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THE USE OF STEEL SLAG AS AGGREGATE IN CONCRETE – ENVIRONMENTAL ASPECTS

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INTRODUCTION

Concrete consists of cement, additives and water, with about 70% of its volume made up of aggregates, whose physical, mineralogical and chemical properties are essential for the load-bearing capacity and durability of a concrete structure. Aggregates can be of natural origin, industrially produced or recycled.

In 2021, approximately 583 million tonnes of natural aggregates such as gravel, sand and crushed natural stone were mined in Germany, with 96% of these materials used for construction purposes [1]. The extraction of these resources means a considerable impact on the natural environment and landscape and is accompanied by noise, dust and long transportation routes to the concrete manufacturer. The enormous demand for materials is not expected to decrease, even in the coming decades. Depending on economic dynamics, demand could even increase according to a scenario from the German Building Materials Association [2]. Industrial by-products, such as steel slag, present an opportunity to partially replace natural aggregates, thereby conserving natural resources and supporting the circular economy. Given the growing political pressure to conserve resources, promote the circular economy and reduce CO_2 emissions, as well as increasing public opposition to activities like gravel exploitation, concrete manufacturers and users are increasingly being compelled to seek alternative aggregates. This has led to a rising interest in steel slag in recent years.

Although air-cooled blast furnace slag (ABS) has been used as an aggregate in concrete or granulated blast furnace slag (GBS) as a clinker substitute for around 100 years without requiring proof of environmental compatibility, steel slag faces regulatory barriers that hinder its use. The applicable environmental regulations for this area of application – Annex 10, “Requirements for construction works with regard to the effects on soil and water (ABuG)” of the Model Administrative Regulation on Technical Building Regulations (MVV TB) [3] – specify not only eluate limit values for the pure aggregate and the concretes produced from it but also solid content limit values for the pure input material. For steel slag, the requirement to meet solid content limit values results in its exclusion from use as a concrete additive. Specifically, the limit for Cr_{total} (600 mg/kg) is consistently exceeded for metallurgical reasons. Although leaching tests demonstrate that the eluates of the pure aggregate comply with the corresponding limit values in most cases, the use of steel slags is still prohibited.

In contrast, in road construction, environmental compatibility is assessed exclusively based on leaching behaviour in accordance with the Substitute Building Materials Ordinance (EBV) [4]. The total content is not considered because the significant factor for environmental compatibility is the release of environmentally relevant parameters, which depends not on their total content but on their mineral binding. Total content does not provide any insight into the release or leaching of potential pollutants.

Due to the differing assessment concepts, a paradoxical situation arises: identical material can be used unbound or bound in road construction, yet it cannot be applied as part of a dense concrete matrix. To help resolve this paradox, a research project was conducted involving extensive investigations into both the technical suitability and environmental compatibility of steel slag as industrial aggregates in concrete.

PROJECT OBJECTIVES

The IGF research project 21567 N [5] "Suitability of Metallurgical Slags for Use as Aggregates in Concrete" focused on a holistic approach that also considered the use of concrete for recycled aggregates. One important objective of the project was the creation of a comprehensive database, which was previously unavailable for concrete applications. This database is intended for discussions with authorities to advocate for regulatory changes that would allow the use of steel slags as concrete aggregates. Another goal of the project was the development of a practical testing method for evaluating volume stability.

This paper addresses the environmentally relevant aspects. The technical aspects are presented in a separate article [6]. Overall, the investigations showed that electric arc furnace slags from carbon steel production (EAF – C) are technically suitable for use as aggregates in concrete, as they demonstrate the required strength development and durability. In contrast, the free lime content in basic oxygen slag (BOS) is often too high to meet the requirements for volume stability. For this reason, only data for EAF slags is presented below.

INVESTIGATIONS CONDUCTED

Four BOS and seven EAF slags were analysed and compared with natural aggregates for the investigations. Both the raw materials and the concrete specimens produced using the aggregates were tested in accordance with the requirements of MVV TB, Annex 10 (ABuG) [3]. Additionally, at the beginning of the project, nine concrete specimens were produced using the aggregates and exposed to outdoor conditions. After a storage period of two years, some of these stored concrete specimens were broken and analysed for leachability.

ENVIRONMENTAL COMPATIBILITY OF ELECTRIC ARC FURNACE SLAG IN CONCRETE APPLICATIONS

The assessment of the environmental compatibility of mineral construction materials primarily involves evaluating the release or leaching of environmentally relevant elements in contact with soil and water. Various laboratory testing methods exist for this purpose, which can be categorised into batch tests, tank tests and column tests. In the field of building construction, the batch test 10:1 (DIN EN 12457-4 [7]) and the tank test (DIN EN 16637-2 [8]) are applied according to the MVV TB, Annex 10 (ABuG) [3] guidelines.

The release of environmentally relevant trace elements is largely dependent on their mineral binding and the solubility of the mineral phases. For this reason, there is often no direct correlation between the solid content and the eluate concentration. In concrete structures, the cement matrix prevents direct contact between the aggregate and water, meaning that leached components can only reach the surface of the structure through diffusion. Due to diffusion resistance and the chemical binding of many components within the cement matrix, only low concentrations of environmentally relevant parameters are to be expected [9,10].

However, as mentioned above, in the regulatory framework for building construction as outlined in MVV TB, Annex 10 (ABuG) [3], both eluate limit values and solid limit values for the input material are specified.

Assessment of the solid contents according to ABuG

The trace element contents measured in aqua regia extracts according to ABuG [3] are shown in Table 1. The results confirm the well-known fact that, for EAF slag, only the parameter chromium exceeds the solid content limit (Cr_{total} = 600 ppm). All other requirements are met. Given the toxicological significance of hexavalent chromium (Cr-VI) – which is classified under the CLP Regulation [11] as acutely and chronically toxic to aquatic environments (Category 1), skin-sensitising (Category 1) and carcinogenic (Category 1B) [12] – the Cr-VI content was also analysed in the samples using the method described in DIN EN 196-10 [13]. The results showed that Cr-VI concentrations consistently fell below the detection limit of 1 mg/kg.

Table 1: Solid contents of electric arc furnace slags in aqua regia extracts compared with the limit values in MVV TB, Annex 10 (ABuG), Table A-3

		EAF 1	EAF 2	EAF 3	EAF 4	EAF 5	EAF 6	EAF 7	Limit values
As	mg/kg	2.17	1.9	1.69	3.92	1.64	1.0	1.09	150
Pb	mg/kg	9.35	2.58	6.3	17.75	2.0	0.2	0.81	700
Cd	mg/kg	0.29	0.07	0.10	0.29	0.1	<0.1	<0.1	10
Cr_{total}	mg/kg	3,053	10,942	5,698	10,378	3,022	5,178	6,265	600
Cu	mg/kg	121	110	173	165	85.9	44.6	249	400
Ni	mg/kg	28.1	27.9	20.8	7.63	10.89	7.1	46.03	500
TI	mg/kg	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	7
Hg	mg/kg	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	5
Zn	mg/kg	274	180	186	116	104	96.8	105	1,500
Cr-VI	mg/kg	< 1	< 1	< 1	< 1	< 1	< 1	< 1	–

cyan = requirement met, red = requirement not met

Assessment of the elution behaviour according to ABuG

The results of the elution tests conducted in accordance with MVV TB, Annex 10 (ABuG) [3], performed on the pure aggregates, the concrete produced from them and the recycled concrete aggregates are summarised in Tables 2 to 5. The batch test (DIN EN 12457-4 [7]) for the pure EAF slags reveals elevated levels of vanadium or chromium exceeding the ABuG threshold values in two cases (Table 2). Notably, EAF 2 exhibited significant chromium release. However, based on extensive data and long-standing experience, this is regarded as an absolute exception. Typically, chromium in slags is bound within insoluble mineral phases, resulting in low release levels. For EAF 7, the vanadium concentration exceeds the ABuG limit. Despite these exceedances, the test results for the concrete specimens made with EAF slag show overall compliance with the limit values (Table 3). Minor exceedances of vanadium are not considered significant, as vanadium is currently excluded from regulatory enforcement due to insufficient modelling data and overly conservative estimates.

The results for recycled concrete aggregates derived from the concrete specimens are presented in Table 4 (after a storage period of 56 days) and Table 5 (after approximately two years of exposure to outdoor conditions) and are compared with the corresponding limit values. Both the limit values for recycled aggregates (Table A-2 of ABuG) and steel slags (Table A-3 of ABuG) are considered in the evaluation. This is because the ABuG limit values for recycled aggregates were established under the assumption that steel slags are not included. As a result, some parameters, such as fluoride, are specific to steel slags. A comparison with the steel slag values helps assess any changes after the material's use in concrete, compared to its original state (without concrete). The results show that all limit values for the recycled aggregates are met. Elevated pH and conductivity values are not considered exceedances, as ABuG specifies that these are not disqualifying if the concrete content is at least 60 wt.%, which is the case here.

Overall, the results demonstrate that even for EAF slags with elevated release rates of certain parameters in their original aggregate form, the release is significantly reduced once bound within the concrete matrix and limit values are met. Even EAF 2, which exhibited noticeable chromium leaching, showed markedly lower chromium concentrations within the concrete matrix. Moreover, the concentrations of relevant parameters, along with conductivity and pH levels, decrease over time. This suggests ongoing carbonation and better incorporation of trace elements into the concrete matrix or cement phases.

Table 2: Eluate concentrations of electric arc furnace slags from the batch test 10:1 (grain size 0/10 mm) compared with the limit values specified in MVV TB, Annex 10 (ABuG), Table A-3 (steel slags)

Pure aggregates
Batch test 10:1 (DIN EN 12457-4, grain size 0/10 mm)

		EAF 1	EAF 2	EAF 3	EAF 4	EAF 5	EAF 6	EAF 7	Limit values
pH value		11.4	11.4	11.0	11.3	11.1	11.6	11.2	11–13
LF*	µS/cm	702	667	292	693	275	872	480	1,500
Cr_{total}	µg/l	7.2	616	4.9	10.3	6.8	1.0	15.1	100
V	µg/l	134	94.1	151	201	132	22.6	323	250
F	mg/l	<0.4	<0.4	0.6	0.5	0.4	3.7	<0.4	5
Cr-VI	µg/l	<10	608	<10	<10	<10	<10	<10	–

cyan = requirement met, red = requirement not met

** Exceedances are not considered exclusion criteria if the concrete content of the material being tested is at least 60% by mass*

Table 3: Cumulatively released quantities in the tank test according to DIN CEN/TS 16637-2 using concrete cubes (0.06 m^2) and 5 litres of eluate compared with the limit values specified in MVV TB, Annex 10 (ABuG), Table A-6. Note: Eluate concentrations < detection limit were set to c=0 for the calculation.

Concrete cubes, DIN CEN/TS 16637-2

		EAF 1	EAF 2	EAF 3	EAF 4	EAF 5	EAF 6	EAF 7	Limit values
Sb	mg/m^2	0.19	0.22	0.21	0.21	0.17	0.08	0.16	5.5
As	mg/m^2	0.12	0.03	0.13	0.16	0.13	0.11	0.11	11
Ba	mg/m^2	79	27	125	89	192	57	192	375
Pb	mg/m^2	0.13	0.04	0.18	0.18	0.31	0.13	0.13	7.7
Cd	mg/m^2	0	0	0	0	0	0.02	0.02	0.56
Cr^{total}	mg/m^2	0.21	1.39	0.68	0.71	0.21	0.39	0.5	7.7
Cr-VI	mg/m^2	0	0	0	0	0	0	0	6.6
Co	mg/m^2	0.07	0.07	0.08	0.09	0.1	0.12	0.08	8.8
Cu	mg/m^2	0.26	0.48	0.77	0.9	0.62	0.93	0.98	15.4
Mo	mg/m^2	1.28	0.14	0.3	0.23	0.23	0.13	0.28	38.6
Ni	mg/m^2	0.05	0.27	0.2	0.21	0.04	0.34	0.4	15.4
Hg	mg/m^2	0	0	0.01	0.01	0	0	0	0.22
Tl	mg/m^2	0.02	0	0	0.01	0	0	0	0.88
V*	mg/m^2	0.72	2.52	3.37	4.63	4.22	7.66	4.12	4.4
Zn	mg/m^2	1.28	3.61	2.25	2.28	1.24	4.88	5.5	63.9
Cl^-	mg/m^2	875	375	700	625	883	933	733	275,500
F^-	mg/m^2	0	0	0	0	0	0	0	826
SO_4^{2-}	mg/m^2	875	375	883	908	817	450	675	264,500

** Limit value is currently on hold*

cyan = requirement met, orange = limit value exceeded but not exclusionary

Table 4: Eluate concentrations of recycled concrete cubes produced with EAF slags from the batch test 10:1 (grain size 2/10 mm) compared with the limit values specified in MVV TB, Annex 10 (ABuG) for steel slags (Table A-3) and recycled aggregates (rec. agg., Table A-2).

Recycled concrete cubes after 56 days
Batch test 10:1 (grain size 2/10 mm)

		Concrete with EAF 1	Concrete with EAF 2	Concrete with EAF 3	Concrete with EAF 4	Concrete with EAF 5	Concrete with EAF 6	Concrete with EAF 7	Table A-3 steel slag	Table A-2 rec. agg.
pH value*		12.4	12.6	12.4	12.3	12.3	12.3	12.3	10–13	7–12
LF*	µS/cm	4,160	5,190	4,530	3,320	3,950	3,370	3,240	1,500	3,000
Cl^-	mg/l	3.7	2.0	4.2	3.9	5.2	2.8	3.2	-	150
SO_4	mg/l	14	1.8	8.2	13	12	9.5	8.1	-	600
As	µg/l	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	-	50
Pb	µg/l	0.7	0.6	0.6	0.3	1.0	0.4	0.3	-	100
Cd	µg/l	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	-	5
Cr_{total}	µg/l	5.7	40.2	9.9	6.6	6.2	11	9.9	100	100
Cu	µg/l	1.5	1.7	1.9	2.2	1.7	1.2	2.6	-	200
Ni	µg/l	0.6	0.3	0.4	0.5	0.3	0.4	0.4	-	100
Hg	µg/l	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	-	2
Zn	µg/l	5.8	6.3	6.4	5.0	5.1	5.0	4.6	-	400
PI	µg/l	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	100
V	µg/l	1.0	0.9	0.5	2.4	1.6	2.2	4.1	250	-
F^-	µg/l	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	5	-
Cr-VI	µg/l	<10	30	<10	<10	<10	11	<10	-	-

cyan = requirement met, orange = limit value exceeded but not exclusionary

** Exceedances are not considered exclusion criteria if the concrete content of the material being tested is at least 60% by mass*

Table 5: Eluate concentrations of outdoor-aged and recycled concrete specimens produced with EAF slags from the batch test 10:1 (grain size 2/10 mm) compared with the limit values specified in MVV TB, Annex 10 (ABuG) for steel slags (Table A-3) and recycled aggregates (Table A-2).

Outdoor-aged (two years) and crushed concrete specimens batch test 10:1 (grain size 2/10 mm)

		Concrete with EAF 1	Concrete with EAF 2	Concrete with EAF 3	Concrete with EAF 4	Concrete with EAF 6	Table A-3 steel slag	Table A-2 Rec. Agg.
pH value*		11.9	12.0	11.9	11.8	11.9	10–13	7–12
LF*	µS/cm	1,908	2,390	1,475	1,453	1,502	1,500	3,000
Cl^-	mg/l	2.1	2.3	3.0	2.5	1.7	-	150
SO_4	mg/l	13	13	16	15	16	-	600
As	µg/l	<0.1	<0.1	0.2	<0.1	0.1	-	50
Pb	µg/l	0.2	0.2	0.3	0.2	0.2	-	100
Cd	µg/l	<0.1	<0.1	<0.1	<0.1	<0.1	-	5
Cr_{total}	µg/l	1.2	27	1.6	1.3	1.1	100	100
Cu	µg/l	1.0	<0.1	3.6	2.4	0.5	-	-
Ni	µg/l	0.3	0.5	0.6	0.3	0.5	-	200
Hg	µg/l	<0.1	<0.1	0.8	<0.1	<0.1	-	100

cyan = requirement met, orange = limit value exceeded but not exclusionary

** Exceedances are not considered exclusion criteria if the concrete content of the material being tested is at least 60% by mass*

ADDITIONAL EVALUATION CRITERIA FOR THE USE OF EAF SLAGS IN CONCRETE

When using aggregates in building construction, it must be ensured that they are not only environmentally compatible but also have no harmful effects on human health. In the case of steel slags (both BOS and EAF slags), extensive studies on human toxicity were conducted as part of the registration under the REACH Regulation [14]. These studies included various exposure pathways, such as ingestion (oral), absorption through the skin (dermal) and inhalation (inhalative).

