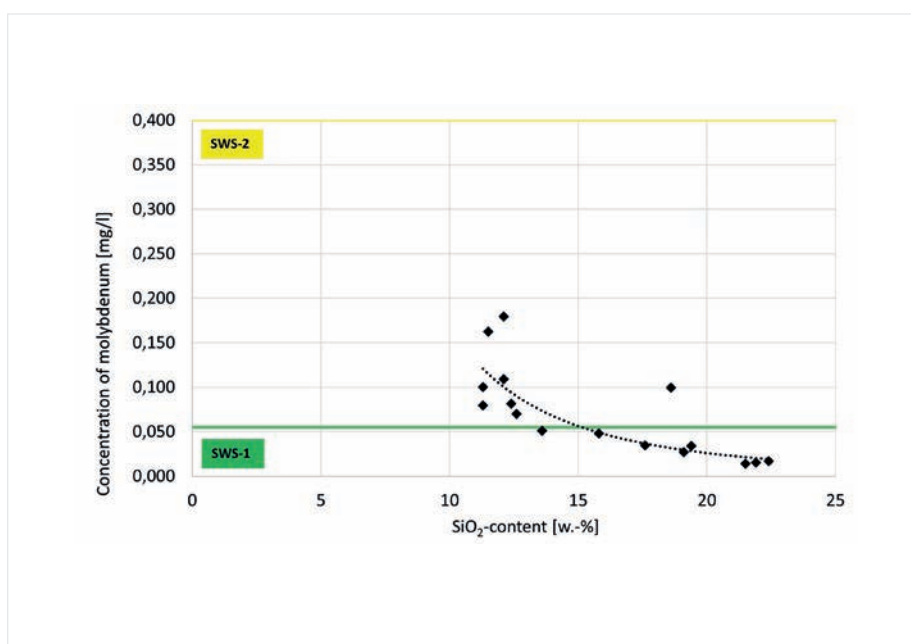


Figure 3: Relationship between Mo concentration and SiO₂ content of EOS during fast cooling without reduction; with limits according to the Substitute Building Materials Ordinance (EBV)

operational workflow and smooth slag pot rotation. In particular, the final experimental campaigns, where approximately 700 tonnes of slag were conditioned in each, would not have been feasible without robust slag pot logistics.

Regardless of this adjustment, preliminary experiments already indicated that rapid cooling of electric arc furnace slag is generally advantageous for its subsequent quality. Therefore, a section of the slag bed was restructured experimentally to allow for the placement of hematite plates. These plates significantly accelerate the heat dissipation from the slag compared to a conventional layer of cold slag.

QUALITY OF THE GENERATED PRODUCTS

The conditioning successfully reduced the leaching of electric arc furnace slag. Depending on the type of conditioning agent and the cooling method, the defined goal of meeting the requirements of material class SWS 1 according to the Substitute Building Materials Ordinance was achieved. The conditioning did not cause any impairment of the physical properties of the slag regarding its use in road construction.

Slag quality

The treated batches were examined according to the specifications of the new Substitute Building Materials Ordinance. The focus was on the shaking method with a ratio of 2:1 in the particle size fractions of 8–11mm and 0–22.4mm, with the fines fraction < 4mm at 45% by mass. Simultaneously, an analysis of the chemical and mineralogical composition

| Comparison slow cooling / fast cooling | High Mo-Scrap Menu with Sand Treatment | Regular Scrap Menu with Sand Treatment | Regular Scrap Menu without Sand Treatment |
|---|---|---|--|
| Mo leaching | -69% | -58% | -19% |

Table 2: Weighted means of the percentage improvement in Mo leaching from shaking procedure 2:1 of quickly cooled EOS (8–11mm), separated by scrap menu and corresponding sand treatment

was conducted to gain insights into the effects of the conditioning agents, as the underlying mechanisms are not yet fully understood.

The use of conditioning mixture 1 in combination with conventional bed cooling successfully reduced the leaching of molybdenum and met the limits of material class SWS 1. However, the leaching of vanadium was negatively influenced, causing the EAFS to not meet the requirements of material class SWS 1. In contrast, a pure treatment with sand under regular bed cooling resulted in a reduced leaching of molybdenum, but not to a sufficient extent to meet the SWS 1 limit of 55 µg/l. A comparison of the results for molybdenum is presented in Table 1.

However, the reducing treatment of EAFS comes with various disadvantages, such as:

- CO₂ emissions during reduction or CO₂ footprint of the reducing agent
- strong foaming/overflowing of the slag pot during treatment
- high costs for the reducing agents.

A pure treatment with quartz sand, without reducing agents, shows no statistically discernible correlation of molybdenum leaching with the

examined parameters, such as the SiO₂ content of the EAFS, as shown in Figure 2. On the other hand, samples treated with quartz sand with rapid cooling show a correlation to SiO₂ content and a correlation between molybdenum concentration and quartz sand conditioning, as depicted in Figure 3.

Based on these findings, several investigation campaigns were conducted, both with a usual and a comparatively high molybdenum input into the electric arc furnace. This confirmed the positive influence of quartz sand treatment and rapid cooling even under worst-case conditions. During these campaigns, one sample was rapidly cooled, while another sample was conventionally cooled in the bed for reference (see Table 2).

By applying this rapid cooling, the limit for molybdenum according to material class SWS 1 could be met in 83% of the batches compared to slow cooling.

However, this rapid cooling, depending on the method, leads to the formation of a firmer slag, posing a particular challenge for the processing technology. One essential aspect is the generation of a uniform particle size band, which is indispensable for efficient marketing. In this regard, the compa-

ny Rauen utilised its expertise to optimise crushing and screening technology so that the conditioned EAFS can be broken and classified similarly well to the conventional, non-conditioned EAFS.

Regarding the building physics properties, there is even a tendency for improvement through conditioning. Thus, the goal of the project was achieved, ensuring that no deterioration occurs due to conditioning to exclude potential losses in marketability of these properties. An example of this is the volume increase in the steam test (168 hours), which averaged 0.8% and reached a maximum of 1.2%. The resistance to crushing was also slightly improved.

Experimental campaign in production operation

The testing of the acquired knowledge was carried out on a large scale in operational production to ensure a robust verification. In this extensive experimental campaign, a total of 30 batches of electric arc furnace slag were successfully conditioned, comprising a total volume of 700 tonnes. These batches were processed together and subsequently thoroughly sampled to evaluate the effectiveness of conditioning at the operational level. In addition to the shaking method 2:1 used so far, the upward perco-

lation method 2:1, which is considered a reference method according to the Substitute Building Materials Ordinance (EBV), was also used for this campaign.

The results obtained demonstrate that the conditioning of electric arc furnace slag leads to a secure compliance with the requirements of material class SWS 2, making a positive contribution to the sustainability and environmental compatibility of the end product in the construction industry.

