INSTITUT FÜR BAUSTOFF FORSCHUNG

RESEARCH PROJECTS FROM RECENT YEARS

CONSTRUCTION MATERIALS

Brief report – The ground granulated blast furnace slag file of the FEhS Institute

When liquid blast furnace slag is quenched in a significant excess of water to form a granulate < 5 mm, the outcome is the largely glassy granulated blast furnace slag (Fig. 1). It has been known since 1861 that this produces latent hydraulic reactions. Ground granulated blast furnace slag has therefore been used since the end of the 19th century as an ingredient in cement. In some countries, it is also used as a concrete additive. Material requirements are defined, for instance, in DIN EN 197-1 and DIN EN 15167-1.

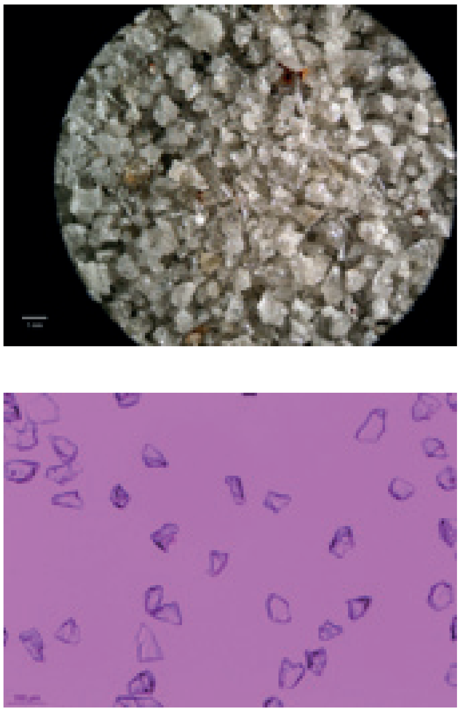

Fig. 1: Ground granulated blast furnace slag under a reflected/transmitted light microscope

Since the beginning of the use of ground granulated blast furnace slag, attempts have been made - albeit only with limited success - to find a correlation between the chemical, physical and technical characteristics of the ground granulated blast furnace slag and in particular the strength development of blast furnace cements. An overview is provided in [1]. The aim was always to draw conclusions from the analytical findings on unknown or modified ground granulated blast furnace slag regarding the behaviour of the cement containing it, and thus avoid the need for time-consuming mortar tests.

The decision to build the ground granulated blast furnace slag file of the FEhS Institute was made back in 1968. The aim was to "record the chemical and physical key data of the ground granulated blast furnace slag", and based on this, to identify correlations between this key data and the reactivity of the ground granulated blast furnace slag. Of major significance is the fact that a standardised procedure has been utilised to this day. The ground granulated blast furnace slag generated industrially or in the laboratory is thus ground to a consistent fineness (4,200 cm^2/g Blaine and comparable grain size distribution parameters), the mixing ratios in the laboratory cements are equal (e.g. 75% by weight ground granulated blast furnace slag and 25% by weight Portland cement clinker), the clinkers are defined (since 2000 only 1 clinker has been used, large unground quantities of which were placed in storage), sulphate content (3.5 or 4.5% by weight, depending on ground granulated blast furnace slag content), and sulphate agent (anhydride and gypsum) are likewise consistent, and the technical cement tests are performed according to DIN EN 196. For around 10 years, this procedure has been supplemented by combinations of 50% by weight of ground granulated blast furnace slag and a CEM I 42.5 R Portland cement, fulfilling the requirements for a test cement with finely ground granulated blast furnace slag as a concrete additive.

The most important results of an initial comprehensive analysis based on 24 ground granulated blast furnace slag varieties were published already in 1978 [2]. The ground granulated blast furnace slag file by now (June 2017) contains 744 data records regarding ground granulated blast furnace slag varieties from around the world. It is presumed to be the largest database in the world for this technically and ecologically beneficial binding agent component. It makes it possible to qualitatively classify previously unknown varieties of ground granulated blast furnace slag. However, the hope that the reactivity of any given ground granulated blast furnace slag could be precisely predicted on the basis of chemical and/or physical parameters has remained unfulfilled. The reason for this is that, even where the fineness of the ground granulated blast furnace slag is consistent, its reactivity is dependent not only on its chemical composition and glass content, but also, for instance, on its thermal history in the blast furnace and the interaction with the respective Portland cement clinker.

The limited correlation between the chemical composition and strength development of blast furnace cement can clearly be seen in Fig. 2. This shows how the 2-day mortar compressive strength of blast furnace cement with 75% by weight of ground granulated blast furnace slag is dependent on the F value defined by Keil in 1942. Only the 251 dataset were used which have been generated by the FEhS Institute member companies for the ground granulated blast furnace slag since 2008. The only thing that can be seen is a trend towards higher strength with higher F values. And even if the parameter TiO2, which still played virtually no role when the F value was defined, is included in the F value, the significance increases only slightly.

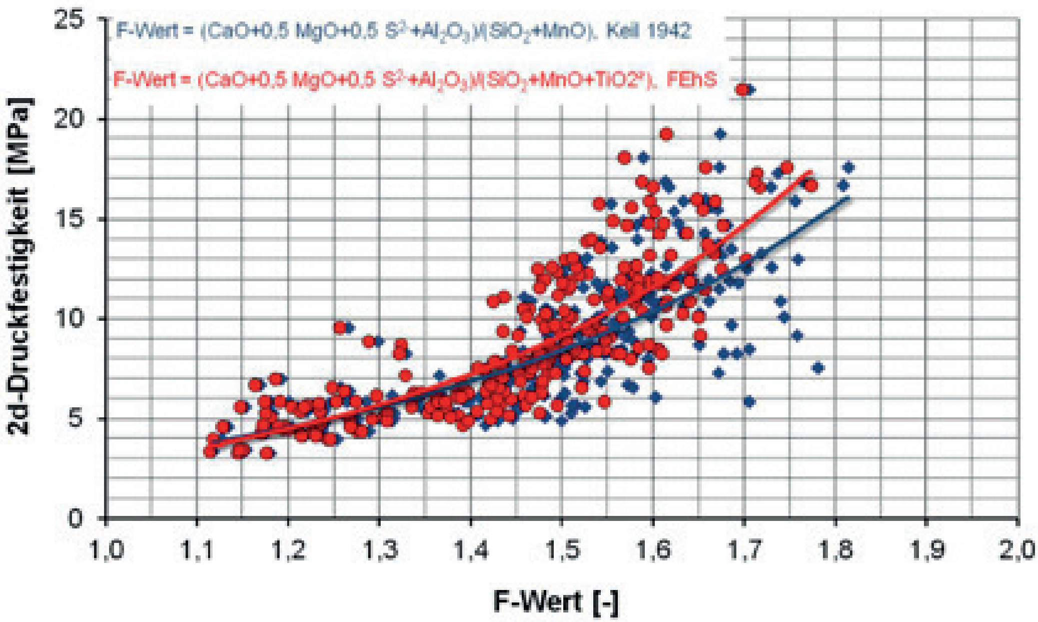

Fig. 2: Dependence of 2-day mortar compressive strength of blast furnace cement with 75% by weight of ground granulated blast furnace slag on the F value

Fig. 2 also shows how different the reactivity of ground granulated blast furnace slag can be (in the sense of strength development), whereas the other boundary conditions remain constant. Precise knowledge of the chemical, physical and technical properties of the ground granulated blast furnace slag therefore remains the basis for the appropriate us of ground granulated blast furnace slag in cement and concrete.

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The creation and expansion of the ground granulated blast furnace slag file are financed almost exclusively using the independent funds of the FEhS Institute. During the period from 01 July 1988 to 31 December 1989, part of the work was funded as part of IGF Project 7588 of the Society for the Promotion of Iron Research (VDEh), through the German Federation of Industrial Research Associations (AiF), within the framework of the programme for the promotion of industrial community research of the Federal Ministry of the Economy and Energy, following a resolution of the German Parliament.

[1] Ehrenberg, A.: Ground granulated blast furnace slag – A high-performance construction material with tradition and a future. Beton-Informationen 46 (2006) No. 4, p. 35–63, No. 5, p. 67–95
[2] Smolczyk, H.G.: The influence of the chemistry of ground granulated blast furnace slag on the strength of blast furnace cements. Zement-Kalk-Gips 31 (1978) No. 6, p. 294–296

CONSTRUCTION MATERIALS

Brief report – Combined use of ground granulated blast furnace slag, mineral coal fly ash and Portland cement clinker for manufacturing optimised cement and concrete

Funding code: AiF 16148 N
Handling period: 01.07.2009–31.12.2011
Project partner: Association of German Cement Works

The aim of the research project was to identify the capabilities and limits of cements, both with standardised and with non-standardised combinations of clinker, ground granulated blast furnace slag and mineral coal fly ash. The background to this is the cement industry trend, which has been increasing since the late 1990s, towards reducing the proportion of Portland cement clinker in the cement portfolio, with its intensive requirements in terms of raw materials, energy and CO_2. It has already been common practice for decades to achieve this through two-component systems consisting of ground granulated blast furnace slag and clinker, and even through three-component systems, which offer the cement manufacturer greater flexibility in terms of materials.