- Oral exposure: When slag is used as a building material in construction (building or road construction), oral intake is highly unlikely and can essentially be ruled out. Nonetheless, in vivo studies have been conducted, confirming that iron and steel slags are non-toxic.
- Dermal exposure: Skin contact with slag is the most likely exposure scenario during construction work. To assess potential health effects, extensive testing has been carried out, including both in vivo and in vitro studies on finely ground slag and its eluates. The results indicate no harmful effects from SWS.
- Inhalation exposure: Inhalation exposure can occur through dust formation during drilling or other mechanical processing. To evaluate this risk, studies were conducted as part of the REACH registration. These included in vivo inhalation studies on rats using finely ground granulated blast furnace slag, as well as in vitro studies on all slag types (air cooled blast furnace slag, granulated blast furnace slag, converter slag, electric arc furnace slag, secondary metallurgical slag). Comparative studies with natural rocks (basalt and obsidian) and standardised reference materials were also performed. The findings demonstrate that iron and steel slags behave similarly to natural rocks, and inhaled slag particles are effectively cleared by physiological mechanisms. No significant cytotoxicity was observed in biological test systems [15].

Overall, both ecotoxicological and toxicological studies confirm that iron and steel slags pose no risk to humans or the environment and do not require classification under the CLP regulation [11]. The key findings of these studies are summarised in the “executive summaries” available on the ECHA website [16] for each slag type.

CHROMIUM IN STEEL SLAGS

As explained above, steel slag as a substance does not pose toxicological hazards. However, in many cases, chromium is considered a contaminant, and there are concerns about its accumulation in the material cycle.

Chromium primarily enters steel slag through the use of steel scrap in steel production. The presence of chromium in the slag is, therefore, a direct consequence of the circular economy in the steel industry and cannot be avoided. The total chromium content (Crtotal) in aqua regia extracts of steel slag can exceed 8,000 mg/kg.

When considering the chromium as a potential contaminant, it is important to emphasise that, like other heavy metals, chromium does not occur in an isolated form in the slag – neither as a pure metallic element nor as potentially harmful chemical compounds. Instead, chromium is primarily incorporated into stable, water-insoluble mineral phases [17]. These mineral phases contain trivalent metals (trivalent iron or aluminium), in which trivalent chromium substitutes for these metals during mineral formation and becomes integrated into the mineral structure [18]. Chromium is primarily found in spinels but can also be present in wuestite and calcium ferrite, with spinel identified as the main host phase ([19, 20]).

Bulk composition measurements and data from the literature – including X-ray absorption near-edge spectroscopy (XANES), thermodynamic modelling and theoretical considerations – reveal that chromium in steel slag is exclusively present in the trivalent form (e.g. 21, 22, 23]). Since only the highly soluble hexavalent chromium (Cr-VI), which is not present in steel slags, is classified as toxic [12, 24, 25, 26], it is the only relevant species from a health and environmental protection perspective. Therefore, a high Crtotal content does not automatically indicate an increased risk. Due to the weather resistance of the mineral phases mentioned [18, 21, 22], the release of chromium from steel slags is low. Results from elution tests show only low concentrations, resulting in minimal input into the soil and groundwater. Chromium release is controlled by the presence of mineral phases that are more soluble than spinels, but these phases account for only a small fraction of the total chromium content.

Under highly alkaline conditions, as found in slag eluates and during concrete and cement production in general, chromium oxidation to Cr-VI can occur under oxidising conditions. Thus, in laboratory eluates, minor Cr-VI concentrations can occasionally be detected (see Tables 3–5). However, from an environmental perspective, these concentrations are not of concern. Firstly, they are most likely artifacts of laboratory testing, and secondly, even if present, Cr-VI would be reduced to Cr-III upon contact with environmental compartments such as soil and groundwater due to the prevailing conditions there (e.g. [27]). Numerous studies and publications confirm that in soils, the presence of Fe(II), sulphides and/or organic matter, as well as the low oxygen concentration in groundwater, effectively reduce Cr-VI to Cr-III, leading to the formation of stable complexes with minerals and organic matter (e.g. [27, 28, 29, 30]). Due to the very low mobility of Cr-III, the overall environmental toxicity risk is significantly reduced since exposure to Cr-III is much lower compared to Cr-VI. A reverse oxidation of Cr-III to Cr-VI could theoretically occur under specific conditions, such as the presence of manganese oxide in a highly alkaline environment. However, such conditions are not typically found in natural environments [27].

From an occupational health standpoint, the low concentrations of Cr-VI occasionally detected in eluates do not pose any significant risk when handling fresh concrete containing slag. This has been demonstrated through dermal toxicity studies on both pure slags and slag eluates, conducted on living animals and synthetic skin models, all of which showed no adverse effects (see text above). Furthermore, a theoretical assessment based on the EU-wide Cr-VI limit for cement (2 ppm) [31] provides additional reassurance regarding safety. If a solid material containing 2 ppm Cr-VI were completely dissolved in water at a water-to-solid ratio of 10:1, the resulting concentration would be 200 µg/L. As shown in the elution test results (Tables 2–5), the Cr-VI concentrations in SWS are consistently much lower.

For completeness, it is important to note that in rare cases, deviations in slag mineralogy may occur during the metallurgical process due to specific steel grades requiring different slag compositions in the furnace. In such cases, chromium may be incorporated into less stable mineral phases, leading to increased release and significantly higher Cr concentrations in the eluate. A notable example is the sample EAF 2 investigated as part of the IGF research project 21567 [5]. However, it is crucial to emphasise that such cases are exceptional, as confirmed by long-term leaching studies and extensive datasets. The objective of environmental assessments should therefore be to identify such slags through suitability testing and ensure that only environmentally compatible slags are used as aggregates.

CONCLUSION

The comprehensive studies on the environmental behaviour of steel slags demonstrate that even in cases where occasional exceedances of limit values occur in the "pure" aggregates, no release of environmentally relevant elements takes place in the finished product, the concrete specimen. Even after crushing the concrete specimens (recycled concrete), there is no significant release of heavy metals from the steel slag. Based on these results, as well as additional extensive research activities and findings, it can be concluded that, considering all potential exposure pathways, there are no dangers associated with the use of steel slags in concrete/cement. Political demands for resource conservation, circular economy and CO_2reduction highlight the importance of using steel slag as aggregate in concrete. However, to facilitate this use, an adjustment of the requirements in MVV TB, Annex 10 (ABuG) [3] is absolutely necessary. The evaluation of aggregates must – similar to the EBV [4] – be based on the release of substances, not on their content in the solid material.

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REDUCTION OF VANADIUM RELEASE FROM ELECTRIC ARC FURNACE SLAGS

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INTRODUCTION

Electric arc furnace slags (EAF slags) are a by-product of steel production in electric arc furnaces, where steel scrap is melted with additives such as lime and dolomite. During the process, crude steel and a molten slag are formed, which crystallise in the slag bed upon cooling and exhibit a complex mineral composition. In Germany, approximately 1.5 million tonnes of EAF are produced annually [1].

Currently, electric arc furnace slag is primarily used as a construction material in road and earthworks [1]. For the application, technical requirements must be met, and environmental compatibility must also be demonstrated. The latter is assessed using leaching tests, which determine whether potential pollutants can be released upon contact with water. The requirements for environmental compatibility are specified in the Substitute Building Materials Ordinance (EBV) [2], which defines material classes and leachate limit values for potentially environmentally relevant substances. Compliance with these defined limits ensures that, when used appropriately, there are no negative impacts on soil or groundwater. One of the substances for which limit values exist is vanadium, whose concentration in some EAF slags produced in Germany exceeds the limit values for the material class SWS-1 and, in some cases, even those for class SWS-2. This significantly restricts potential applications and may result in increased landfilling.

In the context of the circular economy and resource conservation, however, the utilisation of EAF slags is essential. Landfilling contradicts the goal of preserving natural resources and is both ecologically and economically disadvantageous. Looking ahead, the significance of EOS will continue to grow, as the traditional blast furnace-basic oxygen furnace route is increasingly being replaced by the direct reduction-electric furnace route as part of the steel industry’s decarbonisation efforts. This new production route, which uses not only steel scrap but also direct reduced iron (DRI) as an iron source, will result in an overall increase in EOS production [3].

Vanadium enters the production process both through steel scrap and through residual gangue from direct reduced iron (DRI) and therefore remains a relevant parameter in evaluating the environmental compatibility of EAF slags. At the FEhS-Institute, research projects were conducted with the aim of reducing vanadium release by treating the slag in its molten state, in order to ensure compliance with material class SWS-1. In a project completed in 2020 [4, 5], the relationship between the mineralogy of EAF slags and vanadium release was largely understood. Initial conditioning trials showed that vanadium release could be influenced by treating the electric arc furnace slag in its molten state. In a follow-up INNO-KOM project, “Concept Development for Reducing Vanadium Leaching from EAF Slag” [6], the previous approaches were further explored and tested on a larger number of samples. The focus was on treating EAF slag with quartz sand to modify the slag’s mineralogy, thereby enhancing the incorporation of vanadium in stable mineral phases and minimising its release. Other parameters regulated by the EBV were also examined to ensure compliance with material class SWS-1.

INVESTIGATIONS CONDUCTED

For the investigations, 10 EAF slag samples from German steel production were analysed. The samples were examined concerning their chemical and mineralogical composition. X-ray diffraction (XRD) with Rietveld refinement was used to determine the mineralogy, while electron probe microanalysis (EPMA) was conducted on a selection of five samples. The EPMA analyses were carried out using the CAMECA SX FIVE FE at Ruhr University Bochum. Backscattered electron (BSE) images and elemental distribution maps were generated to identify the vanadium distribution and the associated mineral phases. Additionally, individual mineral phases were chemically characterised using wavelength-dispersive X-ray microanalysis (WDS).

The leaching behaviour of the samples was examined for two particle size fractions (5/8 mm and 0/22 mm) using shaking batch tests at liquid-to-solid ratios (L/S) of 2 [7] and 10 [8]. Furthermore, the "Availability Test" [9] was applied to determine the maximum leaching potential.

In the batch tests, the sample was agitated for 24 hours with demineralised water at the respective liquid-to-solid ratio (L/S = 2 or L/S = 10). After shaking, the eluate was obtained by filtration and subsequently analysed. In the "Availability Test", a finely ground sample (< 125 µm, 16 g) was first leached for three hours at an L/S ratio of 50 while maintaining a constant pH of 7. A magnetic stirrer ensured proper mixing. The solid residue was then separated by filtration, returned together with the filter, and leached again for three hours with demineralised water (L/S = 50:1). In the second stage, the pH was adjusted to a constant value of 4. The eluates from both stages were combined and analysed.

For the melting experiments, five slags with different vanadium release rates were selected. The objective here was to specifically change the mineralogical composition of the slag and to determine whether modifying certain influencing factors could lead to an improved mineral incorporation of vanadium in the cooled slag. Several sub-samples of the selected slag (5/8 mm fraction) were melted in MgO crucibles in a Tammann furnace at approximately 1,600°C and subsequently cooled under varying conditions. The narrow particle size distribution was chosen to ensure good comparability between parallel samples and to minimise effects caused by differences in fine particle content.

Initially, reference experiments were conducted in which the slags were cooled at room temperature after melting. These conditions closely resemble those occurring in slag beds and thus help to avoid artifacts that could distort the results. The findings from these reference experiments serve as a baseline for further tests, in which parameters such as cooling rate and conditioning agents were varied.

CHARACTERISATION OF THE SAMPLES ANALYSED

The EAF slag samples analysed exhibit a composition typical of electric arc furnace slags (Table 1). As expected, the samples are rich in iron and calcium, aligning with the characteristics of common EAF slags. The vanadium content of the ten samples ranges between 575 mg/kg and 3,510 mg/kg. X-ray phase diagrams were created for all samples, with the results summarised in Table 2.

The primary mineral phases in the slags investigated are wuestite ((Fe,Mn,Mg)O) and calcium silicates. Calcium silicates are silicate minerals rich in calcium (Ca^{2+}) and silicate ions (SiO_4^{2-}), often incorporating other cations such as magnesium (Mg^{2+}), iron (Fe^{2+}, Fe^{3+}) or manganese (Mn^{2+}). Relevant calcium silicate phases include larnite (β-Ca_2SiO_4), kirschsteinite ($CaFeSiO_4$), bredigite ($Ca_{14}Mg_2(SiO_4)_8$), merwinite ($Ca_2Mg(SiO_4)_2$), glaucochroite ($CaMnSiO_4$) and diopside ($CaMgSi_2O_6$). These minerals crystallise in different crystal systems: larnite has a monoclinic structure, while the other identified phases crystallise in an orthorhombic system. These structural differences can influence the incorporation of foreign ions and the stability of the minerals under various thermodynamic conditions. In most samples, larnite is the predominant calcium silicate phase. However, sample EOS 3 is an exception, as it has the lowest larnite content among all samples investigated. Instead, kirschsteinite ($CaFeSiO_4$) and glaucochroite ($CaMnSiO_4$) are the dominant phases in this sample. Other significant phases in the EAF samples include gehlenite-åkermanite phases (melilite series) with the composition $Ca_2(Mg,Al,Fe)Si_2O_7$, brownmillerite ($Ca_2(Al,Fe^{3+})_2O_5$) and spinel ($(Fe,Mg,Mn)(Al,Cr)_2O_4$).