Regarding the specific elements molybdenum and vanadium, the results show a differentiated development. Although the leaching of molybdenum is slightly above the limit of SWS 1, indicating the effectiveness of conditioning, there is still room for further optimisation. On the other hand, the study illustrates that rapid cooling is required to achieve the requirements of SWS 1 with respect to vanadium. These findings highlight the need for precise control of the cooling process to achieve the desired quality properties of the slag while complying with regulatory requirements.

Furthermore, experiments were conducted to substitute quartz sand with foundry sands, which are currently predominantly landfilled. This could make a significant contribution to the circular economy, even though the effectiveness of conditioning has been less successful than with natural material.

The successful implementation of this large scale experimental campaign marks an extremely successful conclusion of the KONDEOS project and is a crucial step towards the sustainable optimisation of electric arc furnace slag conditioning in the context of road construction. The insights gained contribute to deepening the understanding of the complex relationships between operating conditions, conditioning processes and product quality. This not only contributes to industrial efficiency but also provides a solid foundation for future developments and innovations.

Separation iron / reduction metal

During laboratory experiments, analyses were conducted on the recovery of separated iron and the quality of the corresponding magnetic fraction. Initially, it was observed that between 7% and 13% of the slag consists of large, nearly entirely metallic particles. These particles have the disadvantage of

potentially affecting the processing of the mineral fraction, as they can lead to increased wear and longer downtime of crushing equipment. However, due to their size and the fact that they consist almost entirely of iron, they can be relatively easily separated through magnetic separation. After undergoing such an initial separation process, the mineral fraction can be further reduced to the desired particle size.

However, this reduction process leads to the release of additional magnetic particles from the slag matrix, either fully or partially, making them extractable through magnetic separation as well. Preliminary laboratory results suggest that an additional 7% to 20% of the magnetic fraction can be separated in this way. Since, for various reasons already described, slag reduction is currently not performed, further research activities would be necessary in the field of slag reduction and subsequent metal separation.

SUMMARY AND OUTLOOK

The project has successfully demonstrated that the results from the laboratory scale can be applied to operational use, yielding similarly positive effects in reducing leaching. The large-scale experimental campaign in production confirmed the effectiveness of electric arc furnace slag conditioning for the secure compliance with material class SWS 2 in road construction. The investigations of molybdenum and vanadium revealed differentiated results. While molybdenum leaching was slightly above the limit of SWS 1, rapid cooling was necessary to meet the SWS 1 requirements for vanadium.

Conditioning mixture 1 proves to be suitable for improving quality, but various factors hinder comprehensive use in operations. Besides costs, the foaming due to the formation of CO and CO₂ poses a problem, as it would require cleaning efforts in the slag pot area, potentially leading to undesired production interruptions. In contrast, conditioning with quartz sand is more manageable and economical. The critical criteria here are the conveying speed and the timing of the addition. This ensures that the slag in the slag pot evenly distributes the quartz sand through kinetic effects alone, and the heat content is sufficient to dissolve the sand. In this way, material class SWS 2 can be reliably adhered to. However, to achieve material class SWS 1, rapid cooling is required as a second step in this process, which so far has

only been implemented for smaller subsets. Further research is therefore needed to cool the slag quickly in operational scale without moisture and without increasing the oxygen partial pressure, to achieve further quality improvement.

ACKNOWLEDGMENT

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INVESTIGATIONS OF SLAGS FROM NEXT GENERATION STEEL MAKING PROCESSES

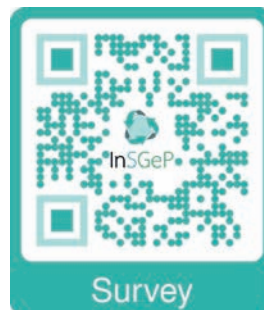


A. Morillon, PhD; D. Algermissen, M.Sc.
(FEhS – Building Materials Institute)

The InSGeP project, titled „Investigations of Slags from Next Generation Steel Making Processes“, is a European research initiative co-funded by the EU Research Fund for Coal and Steel (RFCS), launched on 1 July 2023. As the steel industry prepares for the transformation of the steelmaking process to reduce CO₂ emissions using direct reduced iron (DRI) with varying reduction degrees, hot briquetted iron (HBI), hydrogen plasma smelting reduction (HPSR) or electrical smelters for low-grade ores, it is crucial to understand the by-products, such as slag, to uphold the commitment to zero waste. To move the transition forward, the InSGeP project is investigating slags resulting from next generation steelmaking. The project relies on the limited amount of slag currently produced from next generation steel production in Europe and abroad as well as on laboratory scale, pilot scale and industrial scale tests that will be performed based on the needs of the partners involved. The project brings together 13 partners from Austria, Belgium, France, Germany, Italy and Spain, including 5 steelworks (voestalpine, Ori Martin, AMMR, Sidenor and Saarstahl), 6 research and technology organisations (FEhS, SSSA, RINA-CSM, K1-MET, CRM

and BFI), 2 suppliers (Tenova and Primetals) and 3 subcontractors, including ESTEP.

To better understand the current situation and future needs of the European steel industry, the project is conducting an anonymous survey. Please scan the following code to access it. For further information please visit the project webpage: www.insgep.eu. <<<



THE USE OF METALLURGICAL SLAGS AS AN INDUSTRIAL AGGREGATE IN CONCRETE

Dr.-Ing. V. Feldrappe; Dr.-Ing. A. Ehrenberg
(FEhS – Building Materials Institute)

INTRODUCTION

In addition to cement, water and concrete additives, concrete consists of around 70 vol.% of aggregates, whose physical, mineralogical and chemical properties are largely responsible for the load-bearing capacity and durability of a concrete structure. In 2022, 253 million tonnes of gravel and sand and 210 million tonnes of crushed natural stone were extracted in Germany. For gravel and sand, the annual area equivalent is 9.4 km² at a „mining thickness“ of 15 m, and a further 3.2 km² for crushed natural stones at 25 m [1]!

48% of gravel and sand is used as concrete aggregate [2]. Even in the coming decades, there is no sign that the enormous demand for materials will diminish. Various scenarios presented by the German Building Materials Association (bbs) assume a demand for sand/gravel of 209-261 million tonnes for the year 2040 [2]. Industrial by-products are one way of partially replacing natural aggregates. This conserves natural resources and contributes to a circular economy. In principle, metallurgical slags such as blast furnace slag (BFS), steel slags (electric arc furnace – EAF – or basic oxygen furnace – BOF – slags) can do this. BFS has been approved for use as an aggregate in concrete for about 100 years [3], and has been used extensively [4, 5]. However, an analogue regulation for other metallurgical slags does not yet exist in Germany, whereas steel slags can already be used as an aggregate for concrete in some other countries [6-10].