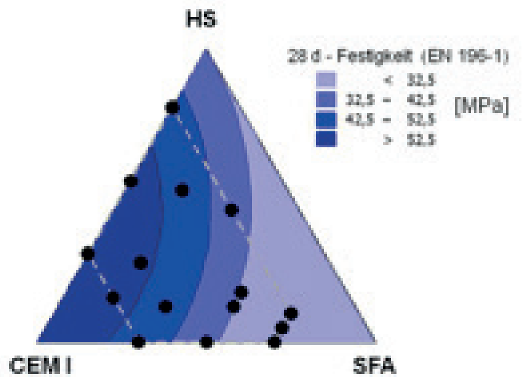

Fig. 1: Statistical test space and 28-day compressive strengths for combinations of ground granulated blast furnace slag, Portland cement and mineral coal fly ash;

Based on the analysis of the factors affecting cement performance capabilities, static test design has been used to create a test matrix with 108 cement types and 15 different compositions (Fig. 1). Static test design makes it possible to reduce the theoretically very large number of potential parameter variations (type, proportion and fineness of the 3 cement components) to manageable dimensions, while simultaneously improving the significance of the results. In order to check the results of the modelling, 7 additional cements were selected and investigated. It has been found that the model created allows the prediction, within the limits of the model and with a very good degree of accuracy, of strength and hydration heat development based on the cement composition and the reactivity of the starting materials.

On these 108 cements, the 28-day mortar compressive strength (DIN EN 196-1) and the isothermic hydration heat over 7 days were calculated. Over large areas of the composition range investigated, it was possible to produce cements with a strength > 42.5 MPa (Fig. 1). From these investigations, it can be determined that marketable cements can also be manufactured in regards to the early strength development and the other requirements of DIN EN 197-1.

Of 4 cements, the hydration products were extensively investigated in order to identify interactions between the various components. SEM imaging was used to characterise the mortar microstructure.

After 2 days of hydration, above all ettringite and calcium hydroxide crystals were identifiable. After 7 days, the particles of clinker, ground granulated blast furnace slag and fly ash were coated with a thick reaction rim of various hydrate phases. After 28 days of hydration, the microstructure of the mortar was relatively dense. The identifiable free surfaces of fly ash spheres and particles of ground granulated blast furnace slag are artefacts produced by breaking the sample (Fig. 2).

Based on the boundary conditions selected for the static test design, the CO_2 emissions can be calculated for the potential combinations of ground granulated blast furnace slag, Portland cement and mineral coal fly ash.

Because of the very small lower specific CO_2 contribution of the ground granulated blast furnace slag and mineral coal fly ash, the CO_2 emissions of the cements decrease in a linear manner as Portland cement clinker content is reduced, irrespective of the relative proportions of the other main ingredients (Fig. 3). The model calculation revealed that compared to Portland cement, with 28-day compressive strengths > 42.5 MPa and > 52.5 MPa, it was possible to reduce CO_2 emissions by 75% and 55% respectively. In particular the previously unstandardised range between CEM III and CEM V cements is very promising in terms of the strengths that can be achieved and the potential CO_2 savings.

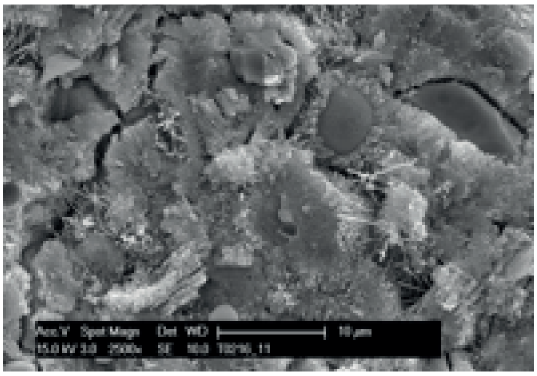

Fig. 2: SEM imaging after 28 days of hydration (Image: VDZ)

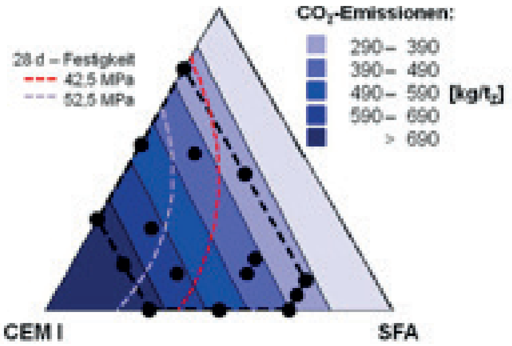

Fig. 3: Statistically calculated reduction in CO_2 emissions

It is also possible to manufacture cements in strength class 42.5 in the range between the CEM IV and CEM V/A cements, which is likewise not covered by the specifications of the existing standard. Based on the results of the technical cement investigations, 8 cements were selected and used in concrete tests for orientation purposes. The fresh concrete properties of the concretes investigated were within the usual range for the two types of concrete produced. With the exception of the two CEM V/B cements, in concretes of type 1 all cements achieved compressive strengths with which strength class C25/30 according to DIN EN 206/DIN 1045-2 could be achieved at an age of 28 days. The investigations of durability predominantly delivered satisfactory results. The AiF project 18228 N conducted between 2014 and 2016 was dedicated in detail to the properties of concretes using the newly developed cements.

In the industrial production of cements with multiple main ingredients and lower clinker contents, knowledge of the influence of the various components becomes increasingly important. The potential of reduced-clinker cements in terms of performance and reduction of the CO_2 associated with their manufacture was successfully identified in this research project. A similar presentation of the work can be found in [1, 2]. The aim of the work was achieved, and the project results already made their way into the revision of the cement standard DIN EN 197-1. The new edition will include some of the combinations that were investigated for the first time in the AiF project, as new cement types. The project is also an example of how IGF industrial community research can promptly result in practical implementation, at least in terms of regulations.

The IGF Project 16148 N of the Society for the Promotion of Iron Research (VDEh) was funded through the German Federation of Industrial Research Associations (AiF), within the framework of the programme for the promotion of industrial community research (IGF) of the Federal Ministry of the Economy and Energy, following a resolution of the German Parliament.

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Bundesministerium für Wirtschaft und Energie
aufgrund eines Beschlusses des Deutschen Bundestages

[1] Feldrappe, V.; Ehrenberg, A.: CEM X-Zemente – Optimierte Zemente mit Hüttensand, Steinkohlenflugasche und Klinker. Report des FEhS – Institut für Baustoff-Forschung 19 (2012) Nr. 2, S. 4–7

[2] Feldrappe, V.; Ehrenberg, A.; Schulze, S.; Rickert, J.: CEM X-Zemente – Möglichkeiten und Grenzen der Leistungsfähigkeit von Zementen mit Hüttensand, Steinkohlenflugasche und Klinker. 18. Internationale Baustofftagung „ibausil", Weimar, 12.–15.09.2012

CONSTRUCTION MATERIALS

Development of application regulations for finely ground granulated blast furnace slag as a concrete additive

Funding code: AiF 16743 N
Handling period: 01.07.2011–31.12.2014
Project partner: Institute for construction research (IBAC) of RWTH Aachen University

In Germany, ground granulated blast furnace slag is traditionally used almost exclusively as a cement constituent. In order to facilitate its technically and economically appropriate application as a concrete additive according to DIN EN 15167-1 in future, the research project pursued three primary objectives: Firstly, a proposal was to be developed for a national application regulation for finely ground granulated blast furnace slag as a concrete additive in the context of European and national standardisation. Secondly, appropriate k-values were to be derived for the ground granulated blast furnace slag varieties typically used in Europe, allowing finely ground granulated blast furnace slag to be categorised in such a way that different k-values could also reliably be complied with. Thirdly, recommendations should be developed for quality assurance in concrete manufacturing. In this research project, for the first time the three application concepts for concrete additives specified in DIN EN 206 (Equivalent Performance of Combinations Concept – EPCC, Equivalent Concrete Performance Concept – ECPC, k-value concept) were simultaneously applied to finely ground granulated blast furnace slag varieties with different characteristics.

