

# Report.

Research projects of the FEhS-Institute 2019

ISSN 0948-4795 | 2019

- 3** Industrial solidification and recycling of sludge from wet dedusting plants in the iron and steel industry  
> Dr.-Ing. P. Drissen, D. Algermissen, M. Sc., Dipl.-Ing. R. Abel
- 13** Occurrence and Utilization of dusts, sludges and mill scale from the iron and steel industry  
> Dr.-Ing. P. Drissen
- 18** Optimizing the acid resistance of concrete with granulated blast furnace slag  
> C. Gerten, M. Sc., Dr.-Ing. A. Ehrenberg
- 26** Glass formation of granulated blast furnace slag and its influence on slag reactivity  
> Dr.-Ing. A. Ehrenberg, Dr. phil. N. Romero Sarcos, D. Hart, M. Sc., Dr.-Ing. H. Bornhöft, Prof. Dr. J. Deubener
- 33** Toxicological investigations of ferrous slag in the context of the REACH registration  
> Dr. K. Jochims, Dr.-Ing. R. Bialucha
- 35** 10<sup>th</sup> EUROSILAG Conference calls for fair treatment of ferrous slag  
> Th. Reiche



# INDUSTRIAL SOLIDIFICATION AND RECYCLING OF SLUDGE FROM WET DEDUSTING PLANTS IN THE IRON AND STEEL INDUSTRY

Dr.-Ing. P. Drissen, D. Algermissen, M. Sc.  
(FEhS – Building Materials Institute)

Dipl.-Ing. R. Abel  
(Volmer Concrete Plant GmbH & Co. KG, Duisburg)

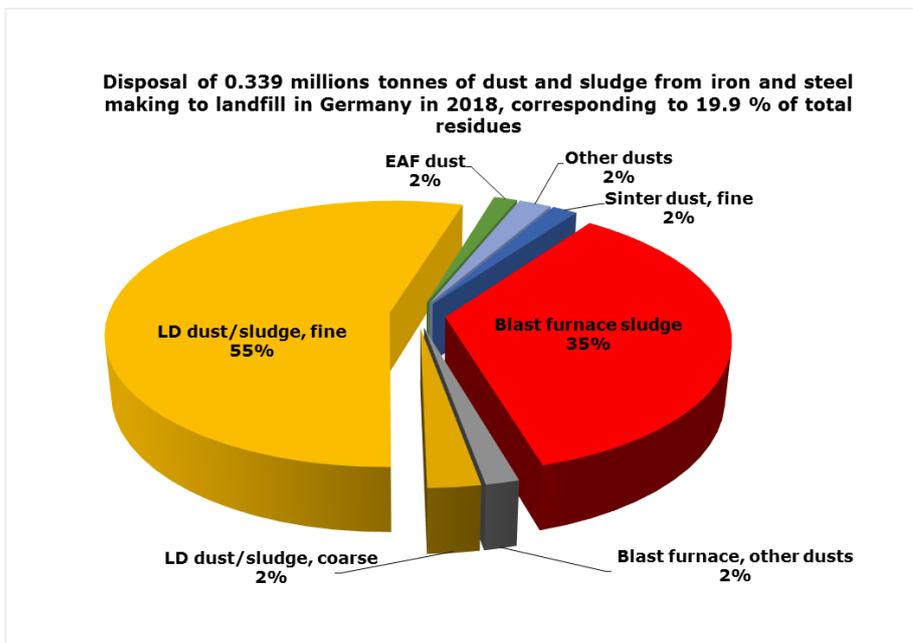


Figure 1: Disposal of dust and sludge quantities of the iron and steel industry to landfill (Germany, 2018)

## INTRODUCTORY REMARKS

The recycling of residues from the flue gas cleaning of the various process stages in the smelting works represents a significant contribution to resource efficiency and environmental relief. While around 80 % of the dusts and sludges from the iron and steel industry in Germany are sent for internal recycling or other use, more than 300,000 tonnes per year are still landfilled (Figure 1).

The fine-grained LD dust/sludge from the dedusting of the LD converters and the blast furnace gas sludge (BF sludge) from the flue gas cleaning of the blast furnaces, which together account for 90 % of the dusts and sludge deposited, are particularly worth mentioning here. The reason for the landfill is the high water content, which makes handling and recycling difficult, but also certain substances. For this reason, only