Due to the manufacturing process, steel slags may contain higher levels of free lime or periclase. When these react with water, the result might be an increase in volume which can lead to spalling or structural damage to the concrete. The relevant European harmonised material standard, EN 12620 [11], does not

yet include an assessment of this important technical property. From a technical point of view, this is the biggest obstacle to the safe use of metallurgical slags as aggregates in concrete. Although the „steam test“ method in accordance with EN 1744-1 [12] and the associated limiting values have been introduced for road construction, these cannot be transferred to concrete construction due to the completely different boundary conditions. From a regulatory point of view, the main obstacle to the use of steel slag as a concrete aggregate in Germany is the limit of 600 mg/kg for the total chromium content of the slag, which is specified in Annex 10 (ABuG) of the Muster-Verwaltungsvorschrift Technische Baubestimmungen (MVV TB) [13], defined by the German Institute for Building Technology (DIBt). This value is several orders of magnitude lower than the content of both current and future steelmaking slags. In some other European countries, the evaluation of the environmental impact is based only on leaching properties, but not on the solid content of heavy metals.

The FEhS-Institut had already worked on a test method for assessing the volume stability of steel slag to be used in concrete in the IGF research project 12968 N [13] from 2001 to 2003. However, no satisfactory method could be derived at that time. The subject was not pursued further, especially as it did not have the urgency that it has today against the background of discussions about limited natural resources, intensified recycling management and the transformation of the steel industry associated with the production of new types of steel slag.

OBJECTIVES

In the new IGF research project 21567 N [15], extensive investigations were carried out between 2020 and 2023 on the technical suitability and environ-

| Parameter | | LDS 1 | LDS 2 | LDS 3 | LDS 4 | LDS 5 | EOS 1 | EOS 2 | EOS 3 | EOS 4 | EOS 5 | EOS 6 | EOS 7 | CUS |
|--------------------------------|-------------------|---------|-------|-------|-------|-------|--------|-------|-------|-------|--------|--------|-------|-------|
| CaO | wt. % | 49.0 | 48.8 | 44.8 | 44.2 | 47.2 | 47.5 | 25.1 | 29.5 | 28.4 | 27.6 | 27.4 | 19.8 | 2.9 |
| MgO | wt. % | 5.2 | 5.2 | 1.6 | 1.9 | 3.0 | 4.7 | 6.6 | 4.5 | 8.8 | 9.7 | 9.7 | 3.9 | 2.0 |
| SiO ₂ | wt. % | 13.1 | 12.7 | 22.7 | 12.0 | 8.9 | 21.7 | 8.0 | 9.2 | 13.3 | 14.4 | 11.7 | 8.4 | 30.3 |
| Al ₂ O ₃ | wt. % | 0.90 | 0.94 | 1.2 | 2.39 | 5.08 | 5.98 | 4.44 | 7.49 | 5.59 | 8.46 | 4.42 | 7.42 | 3.51 |
| Fe _{total} | wt. % | 16.8 | 17.5 | 16.2 | 20.9 | 16.7 | 22.9 | 28.4 | 32.0 | 23.9 | 18.9 | 26.7 | 32.7 | 39.0 |
| Cr ₂ O ₃ | wt.-% | 0.14 | 0.16 | 0.21 | 0.50 | 0.28 | 2.34 | 2.17 | 2.74 | 1.81 | 2.18 | 1.08 | 4.17 | 0.11 |
| Cr-VI | mg/kg | < 1.0 | | | | | | | | | | | | |
| Chloride | wt. % | < 0.001 | | | | | | | | | | | | |
| Free lime (Franke) | wt. % | 9.5 | 11.7 | 0.41 | 3.9 | 11.0 | < 0.20 | 0.44 | 0.40 | 0.22 | < 0.20 | < 0.20 | <0.20 | <0.20 |
| Free lime (XRD) | wt. % | 8.4 | 6.8 | 0.1 | 1.9 | 3.6 | 0 | 0 | 0 | 0.3 | 0 | 0 | 0 | 0.1 |
| Periclase (XRD) | wt. % | 0 | 1.8 | 0 | 0.3 | 1.1 | 2.4 | 0 | 0 | 0.1 | 0 | 0 | 0 | 0 |
| Apparent density | g/cm ³ | 3.49 | 3.49 | 3.35 | 3.62 | 3.46 | 3.43 | 3.51 | 3.98 | 3.71 | 3.67 | 3.83 | 3.89 | 3.71 |

Table 1: Chemical, mineralogical and physical characteristics of the 13 industrial aggregates (LDS = BOF slag, EOS = EAF slag, CUS = copper slag)

mental compatibility of steel and copper slags as industrial aggregates in concrete. The main tasks of the research project were

- to develop a practical test method for the evaluation of volume stability in concrete
- to assess the technical properties of concretes made with slag aggregates
- the evaluation of environmental properties.

This article deals with the technical aspects of the project. Another article will deal with the environmental aspect, discussing in detail the relevance of solid limit values for heavy metals and the elution behaviour of aggregates, concretes made with them and recycled aggregates obtained from these concretes.

MATERIALS AND CONCRETE MANUFACTURING

Aggregates

13 different metallurgical slags were used within the project (Table 1). Commercially available fine and coarse fractions of screened quartzitic aggregate from the Lower Rhine region and crushed calcitic aggregate from the Sauerland region were used as natural references.

All aggregates were analysed according to the requirements of DIN EN 12620. Their water absorption capacity was of particular interest.

Initially, the industrial aggregates had to be crushed and screened into the required fractions. Aggregate mixes were produced from the individual fractions in the A/B range of the grading curve in accordance with Annex L of DIN Technical Report 100. For that, the „least squares method“ was used. For the development of the volume stability test method, aggregate mixes were produced with the maximum particle size defined in the statistical design (Table 3) described below. Aggregate mixes with a maximum particle size of 16 mm were uniformly used for the concretes to be tested for technical concrete properties.

Table 1 summarises some chemical, mineralogical and physical parameters of the 13 industrial aggregates. Chemical analyses were carried out using XRF (major and minor constituents), ICP-MS (trace elements), infrared spectroscopy (CO₂, H₂O) and titration (Franke method for free lime, chloride). Mineral phases were determined by quantitative XRD including Rietveld analysis. The apparent density was determined according to DIN EN 1097-6.

In terms of volume stability, the free lime content of the aggregate is certainly the most important factor. This particularly applies to the BOF slags due to the overdosage and/or insolubility of lime, whereas the EAF slags are not critical in this respect. For EAF slags an excessively high periclase content may be

| Concrete for | | | XC4 Lab | XF3 Lab | XF4 Lab | Demonstrator test | |
|-----------------------------|-----------------------|-------------------|----------------|------------|------------|-------------------|--------------|
| | | | | | | Lab | RMX Plant |
| Cement content | | kg/m ³ | 320 | 360 | 360 | 300 | 302 |
| Water/cement ratio | | - | 0.60 | 0.50 | 0.50 | 0.60 | 0.60 |
| Air content | | vol.-% | 1.5 | 1.5 | 5.0 | 1.5 | 1.5 |
| Plasticiser | | wt.% of c | - | - | - | 0.4 | 0.7 |
| Aggregate | | l/m ³ | 687 | 686 | 650 | 694 | 690 |
| Fine aggregate 0/2 mm | natural industrial | Vol.-% | 0 32.5-36.5 | | | 35.0 0 | 39.2 0 |
| Coarse aggregate 2/8 mm | natural industrial | | 0 27.0-36.0 | | | 25.0 0 | 27.5 0 |
| Coarse aggregate 8/16 mm | natural industrial | | 0 31.0-37.5 | | | 0 40.0 | 14.9 18.4 |

Table 2: Concrete compositions for the evaluation of the concrete properties

| Influencing factors | Unit | Variation range |
|--------------------------------|-------|-------------------|
| Free lime content of aggregate | wt.-% | high; middle; low |
| Max. aggregate size | mm | 4; 8; 16 |
| Water/cement ratio | - | 0.40; 0.50; 0.60 |
| Test temperature | °C | 60; 80 |
| Time of testing | d | 1 – 14 |

Table 3: Factors affecting volume stability and their range of variation

problematic, resulting from refractory materials. With regard to the free lime content, it should be noted that the values measured by different methods may differ significantly.