Table 1: Bulk composition of the samples analysed

	EAF 1	EAF 2	EAF 3	EAF 4	EAF 5	EAF 6	EAF 7	EAF 8	EAF 9	EAF 10
					M. %					
FeO	45.5	30.8	22	26.8	24.5	31.5	34.4	41.6	36.3	23.2
CaO	17.8	25.6	27.8	26.6	27.5	28.8	27.4	20.9	28.8	26.6
SiO_2	7.52	9.47	24.4	7.53	15.3	13.3	11.7	8.86	7.71	14.7
Al_2O_3	7.34	5.75	7.29	3.79	8.24	5.62	4.42	7.36	4.58	9.87
MgO	3.69	11.6	4.29	15.8	9.47	8.82	9.7	4.42	6.55	12.4
MnO	5.76	7.04	6.37	11.1	7.43	3.26	2.68	6.48	6.03	6.25
Cr_2O_3	3.84	3.79	2.32	3.02	2.18	1.79	1.08	2.88	2.3	1.89
P_2O_5	0.35	0.33	0.32	0.27	0.37	0.30	0.20	0.32	0.41	0.28
TiO_2	0.39	0.33	0.43	0.37	0.62	1.02	1.06	0.40	0.35	0.64
SO_4	0.21	0.42	0.33	0.24	0.24	0.24	0.21	0.33	0.63	0.24
F	0.01	0.02	0.03	0.02	0.02	0.07	0.05	0.07	0.04	0.03
					mg/kg					
V	869	1,720	937	3.510	897	656	575	661	1,180	851

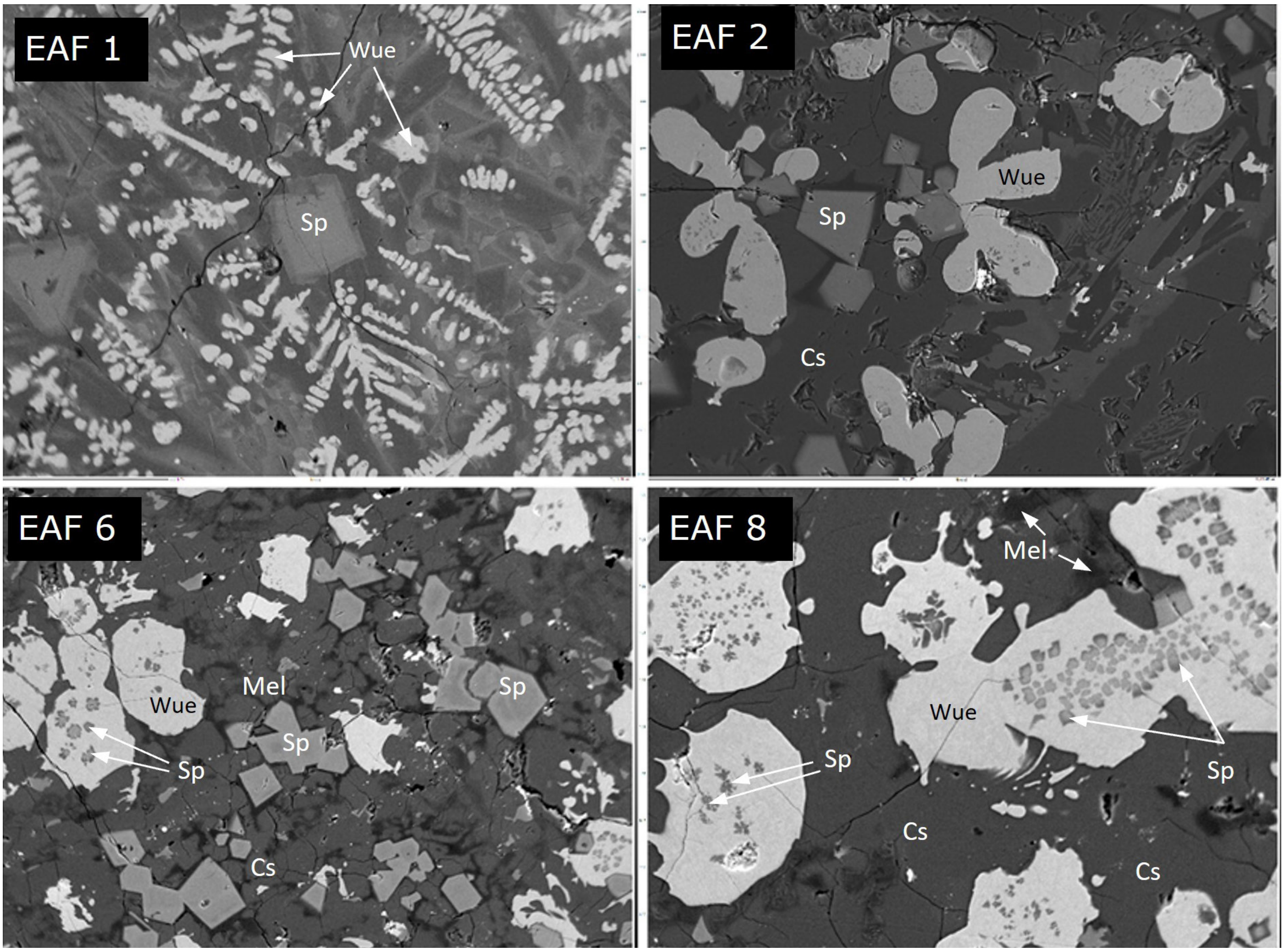

Figure 1: BSE images of representative areas of the samples investigated. Sp = spinel, wue = wuestite, CS = Ca-silicate, Mel = melilite

Table 2: Mineralogical composition of the samples analysed

Mineral name	Chemical formula	EAF 1	EAF 2	EAF 3	EAF 4	EAF 5	EAF 6	EAF 7	EAF 8	EAF 9	EAF 10
Wuestite/ Mg-wuestite	FeO/(Mg,Fe)O	24.1	33.3	10.2	32.8	25.8	39.7	34.8	37.8	18	29
Larnite	β-Ca_2SiO_4	13.9	33.1	2.5	25.2	13.0	17.9	31.2	19.3	30.4	10.3
Other Ca-silicates	$Ca_2{-}_xM_xSiO_4$	6.7	14.8	53.4	9.3	28.4	28.7	9.4	-	-	20.1
Melilite	$Ca_2MgSi_2O_{7}$- $Ca_2Al(AlSi)O_7$	22.5	4.1	24.4	5.9	14	9.3	15.2	16.6	-	9.7
Brownmillerite	$Ca_2(Al,Fe^{3+})_2O_5$	-	-	-	8.6	-	-	-	9.4	23.3	7.2
Magnesioferrite	$MgFe_2{}^{3+}O4$	-	-	4.6	-	-	-	-	-	-	-
Spinel/ magnetite	$MeMe_2O_4$	31.7	10.3	-	14.2	9.2	3.4	3.5	16.8	27.3	22.7
Hercynite	$Al_2Fe_2O_4$	-	-	-	-	5.5	-	-	-	-	-
Others	(< 5 M.%)	1.1	4.4	4.9	3.9	4.0	0.9	4.9	-	1.0	0.8

Melilite: gehlenite/åkermanit; other Ca-silicates: kirschsteinite ($CaFeSiO_4$), merwinite ($Ca_2Mg(SiO_4)_2$), galucochroite ($CaMnSiO_4$), bredigite ($Ca_{12}Mg_2Si_8O_{32}$) and diopside ($CaMgSi_2O_6$)

As part of the electron probe microanalysis (EPMA), backscattered electron (BSE) images were initially taken from representative sections of five selected samples. Figure 1 exemplarily presents the BSE images of samples EAF 1, EAF 2, EAF 6 and EAF 8. In general, nearly all phases detected via X-ray diffraction (XRD) were also observed using the microprobe. Wuestite appears in the BSE images as bright-reflecting, often rounded and, in some cases, skeletal structures. Spinel can be recognised by its characteristic triangular or octahedral cross-sections, with partial zoning visible. Phases with lower iron content, such as calcium silicates and melilite, appear darker in the BSE images.

For the quantitative determination of elemental contents, wavelength-dispersive X-ray spectroscopy (WDS) was performed on the main phases of each sample. The number of measurements per phase varied based on its abundance. A comprehensive dataset is available in the final report [6] and is not reproduced here. Figure 2 presents the vanadium content in various mineral phases of the five samples investigated. The results show that vanadium is incorporated into various phases, with its primary host depending on the sample's chemical composition and cooling conditions. In EAF 1 and EAF 6, spinel has the highest vanadium content, whereas in EAF 2, EAF 8 and EAF 9, vanadium is most enriched in calcium silicates. Additionally, wuestite and melilite can contain notable amounts of vanadium.

The combined quantitative mineralogical analyses and ESMA measurements provide an estimate of how total vanadium is distributed among the different mineral phases. The calculated values are presented in Table 3. In the original samples, vanadium is predominantly bound in calcium silicates, with larnite being the most common phase, as mentioned earlier. EAF 1 is an exception, where most of the vanadium is incorporated in spinel. However, even in sample EAF 6, where spinels contain the highest vanadium amounts (see Figure 2), 68% of the total vanadium is still incorporated in calcium silicates due to their greater abundance. After treatment with SiO_2, this distribution shifts, as described in the following section.

VANADIUM LEACHING BEHAVIOUR

As described earlier, most vanadium is bound in calcium silicates. Previous studies [4] and literature sources (e.g. [10], [11]) indicate that easily soluble calcium silicates are primarily responsible for vanadium release. Among these, larnite (Ca_2SiO_4), which is the dominant calcium silicate phase in most samples, exhibits the highest solubility [12]. Spinels, on the other hand, are known to be highly resistant to dissolution and weathering processes (e.g. [13], [14]), meaning that vanadium release from these phases is negligible. Consequently, larnite is the main contributor to vanadium release, which is also associated with an increase in calcium concentration in the eluates.

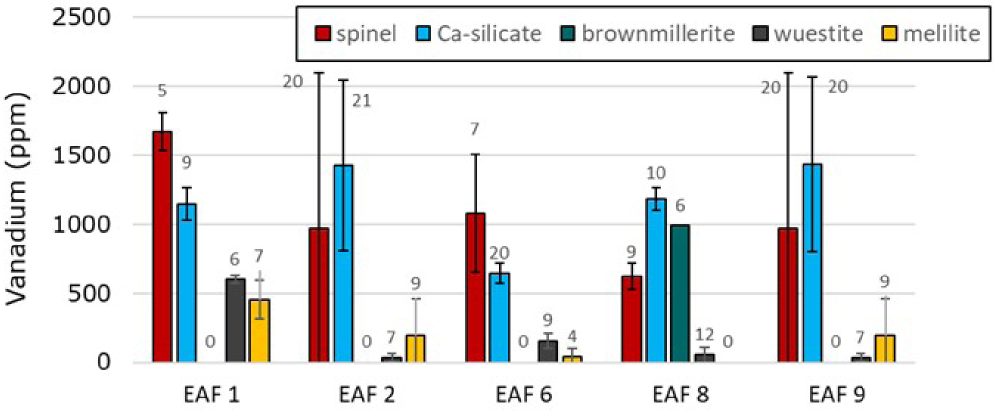

Figure 2: Measured vanadium content (mean values in mg/kg) in the main mineral phases of the samples. The standard deviation is represented as bars. The numbers indicate the number of measurement points (n).

Table 3: Relative distribution of vanadium (%) across mineral phases in original samples and samples after SiO_2 treatment

	Original	10% SiO_2	Original	10% SiO_2	Original	10% SiO_2	Original	10% SiO_2
	EAF 1		EAF 2		EAF 6		EAF 8	
Ca-silicate	23	6	**76**	17	**68**	32	**62**	15
Wuestite	18	16	6	**61**	19	15	4.4	8.9
Spinel	**48**	**77**	17	21	7.8	**53**	21	**74**
Melilite	10	0.4	1.4	0.9	3.0	-	-	2.8
Hercynite	-	-	-	-	2.1	-	-	-
Brownmillerite	-	-	-	-	-	-	13	-

The measured vanadium and calcium concentrations from the 2:1 and 10:1 leaching batch tests for both grain size fractions (5/8 mm and 0/22 mm) are shown in Figure 3. The figure also includes the limit values for the EBV [2] material class SWS-1, as well as the SWS-1 limits according to TL Gestein-StB [15], which was the applicable regulation prior to the introduction of the EBV, for the 10:1 leaching test.

The results show that many samples exceed the SWS-1 limit values of both regulatory frameworks, while some remain below the limits. Exceedance is particularly observed when the calcium concentration in the leachate is above 100 mg/L. This aligns with the well-established relationship between calcium and vanadium [4, 5]. When calcium concentrations exceed around 100 mg/L, the previously observed positive correlation – where calcium and vanadium are released together from calcium silicates – fades. Instead, higher calcium levels cause a noticeable drop in vanadium concentrations.

This effect is less evident in the 10:1 leaching test compared to the 2:1 test, as the higher water-to-solid ratio in the 10:1 test typically leads to lower calcium concentrations. The underlying

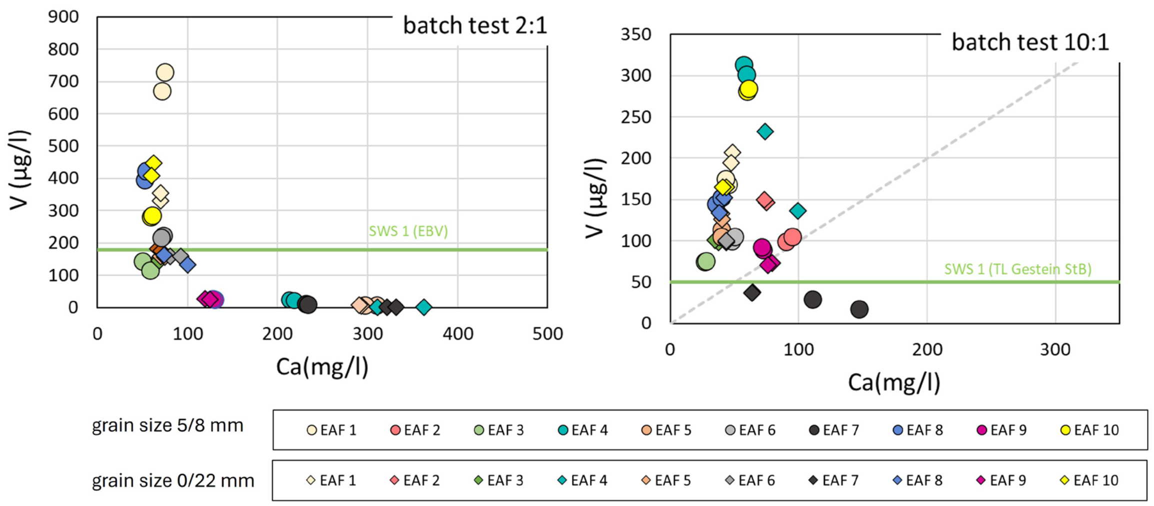

Figure 3: Vanadium and calcium concentrations in the eluates from the 2:1 leaching test (left) and the 10:1 leaching test (right)

mechanism is the exceeding of the solubility limit of calcium vanadate ($Ca_3(VO_4)_2$), causing vanadium to precipitate as a poorly soluble calcium vanadate [16, 17]. As a result, the actual vanadium release cannot be accurately quantified in such cases.

In the “Availability Test”, the described masking effect does not occur because the solubility product of calcium vanadate is not exceeded at the given conditions (pH ≈ 6). This makes the “Availability Test” particularly suitable for assessing the actual release of vanadium. Even though calcium concentrations are high in this test, the lower pH value prevents the formation of calcium vanadate. To highlight the absence of this masking effect, Figure 4 compares vanadium concentrations from the 2:1 and 10:1 leaching tests with those from the “Availability Test” for all samples investigated. The much higher vanadium concentrations in the “Availability Test” are clearly visible. A striking example is sample EOS 2, which shows low vanadium concentrations in the leaching tests – likely due to calcium’s masking effect – but significantly higher values in the “Availability Test”.

Table 4 also summarises the percentage of vanadium released in the different leaching procedures. While the batch leaching tests result in eluates in which at most around 3% of the total vanadium is detected, the “Availability Test” shows that up to 11% can actually be mobilised.

MELTING EXPERIMENTS ON LABORATORY SCALE

As part of the melting experiments, various approaches were tested within the project to investigate the effects of different parameters on mineralogy and vanadium release. In addition to cooling rates, different conditioning agents were examined, including SiO_2 (quartz sand), MgO, Al_2O_3 (bauxite) and borax ($Na_2B_4O_7$). Furthermore, combinations of multiple influencing factors, such as simultaneous SiO_2 addition and rapid cooling, were explored.

The experiments with borax aimed to determine whether incorporating boron into the crystal lattices of calcium silicates could improve their water resistance and thus reduce vanadium release. Borax is commonly used in metallurgy to stabilise slags that tend to disintegrate. It stabilises β-dicalcium silicate (Ca_2SiO_4) and prevents its transformation into the γ-phase, which promotes disintegration.