Component	BF sludge Steel mill A		BF sludge Steel mill B		LD dust Steel mill A		LD sludge Steel mill B	
	mean	SDV	mean	SDV	mean	SDV	mean	SDV
Residual moisture	42.6	12.1	39.4	17.2	9.2	3.3	10.4	6.6
Fe <sub>total</sub>	15.3	7.0	26.7	2.4	58.9	2.5	47.7	18.2
SiO <sub>2</sub>	11.7	7.4	7.1	1.9	1.3	0.2	3.6	0.6
Al <sub>2</sub> O <sub>3</sub>	3.0	1.4	2.6	0.1	0.3	0.1	0.7	
C <sub>total</sub>	27.2	9.2	27.6	1.4	1.1	0.5	0.8	0.7
C <sub>inorg.</sub>	11.7	3.5	5.6	1.8	1.0	0.3	0.8	0.7
C <sub>elementary</sub>	16.4	3.2	14.8	12.1	0.2	0.3	< 0.1	
C <sub>organic</sub>	8.9	10.5	12.5	12.0	0.3		n.b.	
CaO	5.2	1.8	7.4	2.6	6.23	0.25	14.8	10.4
MgO	1.4	0.9	1.14	0.27	0.80	0.23	7.66	13.63
K <sub>2</sub> O	1.2	1.0	0.2	0.05	0.35	0.20	0.05	0.04
Na <sub>2</sub> O	0.63	0.33	0.15	0.07	0.43	0.15	0.05	0.02
S <sub>total</sub>	1.4	0.8	1.2	0.1	0.3	0.1	0.5	0.9
Zn	4.1	2.4	2.9	0.7	1.2	0.2	0.5	0.6

Table 1: Composition of sludges and dusts in M. %

partial quantities can be recycled after suitable treatment in the different process stages of the smelting works or must be processed in specially designed aggregates. With the landfilling of LD and blast furnace gas sludge, both scarce landfill space and roughly 110,000 tonnes of Fe and 30,000 tonnes of carbon are lost annually. Table 1 shows some sample compositions of sludge and dust.

This was the reason to investigate the processing of LD and blast furnace gas sludges to produce cement-bound agglomerate bricks in order to facilitate better handling and dosing and thus create the prerequisites for better recycling of these sludges in the smelting works. As part of a project supported by the Deutsche Bundesstiftung Umwelt (DBU) (German Federal Foundation for the

Environment), a joint project was carried out with Volmer Betonwerk GmbH & Co. KG, Duisburg, Germany. Extensive laboratory tests were conducted to identify major obstacles to the agglomeration of sludges and to develop solutions [1, 2]. In the follow-up project, which was also funded by the DBU, the focus was on the industrial implementation of the results [3]. The aim was to produce agglomerated bricks with a sufficiently high pressure and drop strength for internal recycling in the steel works by means of stone presses.

## PROCESS ENGINEERING FEATURES

### Influence of zinc

Laboratory tests had shown that it is possible to solidify LD sludges with 10 % Portland cement, whereby the addition of supporting

grain in the form of mill scale proved to be advantageous [1].

However, the analogous production of agglomerated bricks from blast furnace gas sludge was not possible. The reasons for this include higher zinc contents, which have an inhibiting effect on the development of the desired early strength unless special cements, such as sulfoaluminate cement, are used [1, 4]. The desired strengths could be achieved by using calcium sulfoaluminate cement or combinations of Portland cement and calcium sulfoaluminate cement. Taking into account the economic efficiency, however, the aim was to dispense with the use of these special cements for an industrial application.

Higher zinc contents can not only inhibit the development of the desired early strength [4], they can also be a limiting factor for the recycling of dusts and sludges into the metallurgical process.

In some blast furnace plants, hydrocyclone technology is used to separate the blast furnace sludge into a Zn-poor and Zn-rich fraction. The hydrocyclone enables a targeted separation into a coarse fraction with a lower Zn content and a fine fraction with a higher Zn content [5, 6]. With this process, the advantage of reducing the zinc content is offset by the space requirement, high investment and operating costs and the high water content of the separating fractions.

Another option is the Ciroval process, a two-stage hydrometallurgical process to remove zinc and lead from fine-grained materials [7]. The first step involves selective leaching of zinc and lead under oxidizing conditions with the addition of hydrochloric acid. In the second step, the filtered solution from the first step is neutralized and zinc, lead and partly iron are precipitated in the form of hydro-oxides. The process is intended to achieve final zinc < 0.3 % and lead < 0.1 % contents. Due to the space required, the requisite auxiliary materials, the residual materials produced and the very moist product, as well as the investment and operating costs, this approach was not pursued further within the framework of the project.

A reduction of the zinc content, in particular of the agglomerate bricks with blast furnace gas slud-

ge, could thus only be achieved by adding further input materials and the cement used as binding agent. This reduces the proportion of sludge per tonne of agglomerate stone. At the same time, however, a material that has so far mainly been landfilled becomes recyclable.