Cements

A commercially available blast furnace cement CEM III/A 42.5 N was used for the development of the test method and the concrete tests. Detailed analysis of the cement showed that all the requirements of DIN EN 197-1 were met.

Concrete compositions

The concretes for the development of the test method were for-

mulated according to the specifications of the statistically design (see Table 3). Both the fine aggregate range up to 2 mm and the coarse range > 2 mm consisted of the same aggregate. Quartzitic natural sand of fraction 0/2 from the Lower Rhine was only used as a fine aggregate in the mixes with limestone chippings. With regard to the use of slag as a substitute for natural aggregates, this procedure represents a „worst-case scenario“ from both the concrete and the environmental point of view. The water requirement of the aggregate was determined based on the respective k-value of the aggregate mix. The required

cement content was calculated from the k-value and the defined water/cement (w/c) ratio of the concrete.

To test the technical properties of the concrete, the concretes were formulated according to the defined limit compositions of the German concrete standard DIN 1045-2 for exposure classes XC4 and XF3/XF4. However, as is usual for concretes with chippings, the cement content was slightly increased to compensate for the negative influence of the crushed aggregate on the workability of the fresh concrete with a higher paste content (Table 2).

A typical ready-mixed concrete mix design for crushed aggregates was used for the demonstrator test and the necessary preliminary laboratory tests. Aggregate mixes with a maximum particle size of 16 mm were used, combining sand or gravel in the fractions up to 8 mm with LDS 3 (BOF slag) as the industrial aggregate for the 8/16 fraction. At the request of the

ready-mixed concrete plant, some of the coarse 8/16 fraction was also replaced with gravel (Table 2).

Concrete manufacturing and storage

All concretes were produced in accordance with DIN EN 12390-2. The water absorption of the aggregates was taken into account during production. To counteract the negative influence of water absorption on the fresh concrete workability, the appropriate amount of water was added to the aggregate beforehand, as is usual when using recycled natural aggregates. This water was not included in the w/c ratio, as it is assumed that it will not increase the porosity of the hardened cement paste later on and thus compromise the durability of the concrete.

All specimens were stored vibration-free in the moulds at 20°C for one day and then, after demoulding, under water at 20°C for 6 days. Volume stability testing began immediately thereafter. The specimens for testing the technological properties of the concrete were further cured for 21 days in a climatic chamber at 20°C and 65% RH, as described in the National Annex to DIN EN 12390-2.

TESTING THE VOLUME STABILITY OF INDUSTRIAL CONCRETE

Development of the testing method

The first step was to define the effects to be analysed and the ranges to be considered. The aim was to assess their significance for volume stability, a test acceleration effect and a possible tendency to artefact formation. The influencing variables and their varying ranges are summarised in Table 3. In addition to the influencing variables, a number of test variables were also analysed to provide a more accurate assessment. In addition to the qualitative visual assessment, changes in the relative dynamic modulus of elasticity, determined by resonance frequency or ultrasonic transit time, and expansions were considered.

The development of the test method was supported by „Minitab 20“ software. From the full matrix of all possible combinations of effects (Table 3), 63 optimal tests were selected using the statistical method of „sequential optimisation“. The tests could take into account potential influences up to 2nd order, i.e. quadratic dependencies. A total of approximately 1600 data sets were included in the statistical analysis. As

a result of the statistical analysis, a test procedure was defined. In a second step, the significance of the procedure was compared with the results of the verification test and the tests on samples stored outdoors.

The concrete properties of those steel slags that showed high volume stability according to the newly developed test method were investigated in the laboratory. In addition to the fresh concrete properties, the focus was on the strength development and in particular the durability. Finally, LDS 3 (BOF slag) was used to verify the results in a demonstrator test in a ready-mixed concrete plant.

Procedure and test parameters

After the water storage, the volume stability test was started after 7 days. The samples were placed in a container of water at 20°C, which was heated to the temperature defined in the statistical design within 6 hours. The samples were kept in the water bath at this temperature for a maximum of 14 days. They were examined after 1, 3, 7 and 14 days.

In addition to visual assessment of the condition of all specimens, length change and dynamic modulus of elasticity were determined on prisms 40 x 40 x 160 mm³ (up to a maximum grain size of 8 mm) and 50 x 50 x 25 mm³ (maximum grain size of 16 mm) using resonance frequency and on 100 mm cubes using ultrasonic transit time, respectively. The results were set in relation to the initial values after heating so that all thermal effects were eliminated, and the relative values could be directly compared and evaluated.

Systematic evaluation of the results showed that the non-destructive methods of measuring the change in length and modulus of elasticity could not be used to reliably assess the volume stability of industrial aggregates in concrete. Significant changes in these measures generally occurred only when the concrete structure was already severely damaged (spalling or cracking). A visual inspection of the specimens is therefore suggested as a targeted evaluation criterion. As shown in Figure 1, a slag to be used as concrete aggregate can only be classified as „volume stable“ if no damage is observed in the concrete produced with it during the 14-day test.



Figure 1: Visual assessment of volume stability. category 1 (left) = no damages = passed test. categories 2 to 5 (right) = damages of various intensities = failed test

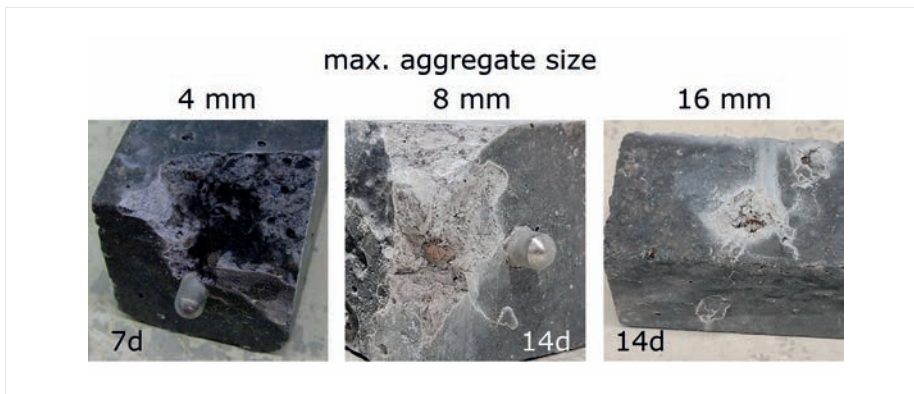


Figure 2: Damage intensities as a function of maximum aggregate size ($w/c = 0.60$; free lime = 1.9 wt.%; test temperature = 60°C)