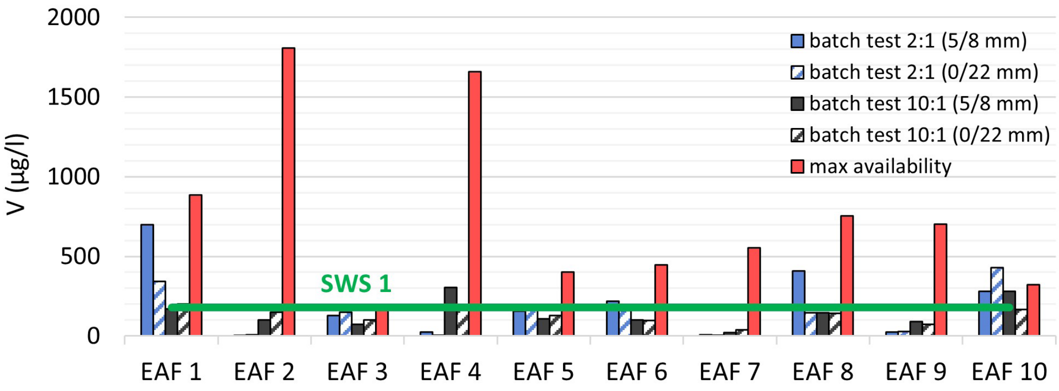

Figure 4: Measured vanadium concentrations in the 2:1 and 10:1 batch leaching tests as well as in the "Availability Test".

Table 4: The amounts of vanadium detected in the elution tests (in %) compared to the vanadium content in the solid phase.

	Solid content	Batch test 2:1 *		Batch test 10:1 *		Max. availability*
		5/8	0/22	5/8	0/22	< 125 µm
	mg/kg	%	%	%	%	%
EAF 1	869	0.161	0.079	0.196	0.231	5.10
EAF 2	1,720	0.001	0.001	0.059	0.086	10.52
EAF 3	937	0.027	0.032	0.079	0.106	2.04
EAF 4	3,510	0.001	0.000	0.087	0.052	4.73
EAF 5	897	0.035	0.040	0.121	0.144	3.35
EAF 6	656	0.066	0.048	0.155	0.151	6.82
EAF 7	575	0.003	0.000	0.392	0.644	9.62
EAF 8	661	0.123	0.045	2.231	2.163	11.4
EAF 9	1,174	0.004	0.005	0.761	0.608	5.98
EAF 10	844	0.066	0.101	3.314	1.939	3.82

** Mean values from duplicate tests*

Effects on the elution behaviour

The individual experiments with MgO and Al_2O_3 showed no improvement in vanadium release. On the contrary, vanadium leaching increased significantly. Due to these negative effects, these approaches were not pursued further.

The results of the melting experiments for the five slag samples investigated (EAF 1, EAF 2, EAF 3, EAF 6, EAF 8) are shown in Figure 5. The diagrams display vanadium concentrations from the 2:1 batch test and the "Availability Test" for both the reference untreated and treated samples. Additionally, molybdenum

Table 5: SiO_2 content and basicity of reference samples (ref.) and samples after treatment with SiO_2 (10% and 5%)

		EAF 1			EAF 2		EAF 3		EAF 6		EAF 8		
		ref.	10%	5%	ref.	10%	ref.	10%	ref.	10%	ref.	10%	5%
SiO_2	M.%	7.91	14.9	12.5	9.53	16.9	22.5	27.8	12.7	15.7	8.52	15.6	13.2
CaO/SiO_2		2.3	1.1	1.4	2.9	1.5	1.3	0.9	2.2	1.8	2.5	1.2	1.5

concentrations (right side of the image) are included, as changes in release behaviour were observed after treatment. The main objective was to reduce all relevant parameters to ensure compliance with the SWS-1 limit values. Given the previously mentioned relationship between vanadium and calcium, calcium concentrations from the 2:1 batch test were also considered.

Experiments with quartz sand addition confirmed, based on solid-phase analyses, that the SiO_2 content increased and the basicity ratio (CaO/SiO_2) decreased, indicating sufficient dissolution of the added quartz sand (Table 5). For samples EAF 1 and EAF 8, tests were conducted with both 10% and 5% SiO_2 additions. Overall, the results reaffirm the previously known effect that conditioning EAF with SiO_2 can reduce vanadium release. This effect was observed consistently across all samples, with a 10% SiO_2 addition proving more effective than 5%. The reduced vanadium release is further supported by the "Availability Test" results, which show low vanadium concentrations even without calcium influence, indicating an effectively improved mineral incorporation. The addition of borax led to a reduction in vanadium concentrations in the 2:1 batch test only for some samples. However, vanadium concentrations in the "Availability Test" remained high, indicating that this treatment did not significantly improve vanadium immobilisation.

However, the effective reduction of vanadium release due to the addition of quartz sand is always accompanied by an increase in molybdenum concentrations in the eluate of the 2:1 batch test. As a result, compliance with the SWS-1 material classification could not be achieved, as molybdenum levels consistently exceeded the limit. In some cases, the increase was so significant that even the SWS-2 class was not met. In contrast, experiments with rapid cooling showed a significant reduction in molybdenum release. Combining both treatment methods – quartz sand addition and rapid cooling – successfully reduced the release of both elements, allowing compliance with SWS-1, as seen in Figure 4. For sample EAF 2, SWS-1 was narrowly missed due to molybdenum, but the treatment still showed clear improvement. The addition of boron may have also influenced the outcome.

Other relevant parameters, such as chromium and fluoride, are not shown in Figure 4. However, for completeness, it should be noted that chromium levels were always below the SWS-1 limit and remained largely unaffected by the treatments. Fluoride concentrations, on the other hand, decreased in two samples that originally exceeded the SWS-1 limit after treatment with SiO_2 and simultaneous rapid cooling.

Overall, the results indicate that the most effective treatment for molten electric arc furnace slags is the combination of SiO_2 addition and rapid cooling. This approach significantly reduces both vanadium and molybdenum release, making it the most promising method for achieving compliance with SWS-1 limits. The large-scale implementation of this treatment was investigated at the electric steel plant Georgsmarienhütte as part of the research project "KONDEOS" [18].

Effects on mineralogy

The addition of SiO_2 alters the mineral composition, particularly the calcium silicates. While the original samples predominantly contain larnite (Ca_2SiO_4), the treatment with SiO_2 leads to the formation of other calcium silicates. Since larnite requires a high CaO content, it is no longer the most stable phase under increased SiO_2 conditions. Instead, phases with a higher silicon content and lower calcium content, such as kirschsteinite and bredigite, become more

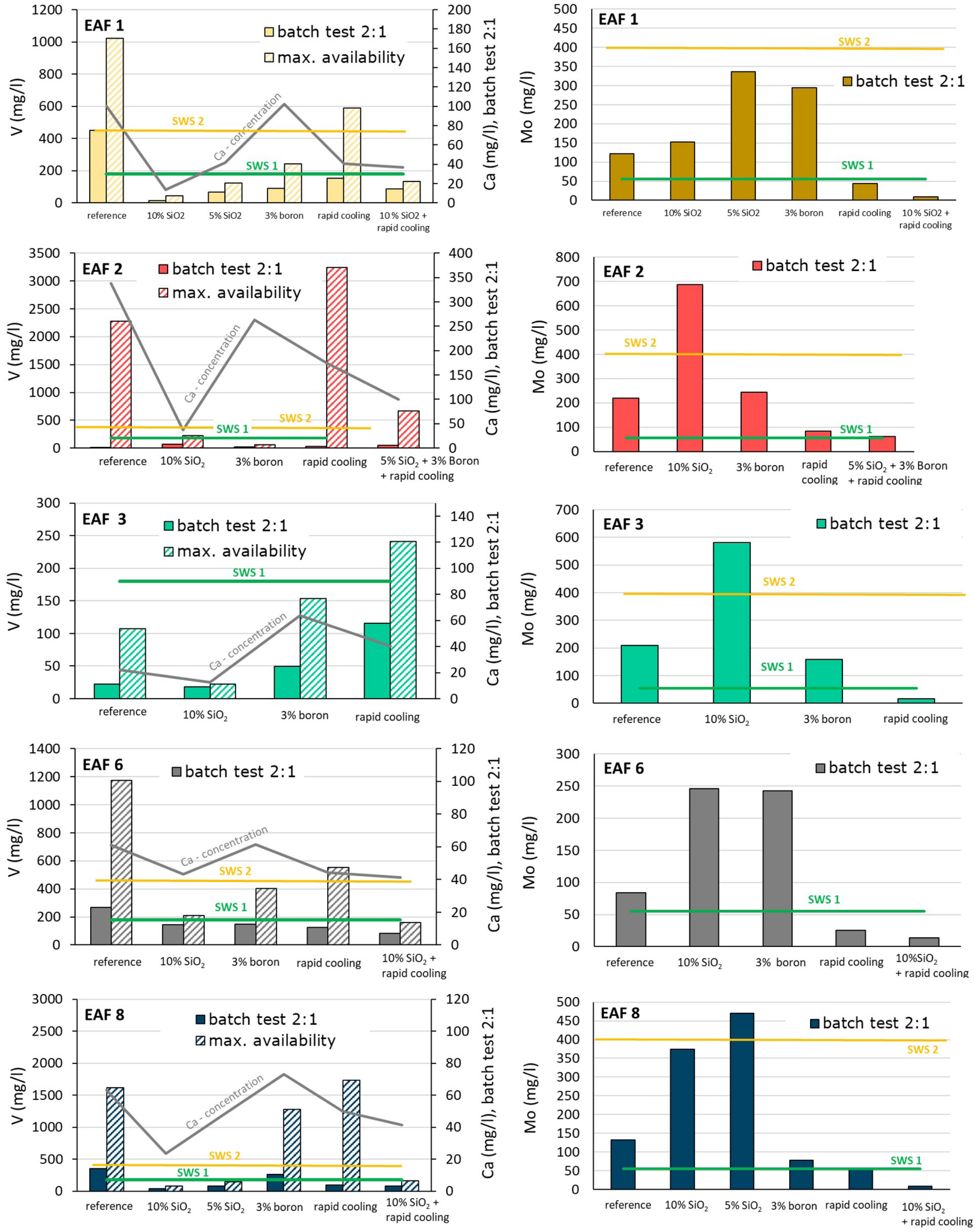

Figure 5: Measured concentrations of vanadium (left) and molybdenum (right) in eluates from reference samples and after various treatments in melting experiments. Additionally, the left diagrams show the calcium concentration from the 2:1 batch test.

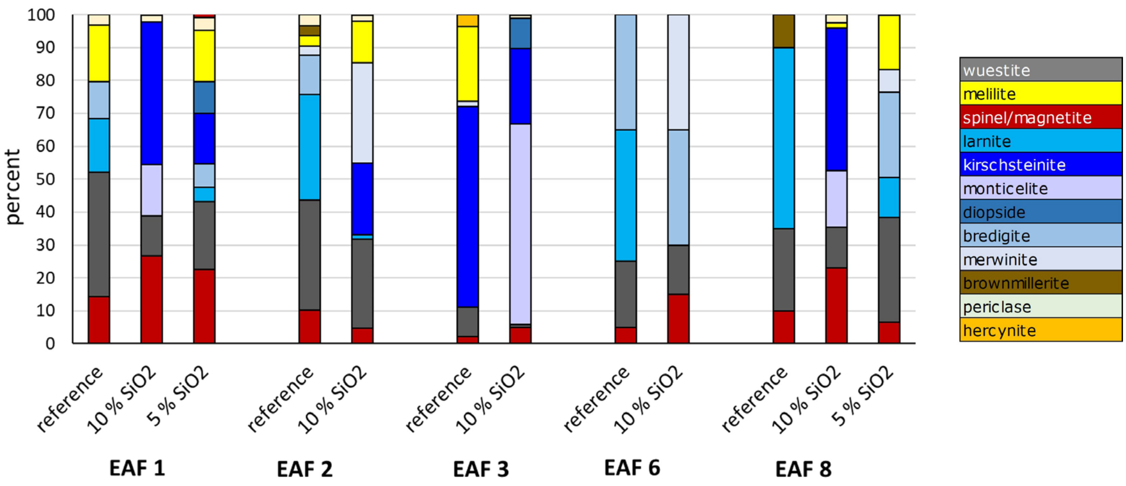

Figure 6: Graphical representation of the detected mineral phases (XRD) in samples from melting experiments with SiO_2 addition.

prevalent, aligning better with the modified CaO/SiO_2 ratio. In most samples, kirschsteinite forms after SiO_2 treatment (Figure 6). In the SiO_2-rich sample EAF 3, kirschsteinite was already present in its original state, while in sample EAF 6, bredigite and merwinite appeared after treatment, but no kirschsteinite was detected.

These changes in the composition of calcium silicates were confirmed by microprobe analyses. Figure 7 presents the compositions of calcium silicates in samples EAF 1, EAF 2, EAF 6 and EAF 8, as determined by microprobe measurements (for sample EOS 8, complete data is not available). A clear shift away from pure larnite composition is observed. The original samples (marked in red) cluster at the upper end of the larnite range, while the treated samples, following SiO_2 addition, have moved to different regions of the diagram.

In contrast, samples treated with boron or rapid cooling show no mineralogical changes. No new mineral phases form, and the composition of calcium silicates remains unchanged.

These mineralogical changes, particularly in calcium silicates, directly influence vanadium release. Since larnite is more soluble than the other phases, it was initially thought that the greater stability of kirschsteinite contributes to lower vanadium release. However, a thorough understanding requires a more detailed analysis of vanadium distribution across individual mineral phases.

Distribution of vanadium across mineral phases

The distribution of vanadium within individual mineral phases was determined using microprobe analysis. As previously shown, the addition of SiO_2 alters the mineralogy, particularly the composition of calcium silicates. The way vanadium is distributed among the slag phases is also affected. As already presented in Table 3, after treatment with quartz sand the vanadium distribution shifts. Samples where vanadium was initially mainly bound to calcium silicates (EAF 2, EAF 6, EAF 8), spinels – partially also wuestite – predominantly incorporate vanadium after the treatment.

Figure 8 illustrates the vanadium concentrations in individual calcium silicates for samples EAF 2 and EAF 8, both before and after SiO_2 treatment. Prior to treatment, larnite (Ca_2SiO_4) was the dominant calcium silicate, whereas after treatment, different calci-

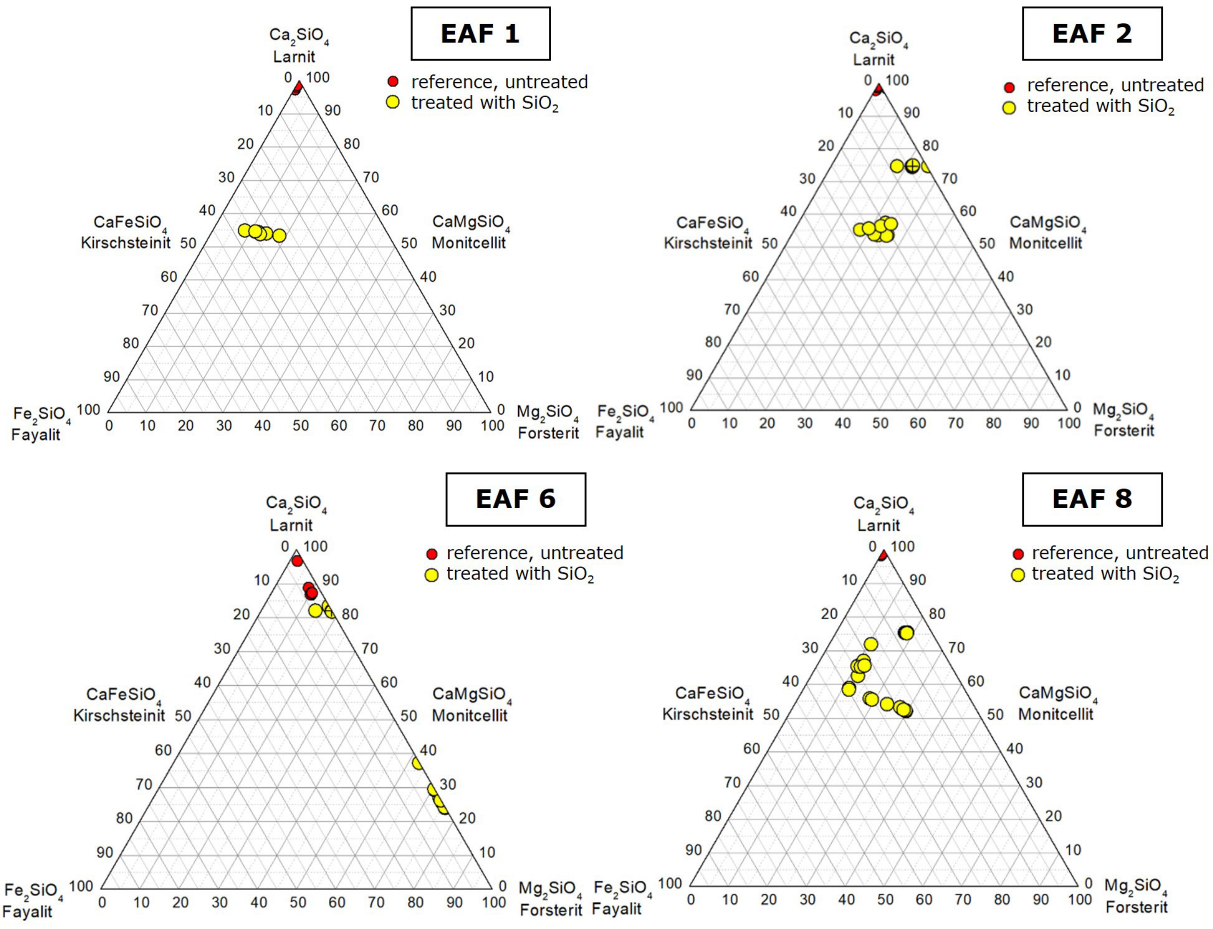

Figure 7: Composition of calcium silicates in reference samples and after treatment with SiO_2.

um silicates formed. The data clearly shows that these newly formed calcium silicates contain significantly less vanadium.