The results of the investigations with 6 ground granulated blast furnace slag varieties, each in 3 finenesses, and each combined with 3 different Portland cements CEM I 42.5 R, demonstrated that all 3 concepts can reliably be applied. It was demonstrated that the technological concrete interaction between the compressive strength of the binding agent, water-cement ratio and compressive strength of the concrete (Walz curve) also applies where finely ground granulated blast furnace slag is used as a concrete additive. The 3 concepts can thus be used in a targeted manner to produce concrete of a defined strength class. The resistance of these concretes to forms of attack that affect durability corresponds to that of concrete varieties with corresponding cements containing ground granulated blast furnace slag.

On the basis of the investigation results and depending on material parameters, 2 different k-values were proposed for finely ground granulated blast furnace slag, at 0.6 and 0.8 (Tab. 1). Categories were defined for the relevant parameters of glass content, alkalinity, TiO2 content and fineness, each with different requirements.

<table>
<tr><th colspan="2">Qualitätskriterium</th><th></th><th>k_1 = 0,6</th><th colspan="3">k_2 = 0,8</th></tr>
<tr><td colspan="2">Glasgehalt</td><td>Vol.-%</td><td>≥ 67</td><td colspan="3">≥ 90</td></tr>
<tr><td rowspan="3">Chemische Reaktivität"</td><td>(C+M)/S</td><td rowspan="2">-</td><td colspan="2">≥ 1,0</td><td>≥ 1,20</td><td>≥ 1,30</td></tr>
<tr><td>F-Wert</td><td>-</td><td>-</td><td>≥ 1,30</td><td>≥ 1,50</td></tr>
<tr><td>TiO_2-Gehalt</td><td>M.-%</td><td>-</td><td colspan="2">≤ 1,00</td><td>1,01 - 1,50</td></tr>
<tr><td colspan="2">Spezif. Oberfläche (Blaine)</td><td>cm²/g</td><td>≥ 2.750</td><td>≥ 5.200</td><td colspan="2">≥ 4.000</td></tr>
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Tab. 1: Proposal for 2 different k-values for finely ground granulated blast furnace slag

These parameters are already included in DIN EN 15167-1, and therefore do not need to be additionally determined.

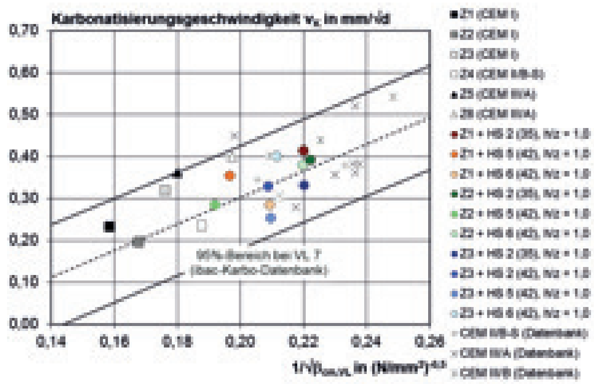

Fig. 1: Carbonation rate of the ECPC concretes after pre-storage at 20°C / 65% RH..

The performance of the specific finely ground granulated blast furnace slag is more effectively utilised in the two performance concepts EPCC and ECPC than it is by the more approximate k-value concept.
There, however, extensive and above all continuous monitoring work is required for combination with various Portland cement types, whereas after definition of one or more k-values dependent on certain material preconditions, no additional technological concrete monitoring is required. Relevant proposals were developed for the application of the concepts and for the necessary quality assurance measures during concrete manufacturing.
Both performance concepts require continuous monitoring of the performance of the specific combinations of finely ground granulated blast furnace slag and CEM I. The ECPC in particular requires the performance of the concrete to be evaluated reliably and in a practice-oriented manner. The basic prerequisite in this respect are capable and generally recognised test procedures and generally applicable acceptance criteria. These are not currently available for all exposure categories. It is therefore currently necessary to perform accompanying testing on a reference sample of concrete. Figure 1 shows that the restrictions mapped for the use of finely ground granulated blast furnace slag as a concrete additive fit well into the range of experience acquired in the use of cements.

The laboratory work was rounded off by a practical test supervised by the research bodies, in which concretes with finely ground granulated blast furnace slag as a concrete additive were used for various exposure classes in the course of building a detached house (Fig. 2). The finely ground granulated blast furnace slag used had

Fig. 2: Practical test of the application of finely ground granulated blast furnace slag as a concrete additive

not previously been a part of the test programme, and for which a k-value of 0.8 was calculated under Table 1. At an age of 28 days, an actual k-value of 0.96 was determined. According to information from the construction company, the concretes demonstrated excellent processability.

The results of the project were published and presented to various groups [1, 2, 3]. The task that now presents itself is to get the results into national and international standardisation work.

Gefördert durch:

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The IGF Project 16743 N of the Society for the Promotion of Iron Research (VDEh) was funded through the German Federation of Industrial Research Associations (AiF), within the framework of the programme for the promotion of industrial community research (IGF) of the Federal Ministry of the Economy and Energy, following a resolution of the German Parliament.

[1] Feldrappe, V.; Ehrenberg, A.: Development of application regulations for finely ground granulated blast furnace slag as a concrete additive. Report of the FEhS Institute for Construction Materials Research 22 (2015) No. 1, p. 14–19

[2] Feldrappe, V.; Ehrenberg, A.: The application of finely ground granulated blast furnace slag as a concrete additive: The performance concepts of DIN EN 206. 19. “Ibausil” International Conference on Building Materials, Weimar, 16 – 18 September 2015

[3] Feldrappe, V.: The use of ground granulated blast furnace slag as a concrete addition. 8th European Slag Conference, Linz, 21 – 23 October 2015

FERTILISERS

Long-term phosphate testing to determine the effect of rock phosphate and Thomas slag on permanent grassland

The use and cultivation of grassland areas at higher altitudes in the central Black Forest region has been fairly extensive in the early 1950s. Fertiliser use was limited to the addition of local fertilisers in the form of slurry or stable manure. Supplementary mineral fertiliser was not generally used. Feed analyses in the region showed that in particular the phosphate content was low. Studies by Bärmann (1953) revealed this situation throughout Germany. For this reason, numerous fertilisation trials were performed during that period, in order to obtain location-specific statements about how fertiliser use influenced yields and feed quality on the one hand, and also to generate practically oriented findings about the significance of individual nutrients on the other. It was in this context that such a trial began in 1954 on a high-altitude meadow in the central Black Forest, near St. Peter. While back then the basic underlying question was quickly answered in favour of mineral fertiliser use, the continuation of the trial today allows the consideration of long-term fertilising practices from an ecological perspective.

The trial is structured as a phosphate form trial and fertiliser showcase trial. The P-trial was designed as an exact test with the conditions "no phosphate", "Thomas slag", and "soft rock phosphate", with quadruple repetition as a series setup with 12 parcels of land (Fig. 1). With mowing predominantly two to three times per year, fertilising and clearing took place annually. As a result of the different lime supply for the two different phosphate forms, the trial areas developed different pH values in the soil, which since 1985 have been balanced out in two of each of the four iterations, by means of differing lime neutralisation based on the result of lime requirement calculations. An overview of the fertiliser quantities can be found in Table 1 (page 16).

Fig. 1: Long-term grassland trial in St. Peter (Black Forest), set up in 1954

Since 1954, a fertiliser trial has been conducted on permanent grassland in the high altitude region of the central Black Forest. The different fertiliser use has a significant impact on yields and on vegetation composition. Phosphate fertilising using Thomas slag continues to result in higher yields and better qualities than using soft rock phosphate. Under conditions of moderate cultivation intensity, the addition of nutrients at the level of harvesting ensures the maintenance of species-rich grassland vegetation (Fig. 2).

During the first year of the trial, the addition of both forms of phosphate already resulted in a different but very significant increase in yields (Fig. 3). Without phosphate fertiliser use, the yields continuously declined until 1973. In the conditions fertilised with phosphate, the yield levels likewise fell until 1968, and then only increased after an increase in nitrate and potassium fertiliser use after 1968. In general, fertilising with Thomas slag resulted in higher yields than fertilising with rock phosphate.

Fig. 2: Differently fertilised parcels of land in the long-term grassland trial in St. Peter (Black Forest) on 31 May 2017

The lime neutralisation performed since 1985 resulted above all in significantly increased yields on the "no phosphate" condition (Fig. 4). By contrast, only a slight increase in yield was recorded for the soft rock phosphate, whereas the Thomas slag showed on average no change in yield as a result of the lime fertiliser use for the trial years compared. In recent years, the additionally limed Thomas slag and rock phosphate parcels have reached equal yields. This coincided with an obviously weather-related general increase in the phosphate content of vegetation, which has been approaching the optimal range in the two phosphate-fertilised conditions. Furthermore, at over 30 kg P2O5/ha, the phosphate fertiliser use in the years 1985 to 1992 was higher than the phosphate removal, meaning that phosphate reserves were able to establish themselves in the soil to an adequate level to cover phosphate requirements, even where less rock phosphate was used. This is indicated by the development of the phosphate content in the vegetation.