Parameter selection and procedure definition

The analyses of the tests, based on a statistical design, provided reliable information on the significant influencing parameters and their contribution to the test acceleration. As expected, the free lime content had the most statistically significant influence on concrete damage after both 7 and 14 days of testing. On both test days, the intensity of damage increased with increasing free lime content of the aggregate. The maximum

aggregate particle size was also significant in both cases. Damage can be detected earlier and more clearly if the maximum particle size of the aggregate is limited to 8 mm, as illustrated by the evaluation of the visual observation for concrete with a w/c ratio of 0.60, a free lime content of the aggregate of 1.9 wt.% and a test temperature of 60°C in Figure 2.

In contrast, the effect of the w/c ratio was not statistically significant. However, trends in damage

intensity could be identified. For example, damage intensity appeared to be lower at a w/c ratio of 0.50 than at higher or lower w/c ratios. The fact that concretes with a w/c ratio lower than 0.50 tended to be more severely damaged at the same test age is probably due to the coarser concrete structure resulting from the poorer workability of a fresh concrete at low w/c ratios, unless this is specifically improved by the addition of superplasticiser. Concrete with a w/c ratio of 0.60 has a naturally higher porosity. This facilitates the ingress of moisture into the concrete. As a result, the free lime reaction can start more quickly, which may lead to more pronounced damage at an earlier stage.

Visual assessment of the specimens also revealed an influence of the surface-area-to-volume ratio, although again this could not be statistically proven. Major damage in the form of spalling tended to occur earlier when prisms were tested rather than cubes. This is

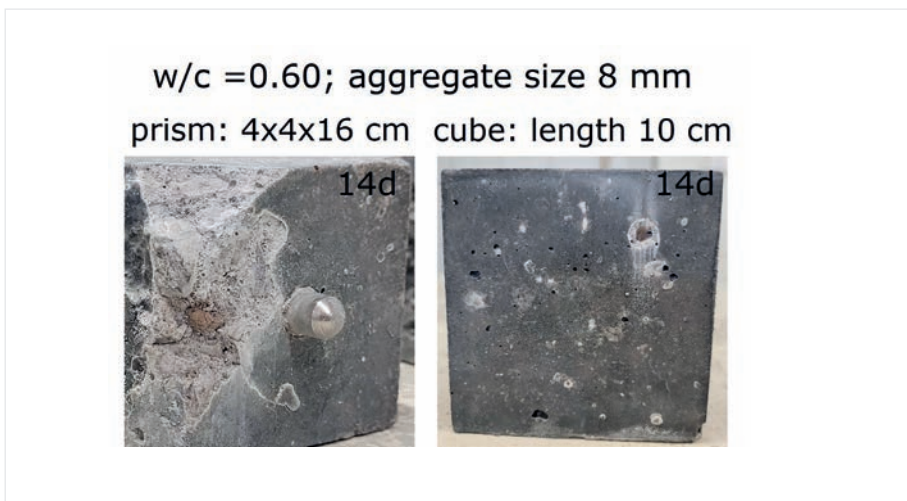


Figure 3: Damage intensities as a function of sample geometry (prism / cube) (w/c = 0.60; free lime = 1.9 wt.%; test temperature = 60°C)

| | |
|----------------------|---|
| Concrete composition | <ul style="list-style-type: none"> ■ w/c ratio 0.60 ■ Max aggregate size 8 mm; aggregates to be crushed, if necessary ■ Binder content defined by k-value of aggregate mix and w/c ratio |
| Geometry of samples | <ul style="list-style-type: none"> ■ Prisms 40 mm x 40 mm x 16 mm |
| Curing regime | <ul style="list-style-type: none"> ■ 1 day in mould at 20°C and > 95% RH ■ 6 days under water at 20 °C |
| Test conditions | <ul style="list-style-type: none"> ■ Test temperature 60°C ■ Heating up to test temperature within 6 h ■ Max 14 days testing |
| Test values | <ul style="list-style-type: none"> ■ Visual assessment after 7 and 14 days ■ Accompanying testing of relative dynamic modulus of elasticity |

Table 4: Frame conditions of a practical test method for evaluating the volume stability of industrial aggregates in concrete

illustrated in Figure 3 for a concrete with a w/c ratio of 0.60, a maximum grain size of 8 mm, a free lime content of the aggregate of 1.9 wt.% and a test temperature of 60°C at the age of 14 test days. Based on the statistical evaluation of the concrete tests, a practical and easy to perform test procedure was defined. Its main features are summarised in Table 4.

Calibration of the test method

To calibrate the test method, 13 industrial aggregates (Table 1)

were tested using the newly developed test method. In parallel, concrete specimens (beams 100 mm x 100 mm x 500 mm) were produced for long-term testing under practical conditions according to the concrete mix design for exposure class XC4 described in Table 2. After 28 days of curing in accordance with the National Annex to DIN EN 12390-3, they were stored outdoors in the open air. All specimens have been and will continue to be inspected at regular intervals and their strain de-

termined. The results available to date are summarised in Figure 4.

All EAF slags and the oxygen/sand-treated BOF slag LDS 3 showed sufficient volume stability in the concrete according to the test procedure. The free lime content of these aggregates was very low (< 0.3 wt.%). In contrast, all the untreated BOF slags had to be classified as „not volume stable“. These BOF slags had free lime content > 1.9 wt.%.

The long-term tests carried out in parallel confirmed the classification of the aggregates according to the new test method. After approximately 600 days of ageing, significant structural defects occurred in the two concretes containing the aggregates with the highest free lime content. The increase in volume due to the free lime reaction was clearly responsible for the damage. On the other hand, the two other concretes containing the industrial aggregates, which were classified as „not volume-stable“, still showed no damage after more than 700 days at the end of the project. However, further long-term tests will show if and when structural damage and expansion occur.

TECHNICAL PROPERTIES OF CONCRETES MADE WITH SLAG AGGREGATES

Fresh concrete properties

The oxygen/sand-treated BOF slag LDS 3 and an EAF slag (EOS 1) were selected to test their suitability in concrete. Both had a high volume stability according to the new test method. The concretes were formulated according to the concrete mix design for exposure class XC4 described in Table 2.