The reduced incorporation of vanadium in the newly formed phases may be explained by their structural properties. Larnite has a monoclinic crystal structure with relatively large interstitial spaces, which may facilitate vanadium incorporation. In contrast, kirschsteinite and bredigite have denser, orthorhombic crystal structures that provide less space for vanadium.

In contrast, the spinels in the SiO_2-treated samples show higher vanadium contents than those in the untreated samples. Figures 9 and 10 exemplarily illustrate the spinel measurements for samples EAF 1 and EAF 2. Additionally, a distinct zoning, with an aluminum-rich rim and an aluminum-poor core is observed. This zoning correlates with the chromium and vanadium contents: while the chromium content decreases with increasing aluminum content, the vanadium content increases. Consequently, vanadium concentrations are higher at the edges of the spinels than in the core.

CONCLUSION

Vanadium in electric arc furnace slags is distributed among various mineral phases. In the samples examined, most vanadium is incorporated into calcium silicates, with larnite being the dominant phase in most cases. Due to its relatively high solubility compared to other calcium silicates, larnite plays a key role in controlling vanadium release from the slag.

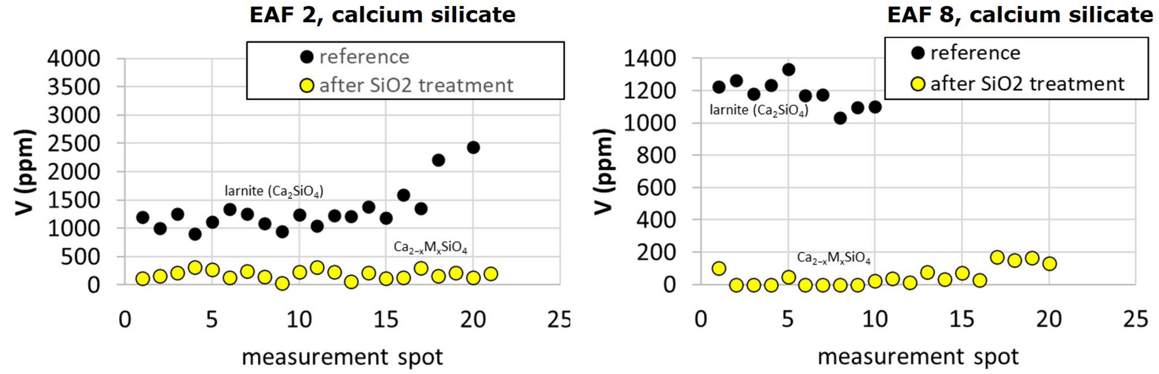

Figure 8: Vanadium content (ppm) at individual measurement spots in the calcium silicates.

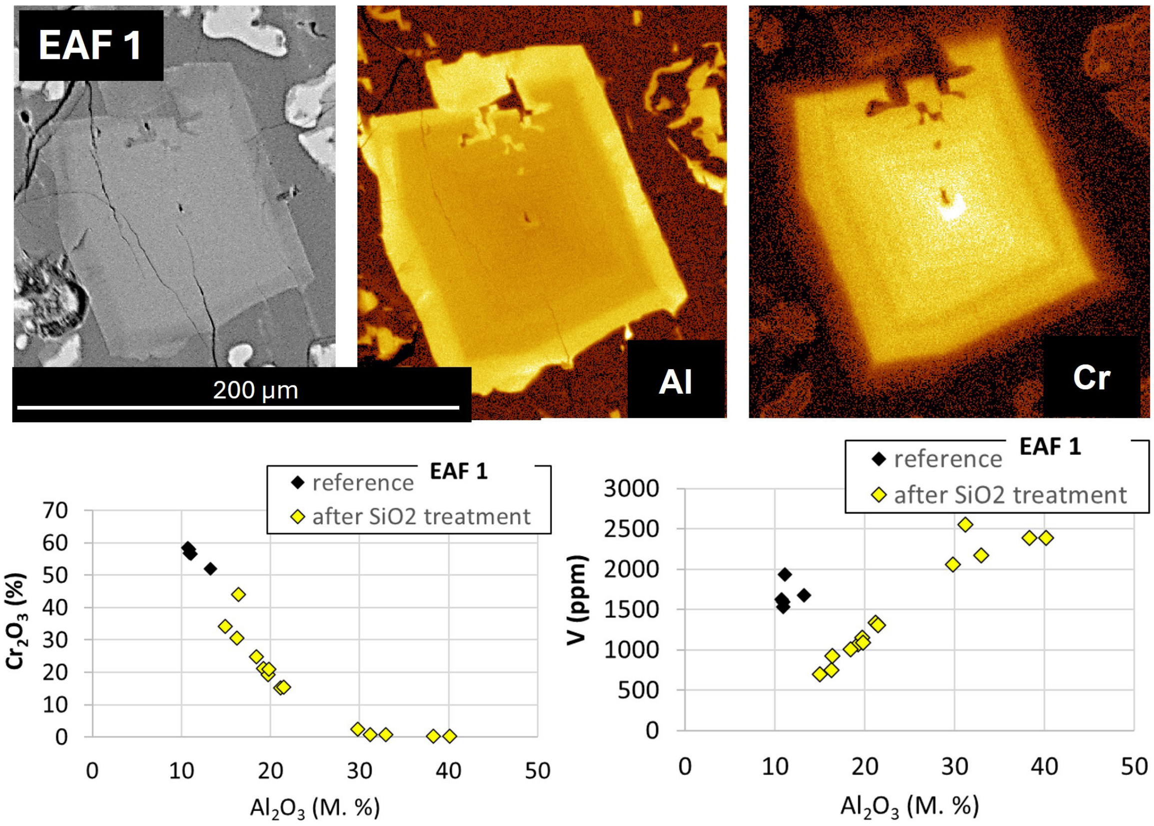

Figure 9: BSE images of a representative spinel grain with corresponding element distribution maps for aluminium and chromium (top), as well as measured contents of Al_2O_3, Cr_2O_3 and vanadium in multiple spinel grains of the sample before and after treatment with SiO_2.

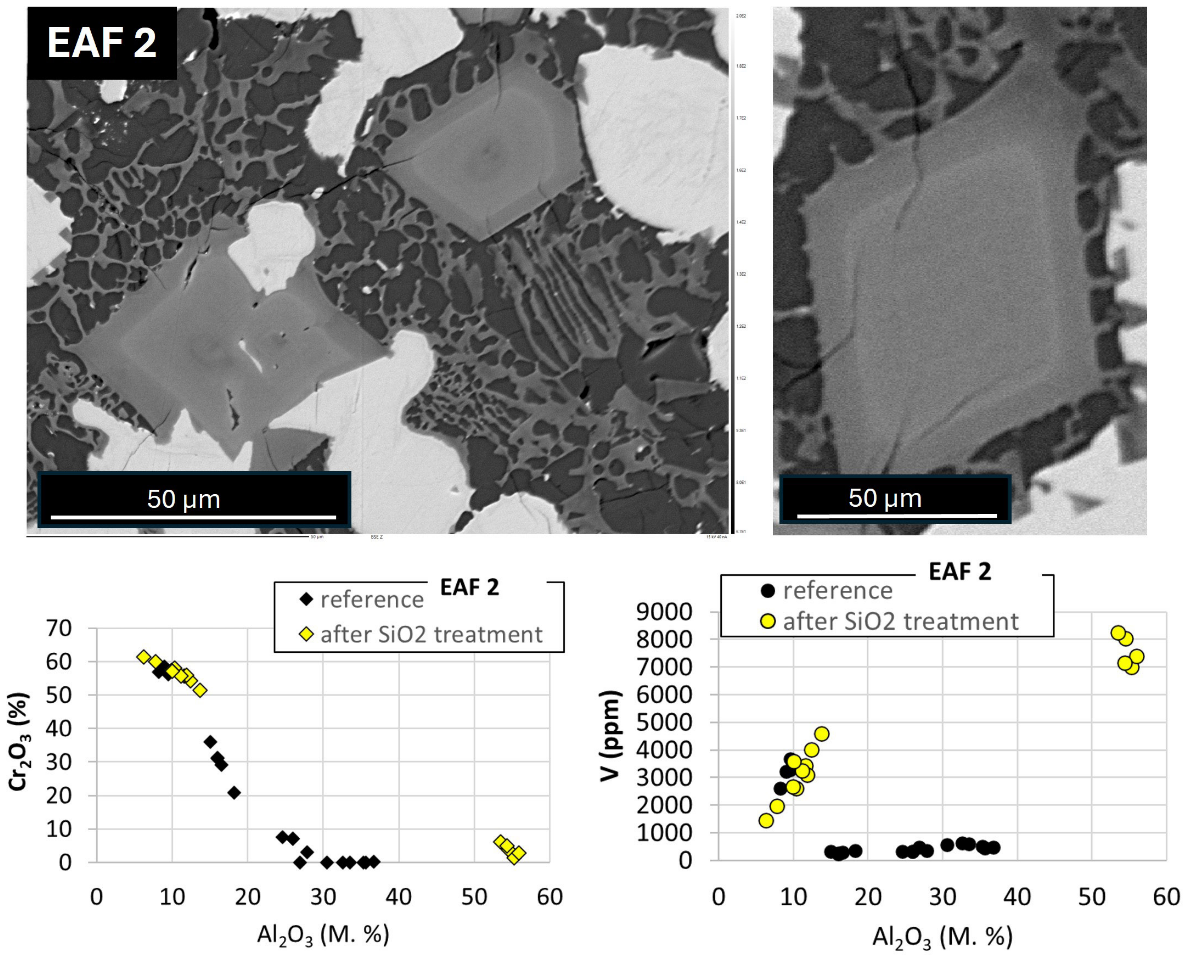

Figure 10: BSE images of representative spinel grains and measured contents of Al_2O_3, Cr_2O_3 and vanadium in multiple spinel grains of the sample before and after treatment with SiO_2.

The addition of SiO_2 to the molten slag alters the mineralogy, replacing larnite with other calcium silicates, often kirschsteinite. This transformation is accompanied by a redistribution of vanadium among the mineral phases. After treatment with SiO_2, spinels usually contain the majority of the total vanadium. This shift results in reduced vanadium release, attributed both to the greater stability of the newly formed calcium silicates and to the strong chemical resistance of spinels, which makes them highly resistant to weathering and leaching.

However, the addition of SiO_2 also increases molybdenum release, preventing compliance with the strictest EBV [2] material classification (SWS-1) through this modification alone. A combination of SiO_2 addition and rapid cooling proves to be particularly effective, simultaneously reducing both vanadium and molybdenum release while meeting the SWS-1 threshold values.

Future research should focus on optimising vanadium incorporation in spinels by identifying conditions that enhance their vanadium-binding capacity. Additionally, further investigation is needed to better understand the mechanisms driving molybdenum release. A more in-depth study of the kinetic aspects of vanadium and molybdenum incorporation into different mineral phases would also be valuable for clarifying the underlying reaction mechanisms and ensuring the long-term stability of the formed phases.

Acknowledgment

The INNO-KOM project “Concept Development for Reducing Vanadium Leaching in EOS” (49VF210006) was funded by the German Federal Ministry for Economic Affairs and Climate Action as part of the INNO-KOM innovation competence programme.

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PRODUCTION AND USE OF FERROUS SLAG IN 2023

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Table 1: Production and use of blast furnace slag in Germany 2023/2022 (in million tonnes)

Production	**2023**	2022
Granulated BFS	**6.27**	6.53
Air-cooled BFS	**0.73**	0.63
Sum	**7.00**	7.16
From interim storage	**0.77**	0.71
Total	**7.77**	7.87

Use	**2023**	2022
ABS for aggregates	**0.18**	0.25
ABS for aggregate mixtures	**0.31**	0.32
GBS for cement production	**7.13**	7.14
GBS for other purposes	**0.08**	0.08
Intra-industrial consumption	**0.07**	0.08
Total	**7.77**	7.87

Table 2: Production and use of steel furnace slag in Germany 2023/2022 (in million tonnes)

Production	**2023**	2022
Slag from oxygen steel making	**2.68**	2.73
Slag from electric arc steel making	**1.24**	1.45
Others (SecMS, etc.)	**0.49**	0.49
Total	**4.41**	4.67

Use	**2023**	2022
Metallurgical use	**0.46**	0.50
Fertiliser	**0.46**	0.49
Construction material	**2.03**	2.10
Others	**0.30**	0.25
Sum	**3.25**	3.34
Final deposit	**0.45**	0.58
To interim storage	**0.71**	0.75
Total	**4.41**	4.67

For decades, ferrous slag (blast furnace slag and steel furnace slag) has been established on the market as a building material and fertiliser all over Europe. The ratio of use continuously exceeds 90% of the production figures. Therefore, the use of slag by-products is an example of a successful circular economy.

GERMANY

The data on production and utilisation in Germany in 2023 is shown in Tables 1 (blast furnace slag) and 2 (steel furnace slag). The data for 2022 is also provided for comparison in each case.

After steel production in Germany of 36.8 million tonnes in 2022, this figure fell slightly to 35.4 million tonnes in 2023 [1]. Accordingly, fewer slag products were also produced: a total of 11.4 million tonnes of blast furnace and steel furnace slag were produced in 2023 (2022: 11.7 million tonnes). In addition, 0.1 million tonnes of stocks were reduced on balance, meaning that a total of 11.0 million tonnes of ferrous slag could be marketed.

A differentiated analysis of the material flows for blast furnace slag shows that granulated blast furnace slag accounts for almost 90% of the total production of blast furnace slag. The proportion of granulated blast furnace slag used for cement production is even almost 92%. This emphasises the importance of CEM II/S and CEM III cements containing blast furnace slag for the cement industry. These cements continue to make an important contribution to CO_2 savings in cement production.

The air-cooled blast furnace slag was primarily processed into construction material mixtures for frost protection layers and gravel base layers, but also into aggregates for asphalt and concrete (approx. 0.2 million tonnes in 2023).