At high altitudes in the central Black Forest, meadows of golden oat grass (polygono trisetion) are widespread. The original vegetation within the test area was characterised as belonging to this type. The fertiliser use had a significant impact on the botanical composition of the vegetation. Under the influence of these fertilisers, the vegetation on the parcels in the fertiliser trial vary between extremely low-nutrient golden oat grass meadows

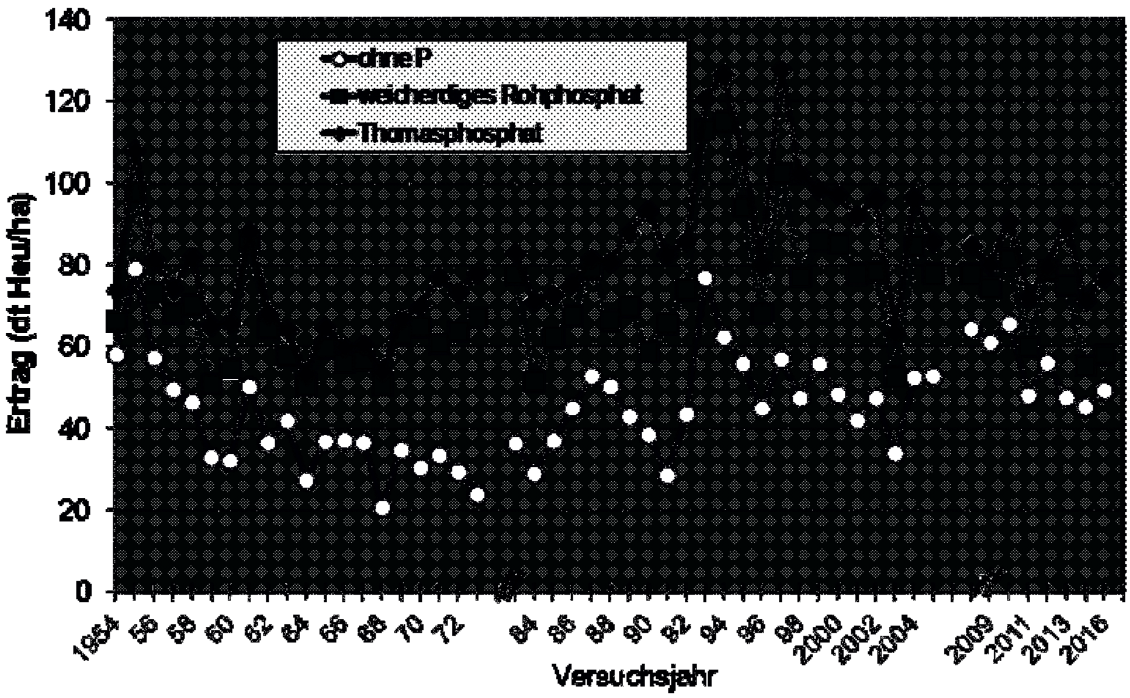

Fig. 3: Yields 1954–2016 in long-term grassland trial in St. Peter, dependent on phosphate fertiliser use without additional liming

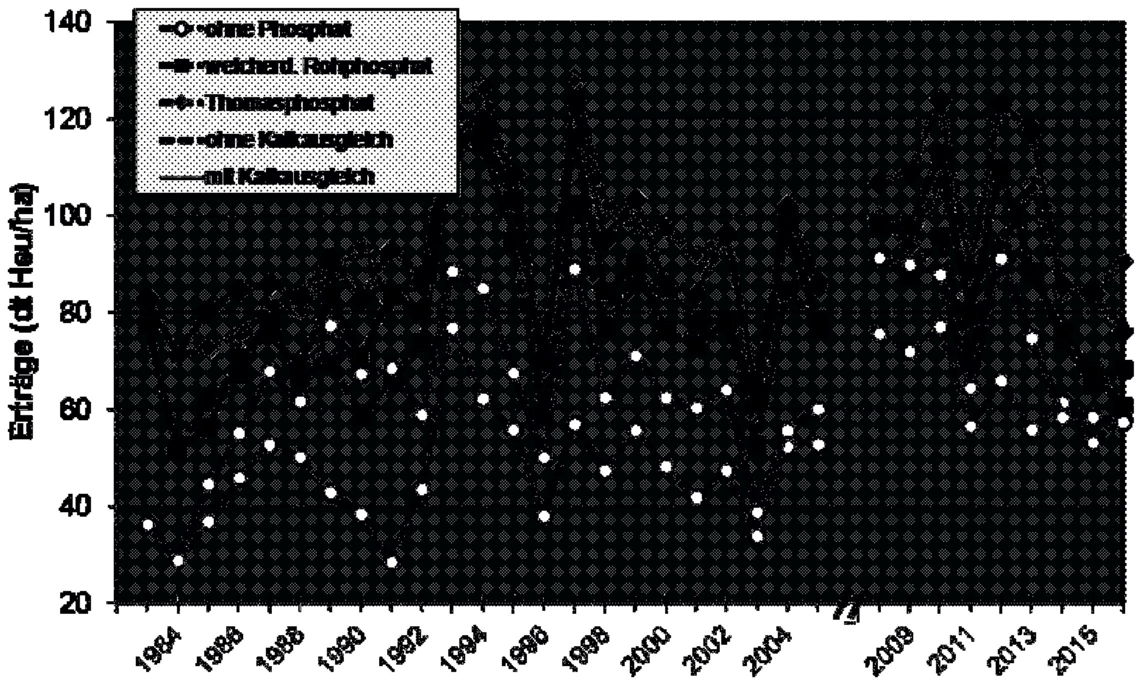

Fig. 4: Yields 1983–2016 in long-term grassland trial in St. Peter, dependent on phosphate and lime fertiliser use

and nutrient-rich subalpine fertilised meadows. Twelve years after the start of the trial, different vegetation types had already established themselves. As expected, the phosphate fertiliser use had significantly increased the proportion of leguminous plants, while the omission of mineral fertiliser use, and also the omission of phosphate fertiliser use, resulted in the dominance of grasses.

In addition, the flowering of herbaceous species was significantly limited. Without phosphate fertiliser use, red fescue, buffalo grass and colonial bentgrass are main constituents.

As a result of liming, the meadow herbs were encouraged, meaning that limed areas were more species-rich than the unlimed areas. As early as 1986, in the second year after the start of additional liming, the addition of lime alone had increased the number of species from 17 to 23, while on the phosphate-fertilised parcels, the number of plan species was between 24 and 30.

Similar ratios can be seen to this day (Fig. 5). The arrows mark the leguminous plants. Through lime and phosphate fertiliser use, the vegetation appears to become more balanced, because heavily dominant species are reduced in prevalence on the fertilised test members.

Typical low-nutrient indicator species, also including a number of rare species such as e.g. the greater butterfly-orchid (platanthera chloranta) and orchis, can be found on the parcels without mineral fertiliser, and those in the phosphate format trial without phosphate fertiliser use. Such vegetation cannot meet the utilisation requirements of agriculture, even where conducted at lower intensity. At moderate utilisation intensity, which regionally consists of two mowings and in some cases an additional pasturage, the addition of nutrients in the equivalent level in which they are removed allows the maintenance of species-rich vegetation with a moderate yield level, which also has high feed quality. Similar fertiliser use practices are also recommended for