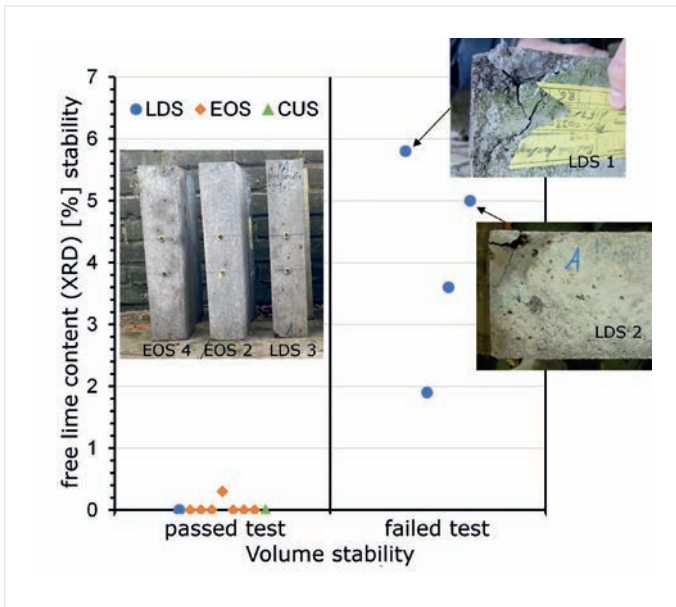


Figure 4: Results of testing with the new method in relation to the free lime content of the aggregates and the results of the long-term tests

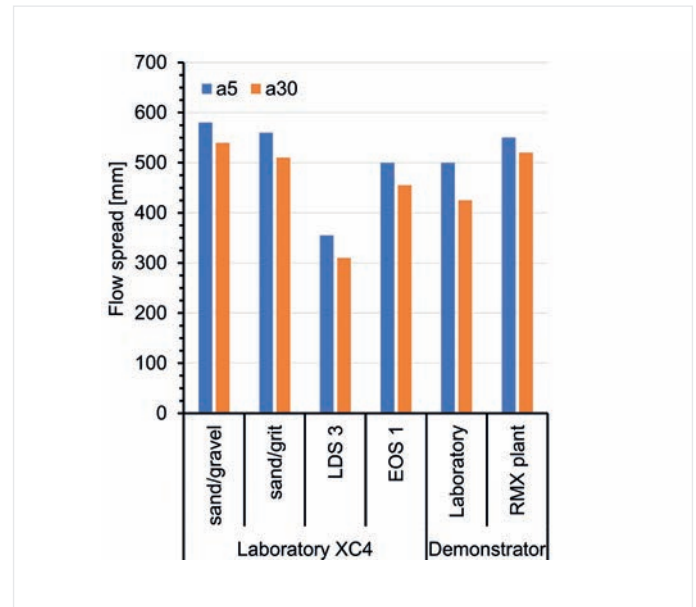


Figure 5: Flow spreads of the concretes 5 and 30 minutes after water addition

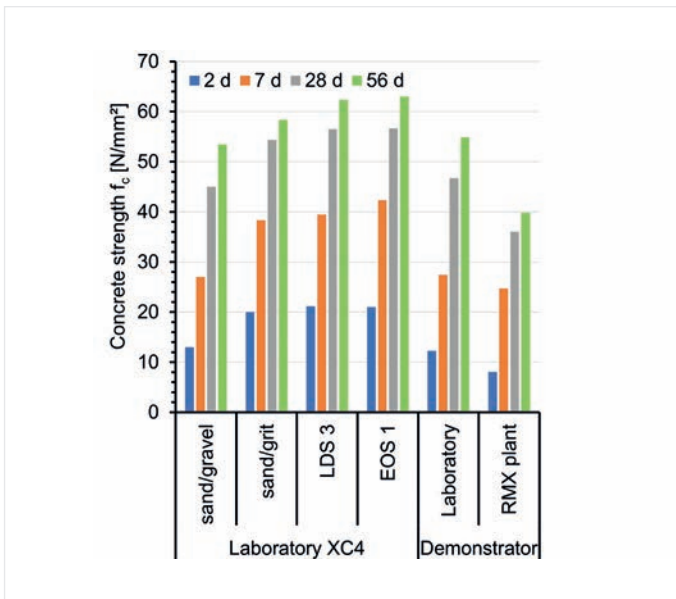


Figure 6: Strength development of the concretes

The flow spreads 5 and 30 minutes after water addition were used as a measure of concrete workability. The results are shown in Figure 5. The workability of the concretes deteriorated significantly compared to the reference concretes. This was to be expected as crushed material was used for both the fine and coarse aggregate fractions in the worst-case scenario considered. For the concrete with LDS 3, the slump was reduced by about 40% and for the concrete with

EOS 1 by about 15%. This is mainly due to the unfavourable grain shape of the fine aggregate fraction.

Strength development

The strength development of the concretes is shown in Figure 6. For the two concretes with the industrial aggregates LDS 3 and EOS 1, the compressive strength is comparable to that of the reference concrete with limestone chippings. Compared to the reference concrete with gravel and sand it is higher, as expected, due to the better binding of the chippings in the cement paste matrix.

Durability

A key property of concrete durability is resistance to carbonation. To assess the carbonation behaviour, the carbonation depths of XC4 concretes stored in a laboratory climate at 20°C and 65% RH (Table 2) were determined over a period of one year. The results were used to calculate the carbonation rate according to EN 12390-10 [16]. This value is compared with the reciprocal value of the compressive strength after 7 days (Figure 7). This figure is based on the approval procedure of the DIBt, which is used to assess the carbonation behaviour of new binder systems in comparison with known systems. The figure also includes results and the 95% prediction range from the database of the Institute for Building Materials Research ibac at RWTH Aachen University, as