The production of steel slag in 2023 was 4.4 million tonnes (previous year: 4.7 million tonnes), of which approx. 2/3 came from the converter process. The use of products from steel slag fell slightly in 2023 compared to the previous year (3.3 million tonnes), which may also be due to the construction measures available. At 2.0 million tonnes (previous year: 2.1 million tonnes), the construction materials market remains by far the most important sales segment in terms of volume. The use for "Others" (0.3 million tonnes) includes measures without formal quality control, e.g. use as landfill construction material. Finally, 0.5 million tonnes of converter lime were used as a high-quality fertiliser in agriculture, and around 0.5 million tonnes of steel furnace slag were used because of their lime and iron content in a resource-saving manner by means of internal recycling.

In total, 11.0 million tonnes of iron and steel slag were used as building materials and fertilisers in Germany in 2023. With a total production of 11.4 million tonnes, this corresponds to an exemplary use rate of 96%.

EUROPE

The European slag association EUROSLAG regularly asks its members for European slag data. Preliminary figures for 2023 are given in Tables 3 (blast furnace slag) and 4 (steel furnace slag). However, these figures must be qualified in 2024 as it has not yet been possible to obtain a satisfactory number of responses.

But based on the hot metal and crude steel production figures provided by Worldsteel [2], a reasonable estimate of BFS production and SFS production can be made. This leads to about 21 million tonnes of BFS and 17 million tonnes of SFS produced in the EU-27 countries plus the UK during the year 2023. The

Table 3: Reported figures on production and use of blast furnace slag in Europe 2023/2022 (in million tonnes)

Production	2023	2022
Granulated BFS	**12.2**	14.0
Air-cooled BFS	**1.4**	1.6
Sum	**13.6**	15.6
From interim storage	**1.1**	1.9
Total	**14.7**	17.5
Estimated production in EU-27 + UK based on Worldsteel figures for hot metal production	20.7	20.9

Use	2023	2022
Cement production and concrete additives	**13.2**	14.7
Road construction	**1.4**	2.7
Others	**0.1**	0.1
Total	**14.7**	17.5

Table 4: Reported figures on production and use of steel furnace slag in Europe 2023/2022 (in million tonnes)

Production	2023	2022
Slag from oxygen steel making	**5.1**	6.1
Slag from electric arc steel making	**2.3**	3.4
Others (SecMS, etc.)	**1.1**	1.8
Sum	**8.5**	11.3
From interim storage	**0.5**	
Total	**9.0**	11.3
Estimated production in EU-27 + UK based on Worldsteel figures for crude steel production	16.9	15.1

Use	2023	2022
Metallurgical use	**0.8**	1.6
Fertiliser	**0.6**	0.7
Construction material	**5.9**	5.5
Others	**0.6**	0.5
Sum	**7.9**	8.3
Final deposit	**1.1**	1.8
To interim storage		1.2
Total	**9.0**	11.3

reported data provided in Tables 3 and 4 presents about 66% of the BFS figures but only 50% of the SFS figures. These are roughly the percentages obtained for BFS for the year 2022 (the data situation is worse for SFS). A comparison between the years 2023 and 2022 was therefore made, even though the validity is limited.

Comparing the production figures, there is a significant decrease in production for BFS especially, as reported above for Germany. There appears to be a difference in SFS production as the estimated sum seems bigger than the previous year.

Comparing the percentages for BFS with those reported from Germany, the figures are quite close together: approximately 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.

Approximately two thirds of the SFS produced is used for construction purposes, for roads, dams or hydraulic structures, for example. Around 9% is used for metallurgical purposes, 7% as fertiliser and a small percentage for other uses. Based on the figures of one single country, an amount of 0.5 Mt of the SFS was taken from interim storage to be used in major construction projects. Twelve percent of the SFS produced was sent to final deposit.

Altogether, the (reported) use is close to the (reported) production, not only in Germany but in most European countries. Steel producing companies acting together with processing and marketing companies continue doing their best to enable a circular economy. <<<

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DURABILITY OF CONCRETE ACCORDING TO THE PERFORMANCE PRINCIPLE – EVALUATION OF LABORATORY TEST METHODS FOR FROST RESISTANCE AND FREEZE THAW AND DE-ICING SALT RESISTANCE

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INTRODUCTION

The durability assessment in the European concrete standard DIN EN 206 [1] and the national concrete standard DIN 1045-2 [2] is based on a descriptive approach. As the descriptive approach is based on past experience, which cannot cover current technical developments, e.g. with regard to new cement types or cement constituents, the European concrete standard already describes additional performance approaches (performance-based design methods). Although in Germany these can only be used in conjunction with general approvals from the DIBt or European technical assessments, public sector clients in particular are increasingly demanding performance tests, for example on the chloride, carbonation, freeze-thaw or acid resistance of concretes. At the European level, Eurocode 2 [3] was published as a draft in 2021, which includes the performance-based concept of exposure resistance classes (ERC). Although the development of a corresponding new EN 206-100 standard has been discontinued, the German Committee for Reinforced Concrete (DAfStb) is working on a national guideline which, as a first step, will regulate this ERC concept for the exposure classes XC1 to XC4 and XD1/XS1 [4], which are mainly used in building construction.

In principle, efficient test methods and a generally valid assessment horizon for the test results are mandatory prerequisites for the use of the performance concept. The laboratory test methods must allow the practical performance of the concretes to be assessed throughout their service life within a manageable test period. The accelerated test conditions must not produce artefacts that are inconsistent with the real conditions in practical concretes, e.g. with regard to the chemical and physical processes in the concrete structure. However, in the case of freeze-thaw resistance, for example, it has been known for decades [5] and described in the DAfStb status report [6] that, for slower-setting concretes containing blast furnace cement or coal fly ash as an addition, the characteristic values determined in laboratory tests are often in contradiction with decades of positive practical experience in construction. It is therefore not possible to apply the test results directly to practice.

One reason for this situation is that test methods were often developed and calibrated using Portland cement concretes, as Portland cement dominated the cement market for decades. This has changed considerably since the 1990s. As the cement industry is one of the largest emitters of industrial CO_2 emissions, the substitution of CO_2-intensive Portland cement clinker by other cement constituents plays an important role in the national, European and global roadmaps of this industry [7]. In Germany, Portland cement today has a market share of only 24%, while Portland composite cements have a share of 53% and blast furnace cements 22% [8]. This trend will continue in the context of the intended decarbonisation of the cement industry, for example by using activated clays or the fines from concrete recycling as a cement component.

The hydration of blast furnace cements, composite cements and concrete additives partly follows different laws from those known for Portland cement. If this behaviour is not taken into account in concrete performance tests, the above-mentioned contradictions with practical behaviour occur. For example, in the laboratory test for freeze-thaw resistance using the CDF method according to DIN CEN/TS 12390-9, unfavourable and impractical pre-setting conditions of the test specimens were found for slower hardening concretes [5, 9-11]. Similar experiences have been reported for other laboratory tests [12-14].

OBJECTIVE

The IGF research project 21835 N [15], coordinated by the FEhS-Institute, was the third project in a joint project coordinated by the DAfStb and consisting of a total of five individual projects, each involving several research institutions, and funded by the Federal Ministry for Economic Affairs and Climate Action (BMWK). The main objective of the project, which was carried out in close cooperation with the Karlsruhe Institute of Technology (KIT) and the Ruhr University Bochum, was to analyse in detail the current test methods for carbonation, chloride penetration, freeze-thaw and de-icing salt and acid resistance and to assess any necessary modifications. The aim was to ensure that concrete durability can be accurately and practically assessed in the increasingly common performance tests that will be carried out in the future. The focus was on various issues relating to the influence of pre-storage of specimens, such as duration and ambient humidity, and time-accelerating test conditions, such as increasing the concentration of the attack medium, on the test results and their evaluation with respect to practical experience.
This article deals only with the results obtained at FEhS for the freeze-thaw resistance test methods. The results obtained by the project partners for the carbonisation, chloride and acid resistance tests will be discussed in later articles.

RAW MATERIALS AND CONCRETE PRODUCTION

Cements

For the tests, different concretes were produced from five commercial cements according to DIN EN 197-1 [16] and a CEM II/C cement according to DIN EN 197-5 [17]. In terms of composition, the cements cover a wide range of cements produced in Germany and will be of great importance for concrete production both today and in the future, albeit in modified form. Table 1 summarises the most important cement properties. They meet all the requirements of the two cement standards mentioned.

Aggregates

Quartzitic aggregates from regional deposits in the Rhine area were used for the tests. An A16/B16 grading curve in accordance with DIN 1045-2 was produced from the individual fractions using the least squares method.

Additive

Where necessary, the consistency of the concretes was adjusted using a commercial PCE-based superplasticiser. For concretes exposed to freeze-thaw and de-icing salt attack, the air content defined for the tests was adjusted using a commercially available air entraining agent. The admixtures were in accordance with DIN EN 934-2 [18].

Concrete composition and pre-storage

DIN 1045-2 defines cements and limiting compositions for the use of concretes in exposure classes XF3 (frost resistance with high water saturation) and XF4 (freeze-thaw and de-icing salt resistance with high water saturation). These combinations are based on many years of practical construction experience and therefore serve as a reference (series B1 and B3) for the evaluation of the results obtained after a modified pre-storage of the concrete test specimens compared to the standard specifications. For example, if the w/c ratio is increased and/or the air void content of the concrete is reduced, it can be assumed that these concretes have insufficient resistance to freezing and thawing with or without de-icing salts. These variation concretes (B2 and

Table 1: Characteristic values of the cements

Parameters		CEM	I 42.5 R	II/A-LL 42.5 N	II/C-M (S-LL) 42.5 N	III/A 42.5 N	III/B 42.5 N
LOI (950 °C)		M.-%	2.99	6.31	6.51	1.4	0.09
Al_2O_3			5.35	4.66	6.34	7.92	9.33
CaO			63.8	63.3	56.0	53.4	48.8
SiO_2			19.0	16.8	20.9	24.5	27.4
Fe_2O_3			2.57	2.21	1.62	1.61	1.22
MgO			1.43	1.30	2.49	3.56	4.70
Na_2O			0.15	0.14	0.15	0.21	0.25
K_2O			0.75	0.64	0.84	0.67	0.57
TiO_2			0.30	0.26	0.40	0.69	0.86
SO_3			3.18	3.04	3.15	3.02	3.29
Cl^-			0.042	0.069	0.086	0.041	0.04
HS content microscopy			-	-	-	42	67
Limestone content			6	15	21	5	2
Blaine fineness		cm^2/g	3,839	3,540	5,478	4,734	5,037
Initial setting time		min	225	205	165	190	220
Water demand		M.-%	29.0	27.5	30.5	31.5	32.0
Compressive strength after	2 d	MPa	28.6	21.2	20.9	19.7	11.4
	7 d		48.7	37.1	35.9	38.9	33.8
	28 d		56.9	44.4	53.3	57.7	55.2
	91 d		61.0	51.2	63.4	68.6	66.1

Table 2: Concrete compositions

Exposure class		XF3		XF4	
Concrete		B1	B2	B3	B4
Cement content	[kg/m^3]	320	320	320	320
w/c ratio	[-]	0.50	0.60	0.50	0.50
Air content	[Vol.-%]	0.0	0.0	5.0	3.0
Aggregate	[-]	A16/B16			

B4 series) must fail a modified test. Reference and test concretes were prepared from the above materials. Their compositions are given in Table 2.

The concretes were produced according to DIN EN 12390-2 [19]. The specimens were either stored in the mould for one day at 20°C, six days under water at 20°C and 21 days in the climatic chamber at 20°C and 65% RH in accordance with the national annex to the standard, or in accordance with the modified pre-storage regime proposed in [20] for seven days in the mould at 20°C, 14 days under water at 20°C and seven days in the climatic chamber at 20°C and 65% RH. The two pre-storage regimes were followed by tests on the microstructure and degree of hydration of the cements in the concretes, as well as tests on freeze-thaw resistance with and without de-icing salts. The actual test method remained unchanged in the test sequence.

RESULTS

Fresh and hardened concrete properties

The fresh concrete properties of all concretes were determined in accordance with the DIN EN 12350 [21] series of standards. The consistency of the concretes was also sufficient for the reference concretes in accordance

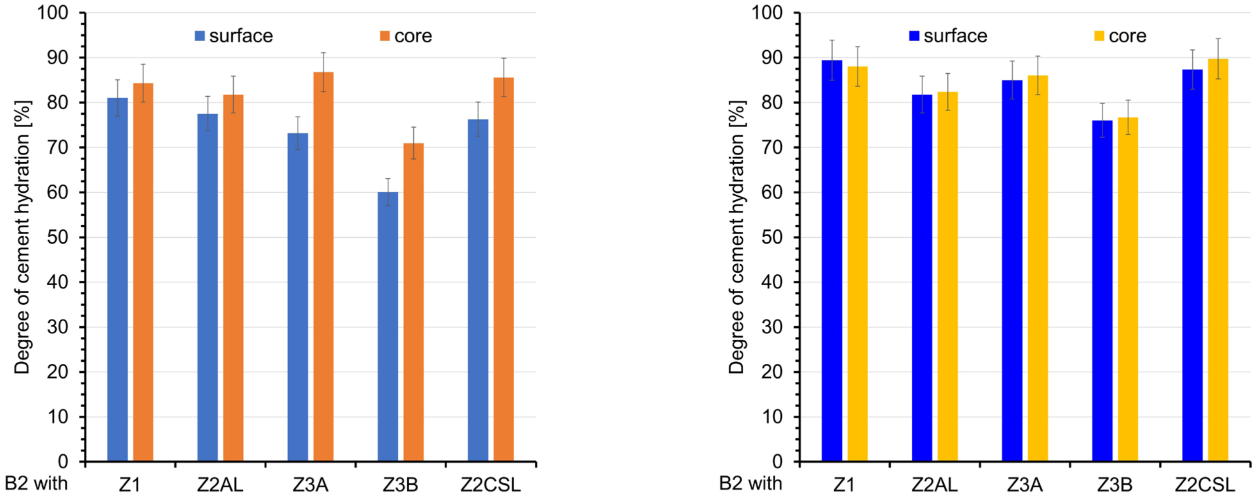

Fig. 1: Degree of hydration of the cements in B2 series concretes; left: Standard pre-storage, right: Modified pre-storage

with the limiting composition of DIN 1045-2, so that the concrete was well compactable and representative test specimens could be produced. The desired air content of the B3 and B4 series (Table 2) was accurately adjusted using a conventional air entraining agent. The compressive strength of the hardened concretes was determined up to an age of 28 days in accordance with DIN EN 12390-3 [22]. The strength development of the concretes was in accordance with the expectations usually associated with the different cements, w/c ratios and air contents.

Degree of hydration of the cements

The degree of hydration of the cements has a major influence on the microstructure of the concrete and therefore on its properties. This includes scaling during freeze-thaw attack in the field and in laboratory tests, which only affects the structural area of the concrete near the surface. It was therefore determined on the concrete specimens. For this purpose, the actual cement content and the content of chemically bound water in the sample analysed were determined in accordance with DIN 52170-4 [24] and related to the maximum water content that can be achieved with complete cement hydration. This maximum water content was calculated using the equation for stoichiometric water binding defined by Stark and Wicht [25], extended by a factor to account for the latent hydraulic main constituent, blast furnace slag [20]. Using this method, the degree of hydration was determined with an accuracy and repeatability of approximately 5%.

The degree of hydration of the cements was determined separately in both the surface and core areas of concretes with different types of pre-storage. The type of pre-storage was not found to influence the degree of hydration of the cements in the core of the concretes. However, the degree of hydration of the cements near the surface was significantly influenced by the type of pre-storage. It was generally lower at the surface than in the core of the concretes stored according to the standard (Fig. 1, left). For the cements with a high hydration rate, such as CEM I or CEM II/A-LL cement, the differences were only slight. However, for the cements with a lower hydration rate, the differences were significant, with values of 11% to 15%. The difference tended to increase with decreasing clinker content. Thus, in the area close to the surface of the concretes, the standardised pre-storage of the concretes mainly affects the hydration of the slow-setting cements.