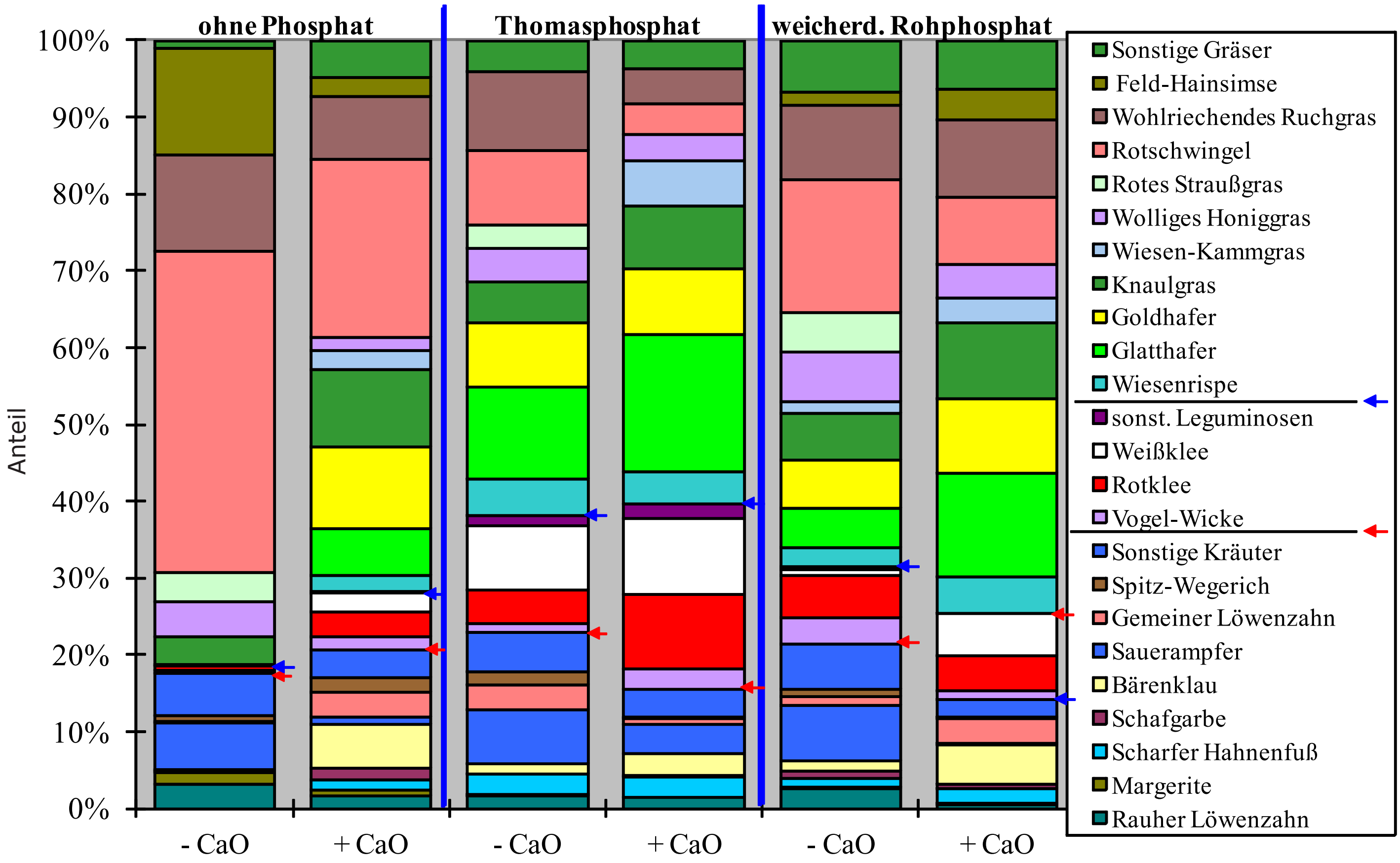

Fig. 5: Vegetation in St. Peter phosphate format trial relative to phosphate and lime fertiliser use 60 years after start of trial

grassland vegetation in nature conservation areas. In the high altitudes of the central Black Forest, tourism also represents an additional significant source of income for the agricultural sector. Species-rich, flowering mountain meadows that shape the landscape are certainly more attractive than low-nutrient grasslands. In order to preserve endangered species, however, it would however be conceivable to establish boundary strips of low-nutrient grassland with corresponding maintenance, while simultaneously compensating the farmer for expenses and loss of income.

Such long-term field trials offer the possibility of measuring the actual behaviour of nutrients and also harmful substances in the soil, and using this data to develop and calibrate simulation programs. In this manner, samples of the soil profile have repeatedly been taken at this location, and the development and displacement of elements has been mapped. For the element uranium, for example, it has been shown that it associates with the phosphor in sedimentary deposits, and thus occurs in rock phosphate. Figure 6 thus shows the distribution of the uranium in a soil profile to a depth of 50 cm below the effect of the fertiliser use.

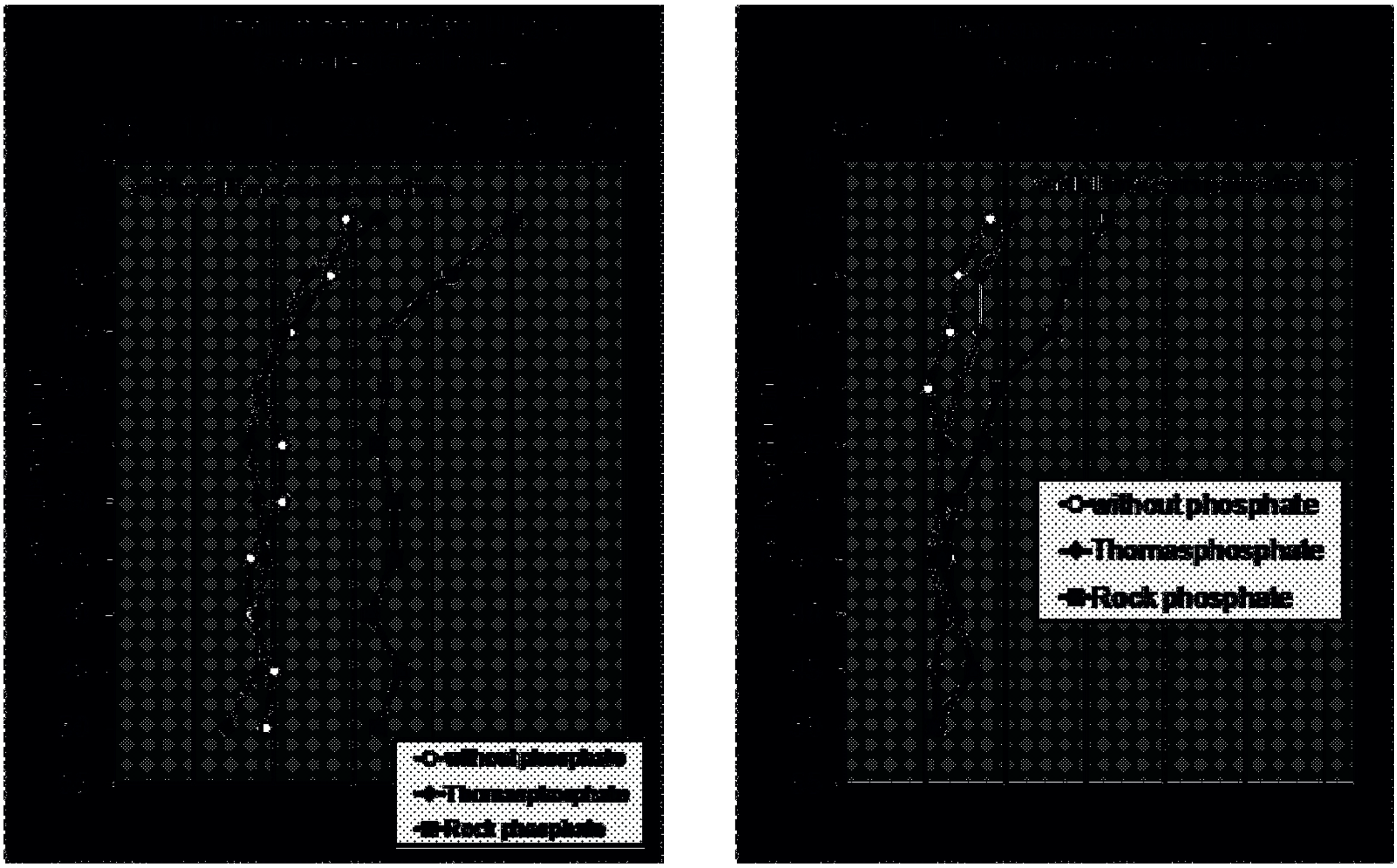

Fig. 6: Uranium content in the soil profile of the St. Peter trial with annual fertiliser use over 60 years with various phosphate formats, with and without lime neutralisation

SUMMARY:

Since 1954, a fertiliser trial has been conducted on permanent grassland in the high altitude region of the central Black Forest. The different fertiliser use has a significant impact on yields and on vegetation composition. Phosphate fertilising using Thomas slag resulted in higher yields and better qualities than using soft rock phosphate. Under conditions of moderate cultivation intensity, the addition of nutrients at the level of harvesting ensures the maintenance of species-rich grassland vegetation.

The results of this trial were developed within the framework of the research project funded by the EU Research Fund Coal and Steel, entitled "Impact of long-term application of blast furnace and steel slags as liming materials on soil fertility, crop yields and plant health (SLAGFERTILISER)". The project report was released as an RFCS publication, and can be accessed under

https://bookshop.europa.eu/en/impact-of-long-term-application-of-blast-furnace-andsteel-slags-as-liming-materials-on-soil-fertility-crop-yields-and-plant-health-slagfertiliser--pbKINA28447/. (Grant Agreement RFSR-CT-2011-00037; EUR 28447 EN)

FERTILISERS

Plant availability of phosphates from sewage sludge and meat and bone meal (MBM) ash after solubilisation in liquid converter slag.