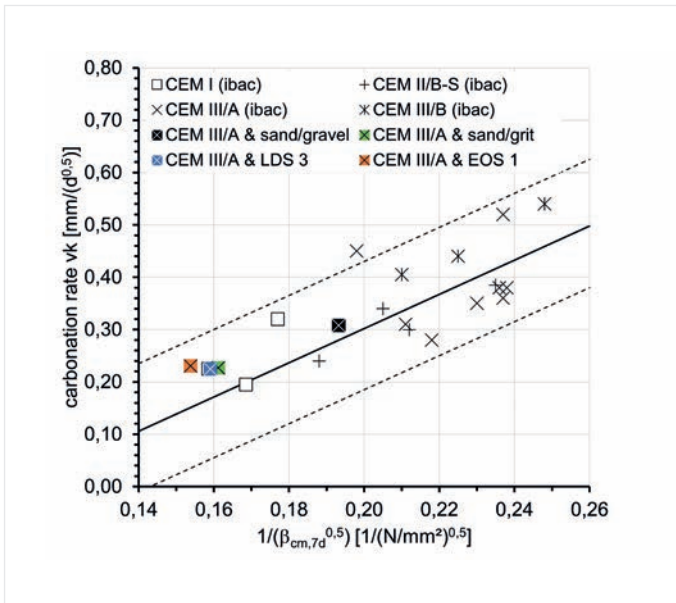


Figure 7: Carbonation rate of the concretes

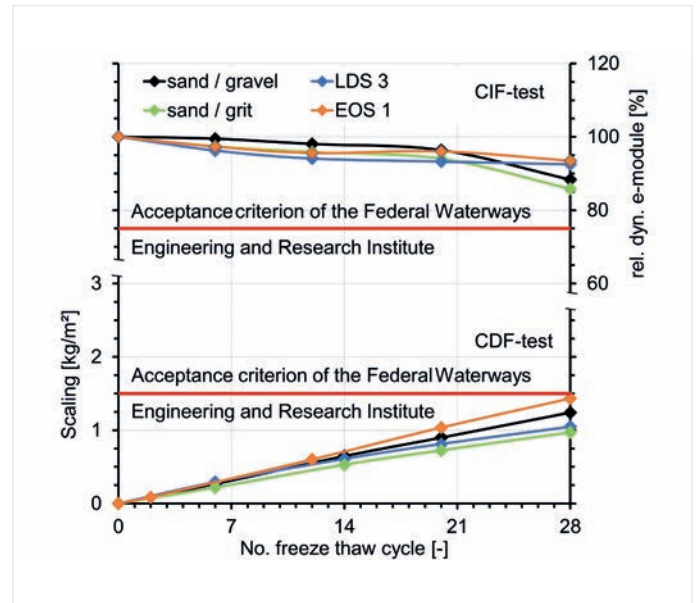


Figure 8: Frost resistance and freeze-thaw resistance; above: relative dynamic E-modulus (CIF test); below: scaling (CDF test)

published in [17]. The two concretes with LDS 3 and EOS 1 behave similarly to the two reference concretes. All concretes are within the 95% prediction range. It can be concluded that the carbonation behaviour of the concretes both with steel slag as an industrial aggregate and with natural aggregates corresponds to the behaviour of the standard concretes.

In addition to the carbonation behaviour, the freeze/thaw resistance of the concretes was investigated as another important durability property. The results are presented in Figure 8. The freeze-thaw resistance was determined using the CIF method in accordance with DIN CEN/TR 15177 [18] on concretes produced using the XF3 mix design (Table 2). The German Federal Waterways Engineering and Research Institute (BAW) defined a maximum change in the relative dynamic modulus of elasticity

(RDM) of 75% after 28 freeze-thaw cycles as the decisive acceptance criterion.

As the aggregates used already had a high freeze-thaw resistance according to DIN EN 12620, it was expected that the concretes produced with these aggregates would also meet the BAW acceptance criterion. As Figure 8 (above) shows, the low reduction in modulus of elasticity confirmed this expectation.

The freeze-thaw and deicing salt resistance was determined using the CDF method in accordance with DIN CEN/TS 12390-9 [19] on concretes of mix design XF4 (Table 2). For this test, the BAW defined a maximum acceptance criterion of 1.5 kg/m² after 28 freeze-thaw cycles. The concretes scaled between 0.97 kg/m² and 1.43 kg/m². Consequently, the criterion was met by all concretes.

DEMONSTRATOR TEST

Based on the laboratory tests, the BOF slag LDS 3 was selected for a demonstrator test to transfer the laboratory results into industrial scale. The test was planned in cooperation with Spenner Herkules GmbH and carried out in one of the group's ready-mix concrete (RMX) plants (Figure 9).

A total of 5 m³ of a typical ready-mix concrete was produced twice. In order to simulate transport to the construction site in the truck mixer, the concrete was moved in the mixing drum of the truck mixer for 45 minutes with the usual slight rotation. Afterwards, fresh concrete properties were tested and specimens for strength development as well as 3 demonstrator elements (2 „Lego bricks“ of 1 m³ each and a wall element of approximately 65 litres) were manufactured (Figures 10 and 11). The durability of the



Figure 9: Demonstrator test at ready-mix concrete plant of Spenner Herkules GmbH



Figure 10: Production of "Lego bricks" in the ready-mix concrete plant of Spenner Herkules GmbH



Figure 11: Production of the wall element in the ready-mix concrete plant of Spenner Herkules GmbH and its storage at FEHS-Institute

concrete will be tested and documented for these demonstrator elements, which will be stored outdoors for the coming years, even after the research project has been completed.

As a first step, a ready-mix concrete mix design was developed in which the coarse fraction 8/16 mm consisted of LDS 3 only, while the fine fraction 0/2 mm and the coarse fraction 2/8 mm consisted of natural sand and gravel. In a second step, concrete was produced,

and its properties measured in the laboratory. The workability of the concrete improved significantly due to the reduced use of LDS 3 and the use of a concrete plasticiser, even though the concrete contained 20 kg/m³ less cement and therefore approximately 19 l/m³ less binder paste compared to the XC4 recipe of the concrete described above (Figure 5). The workability and strength development were in line with the manufacturer's requirements (Figures 5 and 6).

Despite these promising results, it was decided to use about 40% natural aggregates in the 8/16 mm fraction, based on the former experience of the manufacturer with concrete containing air-cooled blast furnace slag. This reduction in slag content resulted in a further improvement in concrete workability. The flow spreads at the test times were now comparable to the reference concretes (Figure 5). The concrete retained its „very soft“ consistency until it was placed after 45 minutes.

For both concretes in the demonstration test (fraction 8/16 mm made from 100% LDS 3 or from 55% LDS 3 and 45% gravel) the strengths decreased with decreasing LDS 3 content in the aggregate mix (Figure 6). This was to be expected since, as described above, the interlocking effect of round aggregates is significantly less than that of crushed aggregates. A coherent explanation as to why the concrete in the ready-mix plant showed a significantly lower strength increase between 28 days and 56 days could not yet be found.

ENVIRONMENTAL PROPERTIES

As mentioned in the introduction, the investigations into the environmental properties of the metallurgical slags and the concretes made with them will be discussed in a separate publication. However, it should already be stated that despite the significantly higher heavy metal content of the slags compared to natural gravel and sand (in particular regarding total chromium), in nearly all cases the leaching data of the slags themselves, of the concretes made with them and of the recycled aggregates made from these concretes fulfilled the relevant requirements. Thus, the conclusion may be drawn that the use of steel slags does not result in environmental problems.

SUMMARY

A key objective of the research project was to develop a test method that can be used to quickly and reliably assess the volume

stability of industrial aggregates in concrete. This objective has been achieved. The outdoor tests on concrete specimens, which were carried out and continued in parallel, have already confirmed the findings of the laboratory tests. A further objective of the research project was to demonstrate the technological suitability of the industrial aggregates for concrete. It was shown that the required strength development and durability properties were achieved. Regarding the workability of the fresh concrete, the problems generally expected when using crushed aggregates were encountered. These were exacerbated by the use of finely crushed steel slag in the 0/2 mm fraction (worst-case scenario). However, these problems can be countered by various measures such as limiting the substitution of natural stone, pre-wetting of the aggregates or adding concrete admixtures to improve the workability.

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PRODUCTION AND USE OF FERROUS SLAG IN 2022

Dr.-Ing. Th. Merkel
(FEhS – Building Materials Institute)

Ferrous slag (blast furnace slag and steel furnace slag) has been established on the market as a product for construction and fertilising for many decades. The ratio of use exceeds 90% of production, so the use of slag by-products is a best practice example of the conservation of natural resources.