The right part of Figure 1 shows examples of the degrees of hydration of the cements in the near surface area and in the core area of the modified pre-stored concretes of Series B2. The differences between the

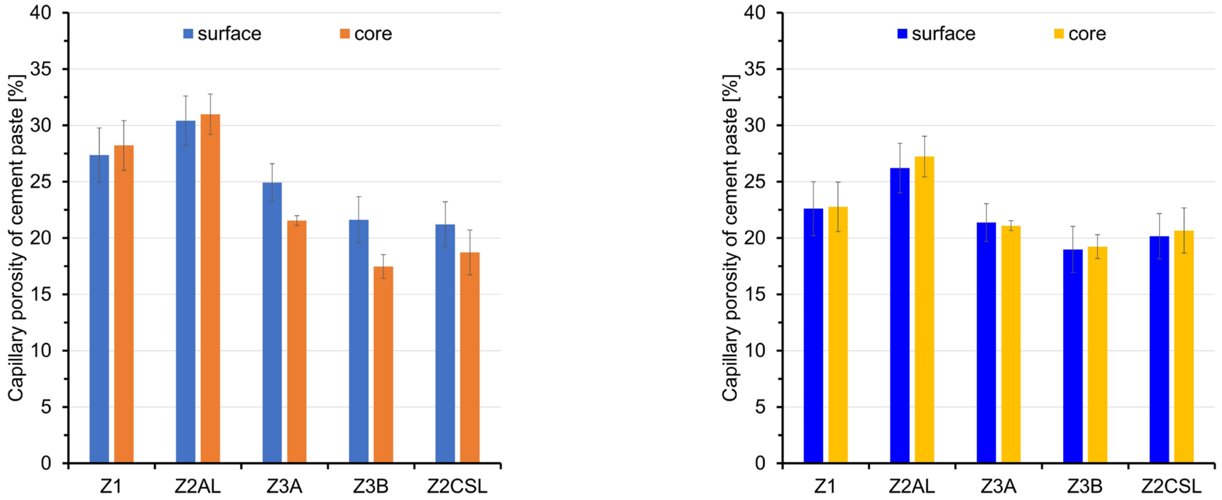

Fig. 2: Capillary porosity of the cements in the concretes with a cement content of 320 kg/m³ and a w/c ratio of 0.50; left: Standard pre-storage, right: Modified pre-storage

areas were small, less than 5%, and within the accuracy of the measurements, which was also the case for the other concrete series analysed. It can be concluded that the modified curing ensures that the cement hydration in the near surface area is not adversely affected. This ensures that the concrete can be properly tested for freeze-thaw resistance. This is, of course, subject to the general conditions in the field ensuring that a sufficiently high degree of hydration can develop in the concrete near the surface. Proper curing of the concrete plays a crucial role in this [26].

Porosity of the concretes

As in the cement hydration tests, the porosity of the concrete samples was determined near the surface and in the core of the concretes. High-pressure mercury porosimetry was used. The results were converted to the cement paste contained in the samples by first determining the aggregate content of the sample using the insoluble residue. The method used is described in detail in [20]. Based on the systematic work of Romberg and Smolczyk [27, 28], a pore radius of 0.03 µm was defined as the lower limit of capillary porosity, while all pores with a radius < 0.03 µm were counted as gel pores. As the effect of air voids in the fresh concrete on capillary porosity was small compared to the w/c ratio, the tests were grouped according to the w/c ratios analysed. This allowed three individual measurements to be statistically analysed. The coefficient of variation for the determination of capillary porosity was approximately 4%.

When the concretes were pre-stored in accordance with the standard, as shown in Figure 2 (left) for the series with 320 kg/m^3 cement and a w/c ratio of 0.50, a significantly higher capillary porosity was found in the surface compared to the core. This was more pronounced for the slower-setting cements CEM III/A, CEM III/B and CEM II/C-M. The near-surface microstructure of these concretes was therefore significantly coarser, which inevitably affected their behaviour in the subsequent freeze-thaw tests.

In contrast, the modified pre-stored concretes did not result in significant differences in capillary porosity between the surface and core (Fig. 2, right). A microstructure similar to that of the core concrete was formed in the surface zone of the concrete. The capillary porosity tests therefore also prove that the modified pre-storage method produces specimens that can be used for proper laboratory testing of freeze-thaw resistance.

Frost resistance

Frost resistance was determined using the CIF method according to CEN/TR 15177 [29]. In both national and international regulations, the only accep-

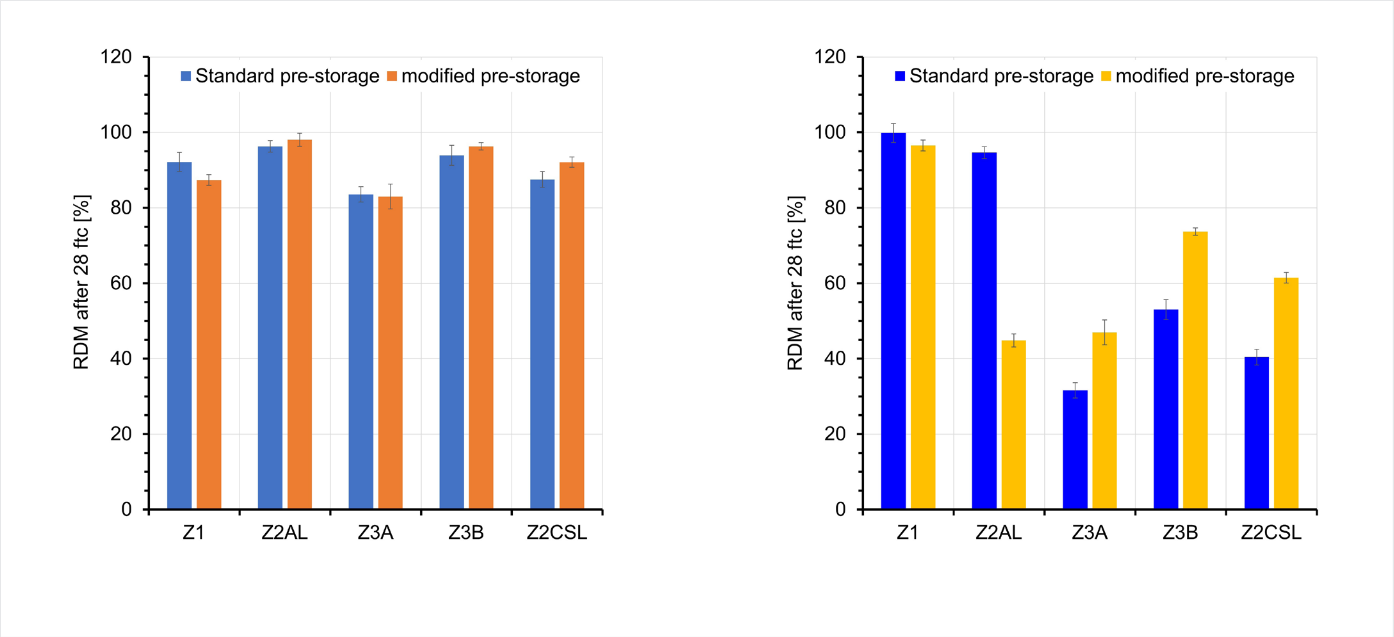

Fig. 3: RDM in the CIF test of the concretes after 28 freeze-thaw cycles; left: Series B1, right: Series B2

tance criteria for high frost resistance with standardised pre-storage of the test specimens have so far been defined in the BAW code "Frost testing of concrete" of the German Federal Waterways Engineering and Research Institute (Bundesanstalt für Wasserbau, BAW). The key acceptance criterion is a maximum change in the relative dynamic modulus of elasticity (RDM) to 75% of its initial value after 28 freeze-thaw cycles. As an additional acceptance criterion, a scaling of ≤ 1000 g/m² and ≤ 1750 g/m² of the 95% quantiles of the test series after 28 freeze-thaw cycles was defined. Concretes from the B1 and B2 series were analysed. While the B1 series concretes were expected to have a high frost resistance as they were composed to meet the minimum requirements of DIN 1045-2 for exposure class XF3, the B2 series concretes were expected to have a lower frost resistance due to the increased w/c ratio.

Irrespective of the type of pre-storage, all concretes in the B1 series had an RDM of between 83% and 98% after 28 freeze-thaw cycles (Fig. 3, left) and reliably met the acceptance criterion. As structural damage can only be clearly determined at an RDM of < 80% [30], the structure of the concretes can be classified as undamaged. As expected, very little material was scaled from the test surface. The specific amount of weathering was less than 0.10 kg/m². The weathering of the modified pre-stored concretes tended to be slightly lower. However, due to the low values, these differences are not considered significant for the frost resistance assessment.

The RDM of the B2 series concretes that did not conform to the standard decreased significantly after 28 freeze-thaw cycles (Fig. 3, right). The only exceptions were the concretes with CEM I cement (both types of pre-storage) and the concrete with CEM II/A-LL cement stored according to the standard. For these concretes, practically no decrease in RDM and therefore no structural damage was observed. The concretes with the slower-hardened cements, which were stored according to the standard, showed RDMs between 31.6% and 53.0%. But the RDMs for the modified pre-stored concretes were slightly higher with values between 46.9% and 73.7%. However, the concrete structure was also damaged in the concrete.

Scaling was low for all concretes, with values well below 1.00 kg/m². Only in the case of the standard pre-stored concrete with CEM III/B cement did the scaling value of 2.11 kg/m² exceed the acceptance criterion. In general, scaling was lower for the modified pre-storage concretes. This, together with the higher RDM, is due to the structure with fewer capillary pores and the higher degree of hydration of the cements in the

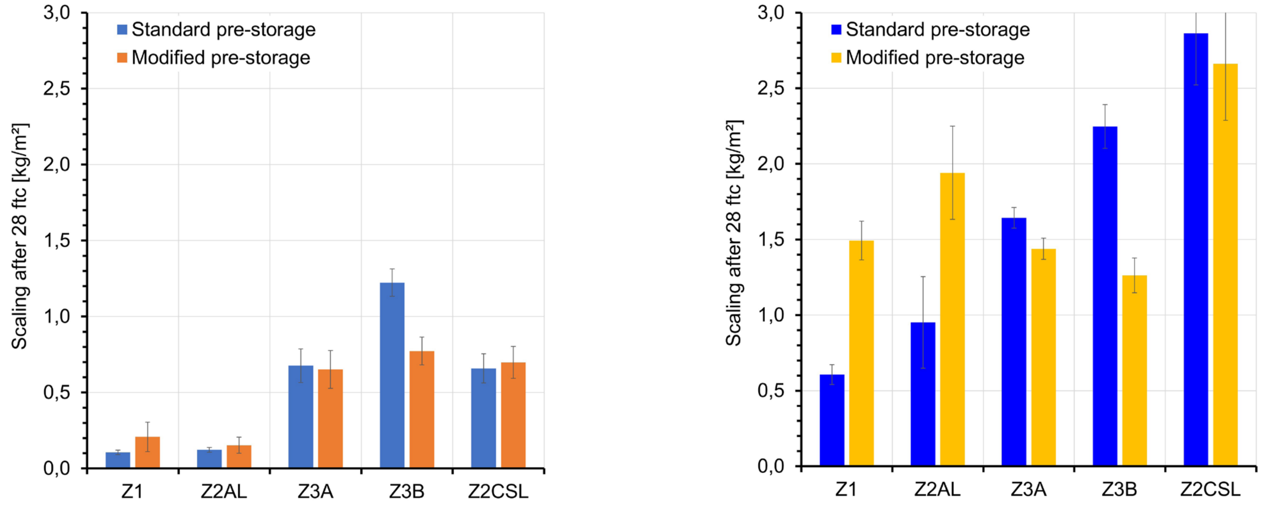

Fig. 4: Scaling after 28 freeze-thaw cycles of the concretes in CDF test: left: Series B3, right: Series B4

surface of the concretes as a result of the modified pre-storing.

Statistical analysis of the individual results of the CIF tests gave no indication that the accuracy of the method was affected by the change in the method of specimen pre-storage. It can therefore be assumed that the frost resistance of the concretes can be assessed with sufficient accuracy with an RDM of 75%.

Freez-thaw and de-icing salt resistance

Freeze-thaw and de-icing salt resistance was tested using the well-established CDF method according to DIN CEN/TS 12390-9 [23]. As for the freeze-thaw resistance, only the aforementioned BAW code defines an acceptance criterion for the freeze-thaw and de-icing salt resistance. A scaling after 28 freeze-thaw cycles of more than 1500 g/m² is not allowed, as well as the 95% quantile of the test series not exceeding 1800 g/m². Series B3 concretes meet the minimum compositional requirements of DIN 1045-2 for exposure class XF4. Therefore, based on many years of practical construction experience, a high resistance to freeze-thaw and de-icing salt can be expected. Concrete with CEM III/B cement is an exception. Its use for exposure class XF4 is generally excluded in DIN 1045-2, except for two special applications. However, no practical experience is available yet for concrete with CEM II/C-M cement. On the other hand, B4 series concretes were not expected to have high freeze-thaw and de-icing salt resistance because they do not meet the standard composition requirements for the air void system.

The scaling after 28 freeze-thaw cycles of the B3-series concretes is shown in the left plot of Figure 4, while that of the B4 series concretes is shown in the right plot.

The concretes of the B3 series with the faster-setting cements CEM I and CEM II/A-LL, stored according to the standard, met the acceptance criterion defined by the BAW. After 28 freeze-thaw cycles, the amount of scaled material was approximately 0.11 kg/m². Concrete made with CEM III/A cement also met the criterion with a scaling of approximately 0.68 kg/m². However, experience has shown that this is not always the case, as illustrated by unpublished results from the FEhS-Institute (Figure 5). The reason for this is an unfavourable near-surface microstructure which can form during standard storage, depending on the content and reactivity of the blast furnace slag, and which can reduce scaling resistance. As described above, the surface structure is not representative of the performance of the concrete and does not match that of comparable and appropriately cured structural concretes [20]. The acceptance

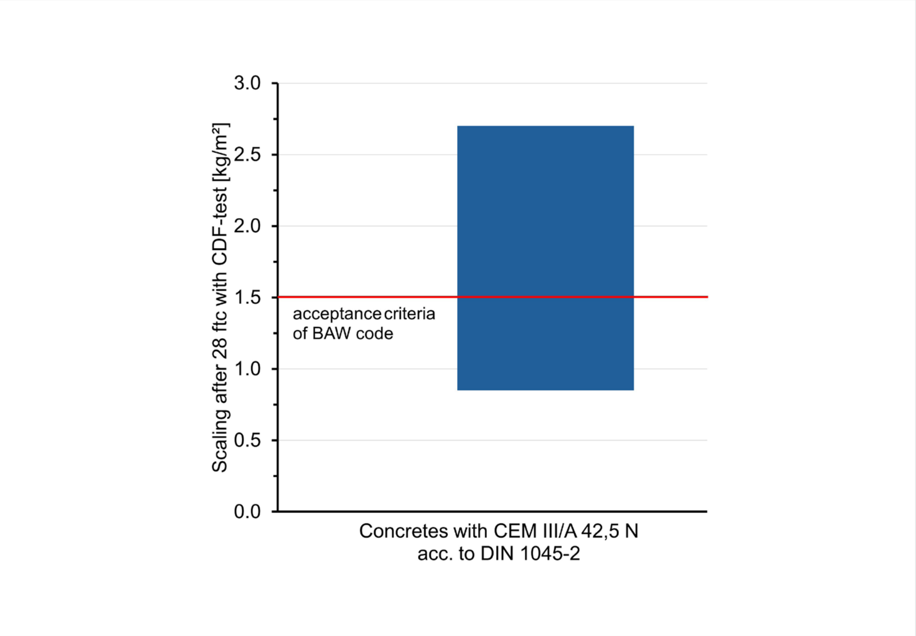

Fig. 5: Scaling of concretes with CEM III/A cement composed acc. to DIN 1045-2 (z = 320 kg/m3; w/z = 0.50; LP content ≥ 4.5 vol.%) in the CDF test acc. to DIN CEN/TS 12390-9 (unpublished results)

criterion of 1500 g/m² was also fulfilled by the two concretes with CEM III/B (1.22 kg/m²) and CEM II/C-M cement (0.66 kg/m²).