There is significant potential for phosphate recycling through the use of ashes from sewage sludge and MBM incineration. From sewage sludge ash alone, the recovery potential is estimated at over 60,000 tonnes per year. Only a small proportion of the phosphate in such ash is plant-available, and for efficient use of the phosphate it must be solubilised using appropriate measures.

In a project coordinated by the FEhS Institute and the German Federal Ministry of Education and Research (BMBF), as part of the BMBF funding programme "Innovative technologies for resource efficiency – Raw material-intensive production processes", an attempt was made to solubilise phosphate-laden mineral ash in liquid BOF slag at the steelworks, and to test the fertilising effect of the treated slag in vegetation trials. The BOF slag required for the process developed here is generated during the production of crude steel in an LD converter. BOF slag, which satisfies the requirements for converter lime as defined in the German Fertiliser Regulation, is used in agriculture as lime fertiliser.

In this project, both in the melt laboratory and on a large scale in the steelworks, ash from the incineration of meat and bone meal (MBM ash) and sewage sludge (SS ash) were melted into converter slag (BOF slag), or were transferred into the molten slag in the converter or slag ladle (Fig. 1). After the slag had cooled, it was crushed and ground for the sieving required for Thomas slag (75% < 0.16 mm; 96% < 0.63 mm). The mineralogical composition of the starting materials and the enriched BOF slag was determined by means of X-ray diffractometry. The phosphate and lime content was determined using the corresponding methods of the Association of German Agricultural Analytic and Research Institutes (VDLUFA).

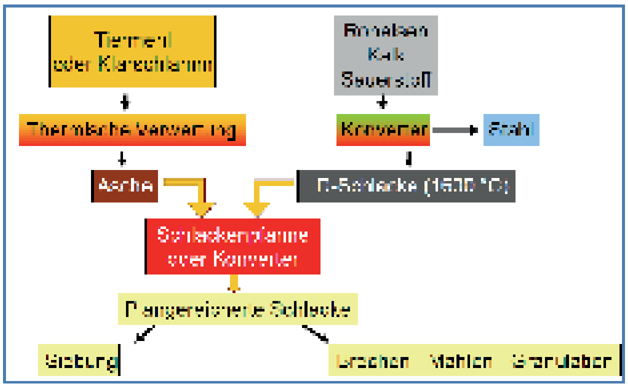

Fig. 1: Schematic diagram of slag enrichment with sewage sludge or meat and bone meal ash in a steelworks

In the laboratory melt tests, phosphate enrichment to just under 10 % P_2O_5. It was found that the BOF slag enriched with SS ash had higher overall proportions of citric acid-soluble phosphates than the slag enriched with MBM ash.

The enrichment of the converter slag resulted in a change in its mineralogical composition.

The minerals in the sewage sludge and MBM ash that contain phosphate, e.g. apatite and whitlockite, were dissolved and converted into calcium silicophosphates. The phosphate bound in apatite and whitlockite is minimally plant-available, while phosphate in calcium silicophosphate - the form of phosphate in Thomas slag - is readily available. This was also demonstrated by vegetation trials, which were performed with the enriched converter slags as compared to solubilised phosphates such as triple super phosphate (TSP) and Thomas slag, non-solubilised rock phosphate, and untreated sewage sludge and MBM ash, in container and field trials.

The plant-available phosphate content in the soil increased in differing manners depending on the fertiliser use. While the rock phosphate and the ash caused a slight increase, the use of the water-soluble phosphate formats and the enriched slags significantly increased the phosphate content in the soil, which was also reflected in the development of yields and the phosphate absorption by the test plants (Fig. 2).

While the rock phosphate and the two ash types achieved at best a slight increase in phosphate content, the two reference fertilisers, and in particular the enriched slag, resulted in significant increases in phosphate content.

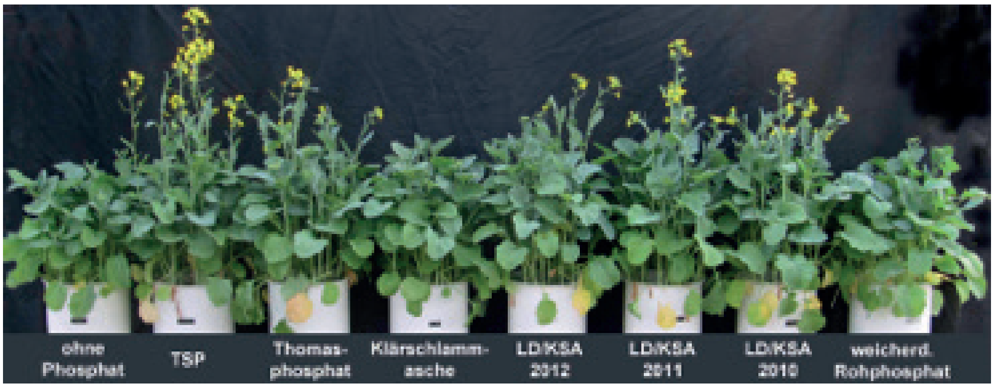

Fig. 2: Development of test culture of rape under the influence of various phosphate fertilisers with solubilised phosphate fertilisers (TSP, Thomas slag), phosphate-enriched slag (BOF/SS ash) and non-solubilised sewage sludge ash and rock phosphate.

In both the container and field trials, the phosphate effect of the enriched slags (BOF slag/SS ash, BOF slag/MBM ash) corresponded to the fully solubilised phosphate fertilisers, and in some cases even exceeded this. Only slight yield effects were derived from the untreated ash and the rock phosphate in all cultures investigated and in all soil types (Fig. 3).

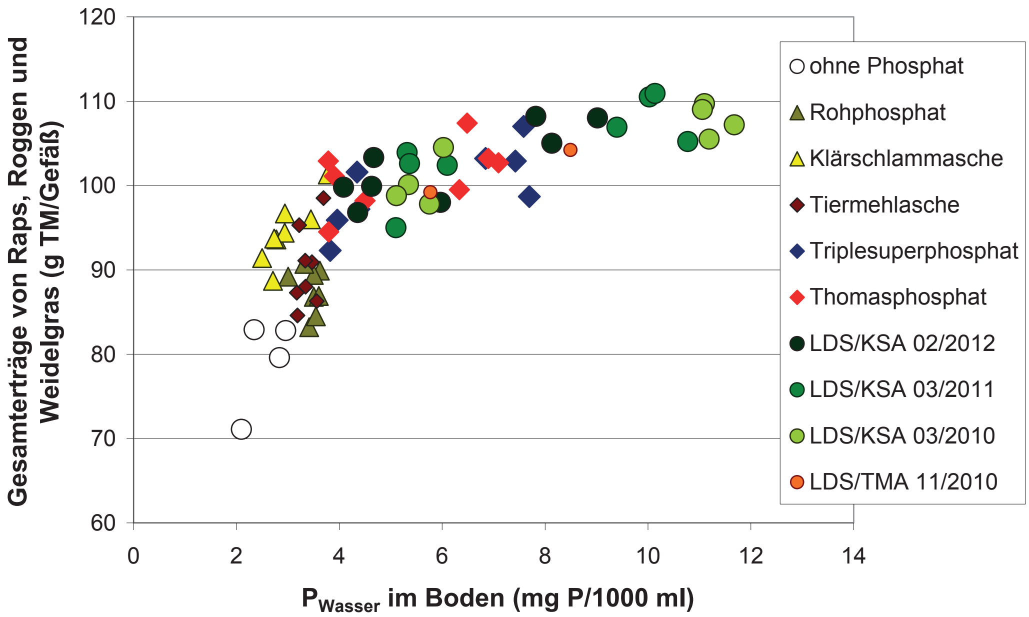

Fig. 3: Total yield of rape, rye and rye grass on the clay soil at Vörden, relative to P_{water} content in soil and phosphate format

In the field trial, significantly increased yield and phosphate absorption resulted from the phosphate fertiliser use. The phosphate absorption after fertilising with enriched converter slag was significantly higher than using triple super phosphate (Tab. 1).