GERMANY

The data on production and utilisation in Germany in 2022 is shown in Table 1 (blast furnace slag) and 2 (steel furnace slag). The data for 2021 is included for comparison.

Table 1: Production and use of blast furnace slag in Germany in 2022/2021 (in million tonnes)

| Production | 2022 | 2021 |
|----------------------|-------------|------|
| Granulated BFS | 6.53 | 6.90 |
| Air-cooled BFS | 0.63 | 0.72 |
| Sum | 7.16 | 7.62 |
| From interim storage | 0.71 | 0.87 |
| Total | 7.87 | 8.49 |

| Use | 2022 | 2021 |
|------------------------------|-------------|------|
| ABS for aggregates | 0.25 | 0.29 |
| ABS for aggregate mixtures | 0.32 | 0.59 |
| GBS for cement production | 7.14 | 7.41 |
| GBS for other purposes | 0.08 | 0.10 |
| Intra-industrial consumption | 0.08 | 0.10 |
| Total | 7.87 | 8.49 |

Table 2: Production and use of steel furnace slag in Germany in 2022/2021 (in million tonnes)

| Production | 2022 | 2021 |
|-------------------------------------|-------------|------|
| Slag from oxygen steel making | 2.73 | 2.82 |
| Slag from electric arc steel making | 1.45 | 1.58 |
| Others (SecMS, etc.) | 0.49 | 0.58 |
| Total | 4.67 | 4.98 |

| Use | 2022 | 2021 |
|-----------------------|-------------|------|
| Metallurgical use | 0.50 | 0.52 |
| Fertiliser | 0.49 | 0.40 |
| Construction material | 2.10 | 2.56 |
| Others | 0.25 | 0.31 |
| Sum | 3.34 | 3.79 |
| Final deposit | 0.58 | 0.44 |
| To interim storage | 0.75 | 0.75 |
| Total | 4.67 | 4.98 |

After a significant increase in steel production in Germany in 2021 to 40.1 million tonnes, this figure fell again in 2022 to 36.8 million tonnes [1]. Accordingly, fewer slag products were also produced: a total of 11.8 million tonnes of blast furnace slag and steel furnace slag were produced in 2022 (2021: 12.6 million tonnes). In addition, interim storage was reduced

by 0.7 million tonnes, meaning that a total of 11.1 million tonnes of ferrous slag could be marketed.

Furthermore, the share of granulated blast furnace slag in the production of blast furnace slag is around 90%. The proportion of granulated blast furnace slag used for cement production is as high as almost 99%.

This highlights the importance of CEM II/S and CEM III cements based on granulated blast furnace slag for the cement industry. These cements continue to make an important contribution to CO₂ savings in cement production.

The air-cooled blast furnace slag is primarily processed into aggregate mixtures for unbound layers, but increasingly also into aggregates for asphalt and concrete (approx. 0.3 million tonnes each in 2022).

The production of steel slag in 2022 was 4.6 million tonnes (previous year: 5.0 million tonnes), of which approx. 67% came from the converter process. The use of products from steel furnace slag fell slightly in 2022 compared to the previous year (3.3 million tonnes, previous year 3.8 million tonnes), possibly due to the construction measures available. At 2.0 million tonnes (previous year: 2.6 million tonnes), the building materials market remains by far the most important sales segment in terms of volume. In addition, 0.5 million tonnes of converter lime were used as a highquality fertiliser in agriculture. Around 0.5

million tonnes of steel furnace slag were used in a resource-saving manner by means of internal recycling.

A total of 11.1 million tonnes of iron and steel slag were used as building materials and fertilisers in Germany in 2022. With a total production of 11.7 million tonnes, this still corresponds to a high usage rate of 95%.

EUROPE

The European slag association EUROSLAG regularly asks its members for European slag data. Preliminary figures for 2022 are given in Table 3 (blast furnace slag) and 4 (steel furnace slag). However, these figures must be qualified as to date it has not been possible to obtain a satisfactory number of responses. The reported data represents about 72% of the BFS and 61% of the SFS figures which were calculated based on the hot metal and crude steel production provided by Worldsteel [2]. In total, about 22 million tonnes of BFS and 19 million tonnes of SFS were produced in the EU-27 countries + UK in 2022.

Table 3: Production and use of blast furnace slag in Europe in 2022/2021 (in million tonnes)

| Production | 2022 | 2021 | Use | 2022 | 2021 |
|----------------------|-------------|------|--|-------------|------|
| Granulated BFS | 14.0 | 15.6 | Cement production and concrete additives | 14.7 | 16.5 |
| Air-cooled BFS | 1.6 | 2.3 | Road construction | 2.7 | 3.1 |
| Sum | 15.6 | 17.9 | Others | 0.1 | 0.3 |
| From interim storage | 1.9 | 2.0 | Total | 17.5 | 19.9 |
| Total | 17.5 | 19.9 | | | |

Table 4: Production and use of steel furnace slag in Europe in 2022/2021 (in million tonnes)

| Production | 2022 | 2021 | Use | 2022 | 2021 |
|-------------------------------------|-------------|------|-----------------------|-------------|------|
| Slag from oxygen steel making | 6.1 | 6.8 | Metallurgical use | 1.6 | 1.4 |
| Slag from electric arc steel making | 3.4 | 4.0 | Fertiliser | 0.7 | 0.4 |
| Others (SecMS, etc.) | 1.8 | 1.7 | Construction material | 5.5 | 7.6 |
| Total | 11.3 | 12.5 | Others | 0.5 | 0.1 |
| | | | Sum | 8.3 | 9.5 |
| | | | Final deposit | 1.8 | 1.7 |
| | | | To interim storage | 1.2 | 1.3 |
| | | | Total | 11.3 | 12.5 |

Comparing the production figures, there is a significant decrease in production especially for BFS as reported above for Germany. A difference seems to be in SFS production as the estimated sum is not so much smaller compared to the previous year.

Comparing the percentages for BFS with those reported from Germany, 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 as aggregate or aggregate mixtures for construction purposes. Only a small amount is used for other purposes such as fertilising and glass production.

About 50% of the SFS produced is used for construction purposes, for roads, dams or hydraulic structures, for example. About 15% is used for metallurgical purposes, 7% as fertiliser and a small percentage for other uses. 10% of the SFS produced went to interim storage to be utilised later, 15% was sent to final deposit.

In summary, the (reported) use is close to the (reported) production not only in Germany but also throughout Europe, which is revealed by the high utilisation rates. Steel producing companies acting together with processing and marketing companies continue doing their best to enable a circular economy. <<<

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FEhS – Building Materials Institute
Bliersheimer Straße 62
47229 Duisburg
Germany

Telephone: +49 2065 9945-0
Fax: +49 2065 9945-10
E-Mail: fehs@fehs.de
www.fehs.de



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