The modified pre-storage changes the scaling behaviour of the concretes in the laboratory test. For concretes with the faster CEM I and CEM II/A-LL cements of the B3 series, the scaling was only slightly higher with values of approx. 0.21 and 0.15 kg/m² respectively. In contrast, they were somewhat lower for the concretes with CEM III/A (0.65 kg/m²) and CEM III/B cement (0.77 kg/m²). Approximately 0.70 kg/m² was scaled off from the surface of the concrete with the CEM II/C-M cement. The results can be explained by the findings on the influence of the modified pre-storage on the microstructure and the degree of cement hydration in the area close to the concrete surface. Accordingly, the concretes made with the faster cements show only a slightly higher degree of hydration at the surface, whereas it increases significantly in the concretes made with the slower cements. This increases their resistance to scaling.

In the case of the B4-series concretes with a reduced air content and a storage according to the standard, scaling increased significantly after 28 freeze-thaw cycles. While the amount of scaled material in the concretes with CEM I (0.61 kg/m²) and CEM II/A-LL (0.95 kg/m²) was still well below the acceptance criterion defined by the BAW code, it was significantly exceeded by the concretes, with CEM III/A, CEM III/B and CEM II/C-M cements with values of 1.64 kg/m² to 2.86 kg/m². Consequently, the concretes with CEM I and CEM II/A-LL would be attested a high resistance to freeze-thaw and de-icing salts, which, however, is not to be expected due to the inadequate composition based on many years of practical construction experience. The performance of the concretes would therefore be incorrectly assessed.

The effect of the type of pre-storage on the test result, described for the B3-series concretes stored according to the standard, was significantly increased for the corresponding B3-series concretes. The amount of scaled material for concretes with CEM I (1.49 kg/m²) and CEM II/A-LL (1.94 kg/m²) increased significantly compared to standard storage. In contrast, the concretes with CEM III and CEM II/C-M had lower scaling of 1.44 kg/m², 1.26 kg/m² and 2.66 kg/m², respectively, due to the improved microstructure in the surface area.

The results were summarised together with the results documented in [20] for different concrete compositions. Figure 6 shows the scaling after 28 freeze-thaw cycles of modified pre-stored concretes with different compositions and cements. Concretes with CEM I, CEM II/A and CEM III/A cements, which were formulated in accordance with DIN 1045-2, showed surface scaling of less than 0.92 kg/m² after 28 freeze-thaw cycles. When the composition of these concretes did not meet the minimum requirements of DIN 1045-2, the scaling of these concretes generally increased to values > 1.13 kg/m². In accordance with practical experience in the construction industry, it is therefore possible to distinguish between concretes with high and insufficient freeze-thaw and de-icing salt resistance at a scaling value of 1.0 kg/m² when modified pre-stored concretes are tested in

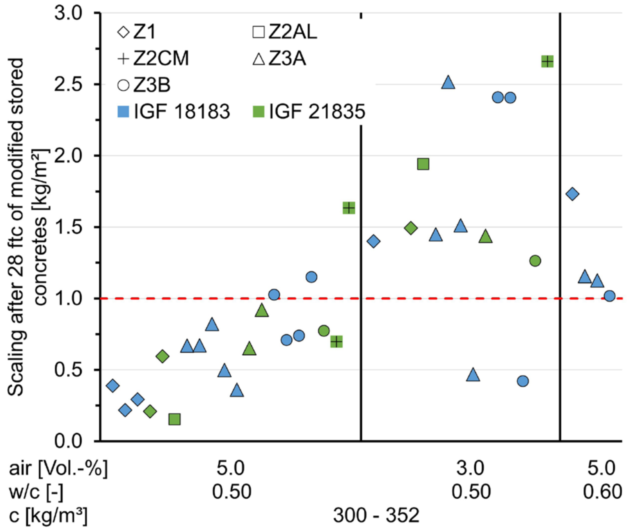

Fig. 6: Evaluation of the freeze-thaw and de-icing salt resistance of modified pre-stored concretes

the laboratory using the otherwise unchanged CDF method. This potential acceptance criterion is shown as a red dashed line in Figure 6. With this acceptance criterion, the concretes made with CEM I and CEM II/A-LL that do not comply with the standard would not be classified as "false positives".

SUMMARY

Performance-oriented concrete design, as described in Eurocode 2 or the DAfStb ERC guideline, can only be implemented with efficient test methods. The durability properties of concrete need to be assessed in a reliable and practical manner. Therefore, the main objective of the research project was to analyse the common test methods for freeze-thaw or freeze-thaw and de-icing salt resistance and to evaluate potential influencing variables.

The degree of hydration of the cements and the porosity of the concretes were investigated. Irrespective of the type of cement used in the concrete, it was shown that changing the pre-storage conditions produced a microstructure in the concrete surface that was comparable to that of the core area and that of field concrete. Effects related to pre-storage, such as the type of cement used or the location of the specimens in the climatic chamber, can be avoided by using the modified pre-storage regime. This makes it possible to accurately assess the performance of the concrete in terms of its resistance to freeze-thaw with or without de-icing salt in the laboratory test.

A selective and appropriate assessment of the freeze-thaw or freeze-thaw and de-icing salt resistance is given by testing modified pre-stored concrete using the CIF (frost) and CDF (freeze-thaw and de-icing salt) test methods established in Germany.

If modified pre-stored concretes are tested using the CIF test method (frost) and CDF test method (freeze-thaw) established in Germany, the frost and freeze-thaw resistance can be assessed accurately and appropriately. However, the acceptance criteria as defined in the BAW code need to be adapted accordingly, as the scaling during the test is significantly influenced by the change in pre-storage. Based on the results of the research projects [15, 20], an acceptance criterion of 1.0 kg/m² can be proposed for the CDF test. With regard to internal damage to the structure, measured as RDM, the CIF criterion of <75% does not currently need to be adjusted, as internal damage to the concrete structure occurs from a RDM of 80% [30] and the influence of pre-storage is rather small.

ACKNOWLEDGEMENT

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NEW LIMIT VALUES FOR CHROMIUM AND VANADIUM CONTENT OF EU FERTILISERS INTRODUCED BY DELEGATED ACT

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THE BACKGROUND

In 2019, after eight years of consultation, the new European Fertiliser Products Regulation (Regulation EU No. 2019/1009) [1] came into force and became applicable on 17th July 2022. On the date of applicability, the EU Fertiliser Regulation No. 2003/2003 was simultaneously repealed. The main aim of the amendment was to strengthen the circular economy and enable secondary raw material fertilisers and recycled fertilisers to participate in the harmonised internal market. Towards the end of the drafting of the new Fertiliser Products Regulation, it was already becoming apparent that some fertilisers that were marketable under Regulation EU No. 2003/2003 [2] would be excluded from participation in the internal market due to the definitions of the new component material categories. For example, N-containing by-products from caprolactam production. Even before the regulation was adopted it was clear that amendments would be necessary after publication in the Official Journal of the European Union. These amendments needed to be made by the date of application of the new regulation.

The Commission was therefore authorised and obliged to subsequently introduce the missing regulations by delegated act by the deadline for applicability. Delegated acts were initially drawn up for the component material categories (CMC) "precipitated phosphate salts", materials from "thermal oxidation" and materials from "pyrolysis or gasification" processes (CMC 12 to 14). These delegated acts are based on the so-called "STRUBIAS report" [3] of the Joint Research Centre (JRC) of the European Commission, in which the three material categories were defined, and the respective source materials were evaluated. In addition, "iron slags" were also included in the category of combustion products due to EUROSLAG and the FEhS-Institute demanding harmonisation for slags. In its elaborations, the JRC took over the application rates from wood ashes instead of determining realistic application rates for slag-based lime fertilisers. In this report, the proposals for total chromium and vanadium limits for the three CMCs mentioned above were developed and then adopted in the corresponding delegated regulations. However, the category of "by-products" was still not regulated.

Based on the "STRUBIAS report" [3], the JRC prepared the report on industrial by-products [4]. The assumptions from the STRUBIAS report on "iron slags" were adopted in this report without any adjustments. Due to the uncorrected adoption of both the application rate as the basis for all further considerations and the derivation of the limit values into the JRC report on industrial by-products, the limit value proposals were also adopted entirely without reflection for the delegated regulation (EU) 2022/973 for industrial by-products (CMC 11) [5] and thus the new limit values for total chromium and vanadium of 400 mg/kg and 600 mg/kg respectively for "iron slags" were introduced into the new European Fertiliser Products Regulation.

EUROSLAG and the FEhS-Institute used every opportunity throughout the legislative process to point out the technical errors in the JRC reports at an early stage to prevent the introduction of the new limits. Discussions were held with the European Commission, members of the EU Parliament and representatives of the German Federal Ministry of Food and Agriculture. Furthermore, the German Federal Ministry for Economic Affairs and Climate Action, the EU Parliament's committees for the internal market, agriculture and the environment, as well as the EU Council, were contacted and informed about the problem. Despite all efforts to remove the proposed limit values for total chromium and vanadium from the delegated regulation with factual arguments and the almost exclusively negative submissions during the public consultation as well as the resistance of Germany and Italy, together with the associations EBIC and EUROSLAG, the Commission saw no need to re-examine the limit values. The Commission believed that placement on the market via national legislation was possible and CE labelling was not necessary. In addition, the accumulation of heavy metals in the soil was to be avoided because this was what the member states wanted (from the Commission's point of view).

THE CLAIM

After the delegated act came into force, the Fachverband Eisenhüttenschlacken e.V., supported by EUROSLAG and the FEhS-Institute, represented by Prof Christian Koenig (Bonn) and lawyer Gregor Franßen, filed an action for annulment against the delegated regulation within the deadline. From this perspective, the EU Commission had no mandate under the Fertiliser Products Regulation to introduce new regulations on health and environmental protection in Annex II of the Regulation by means of delegated regulations. The EU Commission is only authorised to introduce regulations on "agronomic efficacy and (application) safety" as these terms were used separately from the regulations on "protection of humans and the environment" in the Fertiliser Products Regulation. Furthermore, no realistic risk assessment was carried out, as is required if new limit values are introduced in Annex I of the Fertiliser Products Regulation by means of delegated acts. Technical errors in the derivation of the limit values were also a subject of the complaint. The JRC had adopted completely excessive application rates for lime (3 t/ha/a) from the "STRUBIAS report" [3] in the report on industrial by-products [4]. The arbitrarily defined target values for Cr and V levels in soil based on the 25th percentile of the precautionary values of a few member states were also adopted. This means that 25% of the precautionary values are below the specified value (100 mg Cr /kg soil and 125 mg V / kg soil) and 75% of the precautionary values are above, with only twelve member states having precautionary values for chromium at all and only five member states having precautionary values for vanadium. An average background value of 60 mg/kg soil for both chromium and vanadium was taken from EU soil statistics [6 cited in 3]. The difference between the background value and the arbitrarily defined target value was assumed to be the maximum accumulation to be tolerated within a period of 100 years. From this, the limit values were calculated based on the excessive application rate of 3 tonnes/ha/a. A toxicological justification as to why these target values are important is not given in the JRC reports, which makes the entire approach most questionable. Finally, a PNECaqua value for chromium was taken from the literature. PNEC stands for **P**redicted **N**o **E**ffect **C**oncentration, i.e. the concentration of a substance up to which no effects are to be expected and whose concentration should not be exceeded. This value was compared with concentrations in leaching tests with pure slag. However, no comparisons were made with real concentrations in soil water and no assessment of the consequences of a possible exceedance was made.

In addition to the scientific aspects, the complaint also criticised the denial of access to the internal market and the socio-economic aspects (disproportionality, waste avoidance, resource conservation, impact on affected industry, etc.) that were not examined. As expected, the EU Commission argued that it also had a mandate to protect the environment and health and that it had assessed all relevant scientific evidence. Furthermore, the EU Commission pointed out that the new Fertiliser Products Regulation applies in parallel to national law and that fertilisers can therefore continue to be marketed throughout Europe in accordance with national legislation and access the internal market by mutual recognition. CE labelling is not required. However, cross-border trade in the course of mutual recognition came to a standstill when the new Fertiliser Products Regulation came into force.

THE HEARING

Both sides reiterated their positions in the written hearing and in the oral hearing. The Commission defended its approach and introduced the VDLUFA position on liming [7] into the proceedings to justify the challenged application rates for converter lime. From this source it incorrectly cited the recommended application rates for lime. For example, the EU Commission did not take into account that the recommendations in the VDLUFA position on liming are not given in tonnes per hectare, but in decitonnes per hectare, i.e. 100 kilograms per hectare, and that these recommendations do not refer to annual applications, but to a crop rotation, i.e. a period of three to four years. The question of the correct application rate was discussed at length with the Court during the oral hearing, with the EU Commission and the JRC repeatedly attempting to justify the underlying application rate of 3 tonnes/ha/a by citing extreme values, recommendations for melioration and unit errors. No other points of criticism of the delegated act were discussed.

THE JUDGEMENT

The Court dismissed the action on all points [8] and justified its judgement by stating that the Commission should be granted a wide margin of discretion. With regard to the precautionary principle, the Court ruled that this could be applied even if a risk had not been scientifically proven. From the recitals to the Fertiliser Products Regulation, the Court concluded that the term "agronomic efficacy and safety" must be interpreted more broadly and also includes the protection of humans and the environment. Furthermore, the Court stated that beyond a REACH registration as fertiliser, in which the safety for the environment and health is proven, the legislator may make further regulations in specialised law. The judgement barely addresses the technical points of criticism. With regard to the detailed discussion during the oral hearing about the correct application rates, the Court merely states that even if the Commission had made a mistake here, this was covered by the wide margin of discretion.

ASSESSMENT

By establishing the wide discretionary scope and the very broad interpretation of the precautionary principle, the Court has essentially given the EU Commission carte blanche. If both are applied generously, any conceivable substance can be banned. The fact that very complex issues are regulated by delegated acts makes it very difficult for the EU Parliament and Council to exercise any meaningful control. It is sobering that the Court did not evaluate the criticism presented in any way and followed the EU Commission's arguments with regard to access to the internal market via national law and mutual recognition. In this context, even a press release from the EU Commission, in which the difficult conditions to access the internal market were cited as justification for the new European Fertiliser Products Regulation, had no probative value.

THE APPEAL

Appeals could be lodged against the Court's judgement, i.e. against errors in the judgement. However, there cannot be a new hearing of evidence. The Fachverband Eisenhüttenschlacken e.V. has lodged an appeal against the judgement in good time, as the Court made errors in reaching its decision.

For example, Article 42 (8) [1] of the new Fertiliser Products Regulation stipulates that the introduction of new limit values must be based on normal conditions of use. The significantly excessive application rate as the basis for all further considerations in determining the limit values does not represent normal conditions of use. Even in the JRC reports [3, 4] it is pointed out at various junctures that this elaboration is not a risk assessment and that "worst-case scenarios" were assumed for the analysis. The Court should have recognised this.

The Court also did not correctly describe the precautionary principle and thus gave the EU Commission too much room for manoeuvre. Instead of demanding a risk assessment, the Court was satisfied with a risk characterisation. Furthermore, the Court did not review the proportionality of the regulations or examine less burdensome measures such as labelling the Cr and V content. Labelling would give the member states the opportunity to themselves control the immission to soil via application regulations at their own discretion. The consequences of non- marketability (conservation of resources, disposal, etc.) were also not examined by the Court.

WHAT HAPPENS NEXT?

Now that the appeal has been admitted, the defendant will also be heard again, i.e. the appeal proceedings will drag on for a long time – the excitement continues ... <<<

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