P-Form	Kalkform	P-Düngung (kg P/ha)	Triticale-Ertrag (dt TM/ha)	P-Entzug (kg P/ha)	pH ($CaCl_2$)	CAL-P_2O_5 mg/100 g
-	Kohls. Kalk	0	**49,0** a	**9,9** a	5,70	5,25
-	Konverterkalk	0	**45,6** a	**9,9** a	5,65	6,25
TSP	Konverterkalk	26	**53,4** ab	**11,0** ab	5,55	5,75
LDS/KSA	Konverterkalk	26	**61,0** b	**12,7** bc	5,63	5,25
TSP	Konverterkalk	52	**55,5** ab	**13,7** c	5,63	7,25
LDS/KSA	Konverterkalk	52	**63,0** b	**15,9** d	5,50	6,75
		GD 5%	11,3	2,0		

Tab. 1: Results in Marienmünster-Vörden field trial 2013

The energy-efficient solubilisation of phosphate-rich sewage sludge and meat and bone meal ash in molten converter slag resulted, after appropriate mechanical processing, in highly plant-available phosphate fertiliser.

SEKROHMET

Reduction of environmental burden through saving primary resources and avoiding carbon dioxide emissions during raw material processing, and utilising the energy content of molten electric arc furnace slag, while simultaneously avoiding dumping of by-products in landfill by converting molten electric arc furnace slag into a material with clinker properties.

The aim of the project was the environmentally friendly production of a material based on liquid electric arc furnace slag (EAFS) that would have comparable properties to hydraulic Portland cement clinker. The EAFS was to be used for both the material and thermal input for the clinker phase formation. The material use of EAFS predominantly takes place today in the form of aggregates for road-building. In the context of future changes in legislation, the use of annually around 1.7 million tonnes of EAFS could be significantly restricted or prohibited, which would result in (partial) dumping in landfill. In the interests of increasing resource intensity and the circular economy, this should be avoided. From both an ecological perspective (CO_2 emissions, raw materials and primary energy requirements) and an economic one (increased value creation from EAFS, contribution to securing steel locations), it is necessary to open up an alternative us of EAFS.

The cement industry is intensive in terms of resources and CO_2. It is based on the use of Portland cement clinker, frequently combined with additional components (e.g. ground granulated blast furnace slag). These are not sufficient, however, to open up a significant additional substitution of clinker. EAFS fundamentally represents an option for the production of a clinker-like material that does not impair the technical properties of the cement (strength development, processing behaviour) or the interests of occupational safety and environmental protection. This application suggests itself, because EAFS already has a similar material composition to Portland cement clinker, is available in molten form, and generates no further material-related CO_2 emissions (no deacidification of limestone). The high thermal content of EAFS, at around 2.3 GJ/t, can furthermore be utilised for the conditioning process.

The reduction tests in the Tammann furnace of the FEhS Institute were performed in a graphite crucible, whose carbon in the form of carbon monoxide reduced the oxides Cr_2O_3, FeO, Fe_2O_3, and MnO from the EAFS. This was confirmed by the thermodynamic calculations for free reaction enthalpy at temperatures of 1,650°C.

The metallic reguli that settled contained a mass fraction of up to 40% by weight, and demonstrated the high recyclable material potential of EAFS. The metal analyses found that to a limited extent this metal can again be returned to the electric arc furnace process, facilitating a substitution of the input material.

The reduced slag remaining alongside the metallic regulus had CaO contents of only 45% by weight, meaning that conditioning with additional lime materials is necessary to create the chemical properties required for clinker.

Due to the high proportion of CaO, the viscosity was now increasing sharply, and it was found that the slag was no longer easy to handle, which on an industrial scale would result in massive problems. The process stages of reduction and conditioning therefore need to take place separately. A possible process for this utilising a rotary kiln could be developed in order to allow handling even on an industrial scale.

The mineralogical analyses of this material showed that important clinker phases such as C3S, C2S and C3A could be formed. By optimising the conditioning, it was possible to use the Bogue calculation model to generate a material that had good technological properties for cement, such as mortar compressive strength and hydration heat.

A further option identified within the framework of the project was the possibility of conditioning to produce ground granulated blast furnace slag, a latent hydraulic material. Instead of using lime, the conditioning process used materials containing SiO_2, which have no negative impact on the viscosity of the slag. Through subsequent granulation of the material, it was possible to produce a ground granulated blast furnace slag that likewise had good technological properties for cement. This treatment requires no second process stage using a rotary kiln process, which makes the economic perspective considerably more favourable. However, the ground granulated blast furnace slag has a considerably lower value than clinker.

This project successfully demonstrated that alternative utilisation options exist for EAFS, with various advantages and disadvantages. Theoretically, EAFS can be conditioned completely into two products, “metal” and either “clinker” or “ground granulated blast furnace slag”; however, this is associated with high economic expenses that cannot be afforded by an electric steelworks. In addition, the reduction process using carbon is very energy and CO_2-intensive, such that is offers no ecological advantages over the former clinker production process.

The project can nevertheless be considered a success, because a large volume of knowledge was obtained for the reduction and conditioning of EAFS, which could help to save energy and resources in future.
This makes a contribution to environmental protection.

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DBU
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SEKROHMET

Reduction of environmental burden through development of a process for the stabilisation and recirculation of sludge from wet dust separation plants in the iron and steel industry

The aim of the project was to develop an environmentally friendly process for the stabilisation and recirculation of sludge from wet dust separation plants at smelting works of the iron and steel industry. This process makes it possible to convert the previously stabilisation-resistant sludge into a state that allows compaction, due to changes in material properties. It is planned that compacted and structurally stable sludge from wet dust separation plants should be returned to the same process stages of the iron and steel industry in which it originated.

The overwhelming majority of sludge from wet dust separation plants is currently dumped in landfill. Sludge contains recyclable materials, predominantly iron and carbon, the reuse of which contributes to saving resources. In Germany alone, their reuse would allow the recycling of 300,000 tpa of sludge that have previously been landfilled. On a purely hypothetical level, this would allow 135,000 tonnes of iron and 40,000 tonnes of carbon be saved each year. This saving of natural resources would furthermore generate a large saving in terms of energy.

Engineered stone, which is structurally stable and thus practical for the handling required in recycling, was successfully manufactured from converter and furnace gas sludge within the framework of the project work. The comprehensive results from the analysis of the chemical and mineral composition, grain size distribution and grain geometry, and influence of supporting particles, were collated in a obstacle analysis, and guided the process of developing formulas for manufacturing this engineered stone from the sludge. The use of different cement types allowed the desired key indicators for the engineered stone to be further optimised.

The newly developed process also makes it possible for the first time to shape sludge into rocks, and then to easily recycle them in the metallurgical processes, as is already the operational practice with dust from dry dust separation plants. The reuse of sludge in solid rock format reduces the quantities of such sludge being landfilled, and thus contribute to the objective of promoting the circular economy and resource efficiency.

The results achieved in the laboratory tests have successfully been used in the Volmer rock factory to produce engineered stone from converter sludge. The use of this engineered stone in the converter process was likewise successful. The metallurgical objective of cooling steel melts through the use of the engineered stone was confirmed.

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Deutsche
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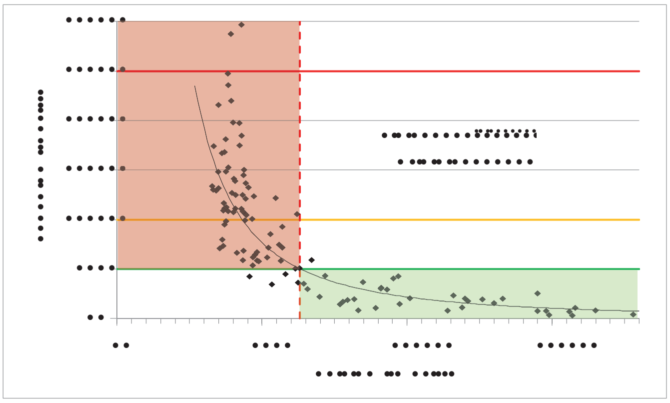
INSTITUT FÜR BAUSTOFF FORSCHUNG

SEKROHMET

Control of slag quality for utilisation in the construction industry

EAF slag is a by-product of electric steelmaking, the annual quantity in Europe is around 10 M tonnes, 8 M tonnes from carbon steelmaking and 2 M tonnes from high alloyed steelmaking. The objective of this project is to increase the utilisation of EAF slag by improving the quality of this slag. The treatments investigated are during the liquid stage of the slag (optimised metallurgical process or additions or cooling procedure) and during/after solidification through water treatment (cooling/washing).



As the regulations in EU countries are not uniform the slag quality classification and utilisation is based not only on the properties of the slag, but also in which country it is used. Therefore, individual solutions have to be found for each slag/steel work. Elements such as Ba, Cr and V were successfully decreased in slag leachate to meet environmental regulations, however solutions for stabilisation of Mo and Se during the liquid stage of the slag were not found. Barium leaching was decreased with the addition of sand without increase in V leaching (the slag was slow cooled). Vanadium leaching was decreased by addition of Ca-rich material (e.g. LF slag). Chromium leaching was decreased by favouring the formation of spinels with aluminium oxide additions.

In pilot scale tests with solidified slag, slag washing and water treatment with iron hydroxide adsorbent was tested. The absorbent is able to remove Mo, V and F- from slag washing water, but the solidified slag washing experiments were not yet successful in decreasing V leaching from the EAF slag.

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ENVIRONMENT

Transferability of laboratory results to practical conditions when using BOF slag in exposed installation

The use of steel slag in base courses without binding agent under dense top courses, or bitumen-bound in asphalt layers, is generally considered non-critical. By contrast, the exposed installation (use in paths, outdoor areas or embankments that are not provided with thick covering layers of e.g. concrete or asphalt) of industrial by-products in general, and thus also of steel slag, has repeatedly been discussed by the environmental authorities.

The aim of one research project was therefore to investigate the long-term behaviour of BOF slag when used in unbound layers. Alongside the technical suitability of the selected BOF slag for exposed rural path construction, in particular its leaching behaviour was investigated in laboratory tests, in semi-technical lysimeter tests, and under practical conditions. To this end, a trial path was built in two sections (see Fig. 1), the base course of which consists of a BOF slag or of limestone for comparison. The analysis of the leachate from the trial path was compared with the results of various laboratory leaching processes and lysimeter tests.

Fig. 1: left: Plot before construction of the trial path; right: Trial path shortly after completion

Based on the testing of technical properties, good suitability of the BOF slag was verified as a mineral material for use in exposed path construction. Investigations of the leachate quantities verify that, even over the seven-year observation period for the trial path, the permeability of the base course is sufficiently high that good infiltration of precipitation water is guaranteed.

The comparability of the laboratory processes with one another is limited by the different boundary conditions, and by the different l/s ratios, which often result in differing material loads. The direct transfer of the results achieved in the laboratory tests to the conditions under the base course of the trial path is not possible, because the l/s ratios in the laboratory tests are significantly higher. Only the respective first stages of the comprehensive column test (DIN 19528) and the up-flow percolation column procedure (DIN EN 14405) constitute exceptions to this.

The structure of the lysimeter tests (Fig. 2) corresponds to the trial path down to a depth of approx. 20 cm below the base course. Nevertheless, different concentration curves were observed for some elements, which is explained by higher l/s ratios, facilitated by forced through-flow, and thus by different material loads.

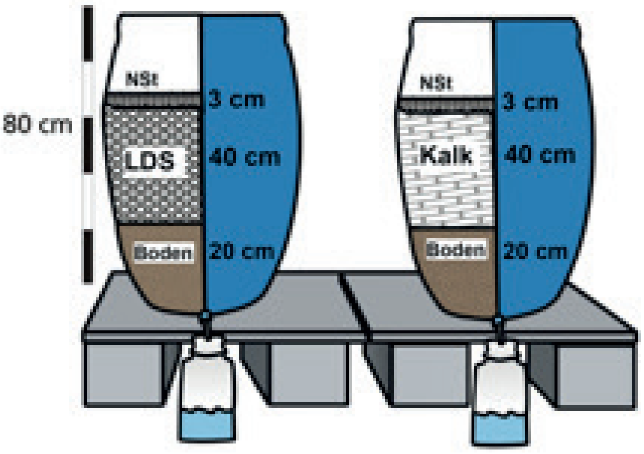

Fig. 2: Sketch (left) and photo (right) of the lysimeter test setup

Already during the initial phase of the trial path, low permeability of the base course was determined for both mineral materials (BOF slag and limestone), which results is a very low level of leaching of the materials. The concentrations of environmentally relevant parameters soil solutions collected centrally below the trial path are therefore so low that there is no cause to fear negative impact on the groundwater.

ENVIRONMENT

Investigations on the leaching of non-percolating construction materials, taking into consideration new German and European regulations, with the aim of sustainable use

Various branches of industry, e.g. the steel industry, coal power plants and foundries, produce not only their actual products, but also what are known as industrial by-products. They can take the form of large chunks, but may also be fine-grained or even powdery. For technical reasons, the possible applications for such fine-grained materials, e.g. in road construction, are limited. There is however the option of utilising them e.g. for the surface sealing of landfills and for site rehabilitation. Further applications exist in the field of earth engineering, e.g. noise control walls. The use of such industrial by-products helps to save natural resources on the one hand, and on the other it saves expensive and increasingly scarce landfill space.

The prerequisite for the use of industrially manufactured fine-grained materials as a construction material is that they fulfil certain requirements in terms of technical properties and environmental safety. Previously, there had only been a few processes available for testing environmental safety that were particularly suitable for fine-grained materials. Batch tests such as DIN 19529 and DIN EN 12457 were fundamentally suitable. However, since the beginning of development work on a Germany-wide regulation for the use of industrial by-products, the Replacement Building Material Ordinance (EBV), column tests have been preferred (DIN 19528), because these are presumed to deliver results closer to the reality of this type of leaching. One problem in the investigation of very fine-grained materials is the low permeability of such materials, the tendency towards stabilisation and swelling (Fig. 1).

Fig. 1: left: heavily compacted, non-percolating mineral coal fly ash in the glass column of the percolation column procedure (DIN 19528); right: stabilised, non-percolating ladle slag in a shattered glass column

DIN 19528 contains the note that "non-percolating materials" can be mixed with 80% sand in order to ensure flow through the sample. Little experience is available thus far with using this special test procedure, however, and it is unclear what effects the addition of sand would have on the results. Furthermore, there is a lack of specifications regarding handling, e.g. how a homogeneous mixture of sample and sand should be achieved.

At the European level, an entirely different approach is taken to the investigation of very fine-grained construction materials. If a material is so impermeable that being flowed through in a test column is no longer possible, the material is considered essentially monolithic. In this case, the GLHC procedure (test method for granular products with low hydraulic conductivity) is used, a special procedure for the DSLT (dynamic surface leaching test) developed for monolithic materials. Virtually no experience has yet been obtained with the GLHC method, however.

Neither investigation approach provides a conclusive decision-making criterion for the minimum degree of permeability beyond which a fine-grained construction material can no longer be investigated using a standard method for granular construction products, and instead needs to be testing using an alternative method for non-percolating materials. The results of this project are intended to provide a decision-making aid in this respect. For this purpose, amongst other things long-term permeability tests are being conducted using triaxial cell testing (Fig. 2).

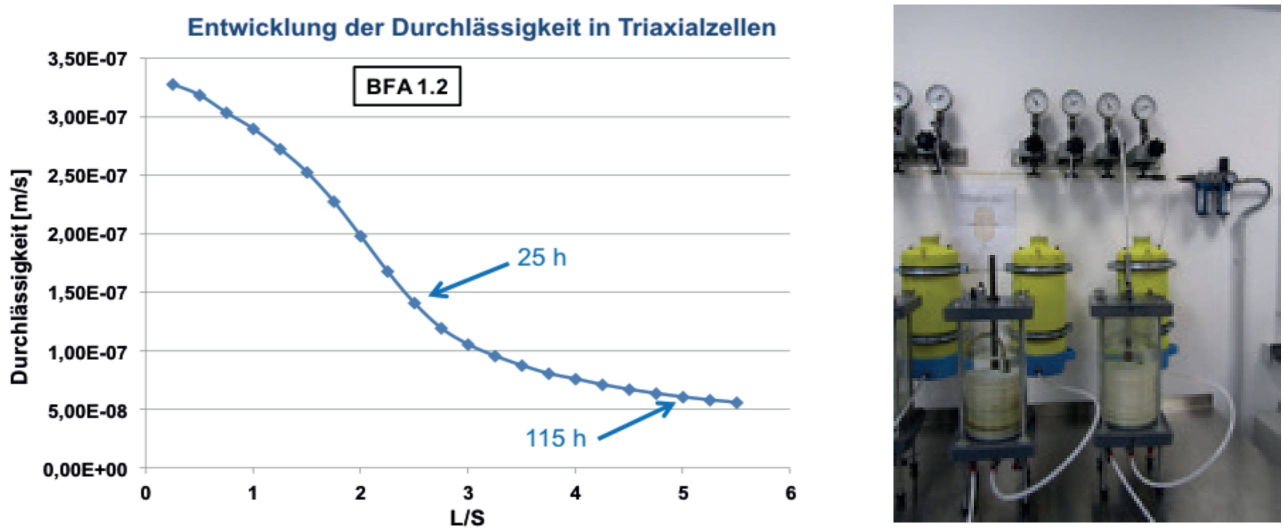

Fig. 2: Development in permeability of a sample of lignite fly ash over the course of the triaxial cell test