#### **Water content**

With regard to the operational production of cement-bound agglomerate bricks from LD and blast furnace gas sludges on stone presses, their sludge-like consistency is of particular importance. The sludge-like consistency is based on the extreme fineness of < 100 µm and the high, strongly fluctuating water contents of 30 to 60 % [1]. A further complicating factor is that the water distribution within the grain band of the sludges shows clear differences [1, 2]. Even after gravity drainage and storage under roof, the residual moisture could only rarely be reduced to below 30 %, and only if stored for several months, with substantial proportions of the physically bound water often being contained in clumps. This water is released by process-related vibration processes and leads to mixtures with apparently suitable moisture quickly returning to a muddy consistency. During the mechanical processing of the mixture into agglomerated bricks, problems such as insufficient filling of the moulds, sticking of the mixture in the mixer or in the storage container as well as on moulds and punches of the brick press then occur. The latter in particular causes cracks to form inside and on the surfaces of the agglomerated bricks and results in poorer strength of the agglomer-

ated bricks. In addition, the stronger adhesive forces between the mould and the press body require higher extrusion forces, which excessively stress the hydraulics and the steel structure of the stone press. This leads to higher wear, cleaning and maintenance work and thus to additional downtimes and increased repair costs. On the other hand, a too low water content leads to incomplete setting of the added cement and the desired strength of the agglomerated bricks is not achieved.

In the production of agglomerate bricks by mixing and pressing different components such as sludges, dusts, additives and binders, the moisture content of the individual components must therefore be adjusted so that the water balance requires the addition of water in the mixer. Only then is it guaranteed that the total moisture content of the finished mixture can be optimized both with regard to a consistency suitable for production and for cement binding.

In order to mechanically solidify sludges from the wet dedusting plants in such a way that recycling in the metallurgical process is possible, a number of tasks had to be solved under practical and economic aspects, which are described below.

#### **DEVELOPMENT OF A DRYING PROCESS FOR THE SLUDGES**

Sludges from the wet dedusting plants of the metallurgical plants are partly dewatered in filter chamber presses, but experience has shown that these only achieve residual moisture levels of about 30 %. The target value for moisture < 8 % is thus not achieved.

The reliable setting of such a low target value is only possible by means of drying in the rotary kiln, which, however, involves high energy costs and additional work and logistics.

Since the drying of sludges in a rotary kiln did not come into consideration for the large-scale production of agglomerate bricks for economic and ecological reasons, mixing with dry, iron-containing filter dusts from oxygen steel production was tested for the necessary pre-drying of the blast furnace sludges in particular. For this purpose, removed blast furnace gas sludge and LD dust were intensively mixed with a wheel loader and stored under roof. In addition to the lower calculated mixed moisture, further drying of the mixture is achieved by the oxidation heat of the metallurgical dust. Temperature measurements in the pile showed a clear temperature increase that favours a further reduction of the water content in the mixtures. The dried mixtures apparently exhibited good homogeneity and consistency with regard to their further processing. This process technology was therefore retained as the basis for further work.

#### **PLANT ENGINEERING AND PROCESS OPTIMIZATION OF AGGLOMERATE BRICK PRODUCTION**

In the technical production of agglomerate bricks from sludges, cement and other feed materials, the material to be pressed is homogenised in planetary counter-current mixers and filled from a storage tank into moulds, hydraulically compacted on the brick press and pressed onto a covering board with punches.

As already mentioned, in the production of agglomerate bricks from mixtures with higher proportions of blast furnace gas and LD sludges, the water balance, the mixing behaviour with regard to the achievable homogeneity and the machinability of the mixtures are critical. A number of complications can therefore occur during production, which have a negative effect on the productivity and quality of the agglomerated bricks.

For example, the uneven distribution of water within the grain band during the mixing process in the storage tank of the stone press can lead to problems. The transmission of vibrations during the compaction process of the press to the storage tank leads to an energy input to the sludge and thus to the partial release of the water. This results in the sludge compacting in the storage tank and the released water settling on the surface. As a result, the material no longer slides evenly and the moulds are filled unevenly and thus compacted differently.

A change in the geometry of the storage tank, combined with a reduction in conicity to reduce the pressure on the material, as well as a decoupling of the storage tank from the stone press to prevent vibration transmission were rejected due to the constructional difficulties and the high investment costs. However, suitable formulations for mixtures with blast furnace gas and LD sludge could be developed and successfully tested within the scope of this project, which significantly reduced the inadequacies of the mixture compaction in storage tanks in advance.

Furthermore, remaining inhomogeneities in the mixture, such as macroscopic sludge lumps, lead to an additional pelletization of the mixture when the filling trolley of the moulds is moved forward. This results in incomplete filling, especially of the front individual moulds, with the problems of different densities and strengths of the pressed agglomerate bricks.

In addition to the problem of the different filling degree, which also leads to different stone heights, the different heights of the wooden boards on which the agglomerated stones are expressed are problematic. The facing boards are subject to natural wear. Due to weather-related stretching and shrinking processes in the wood, there are additional height differences of up to 1 cm from board to board, which further intensify the individual height differences of the agglomerate bricks.

It was therefore a further goal to optimize the filling process with the subsequent pressing, taking into account the different wooden board heights. For this purpose, a new control system was put into operation with which various process parameters such as the number of vibrators, starting point and duration of the pre-vibrations, the control of the vibratory plates and the height of the wooden boards can be recorded or freely selected during production. This allows direct reaction to variations in the raw material mixture and varying water contents of the raw materials caused by different weather conditions.

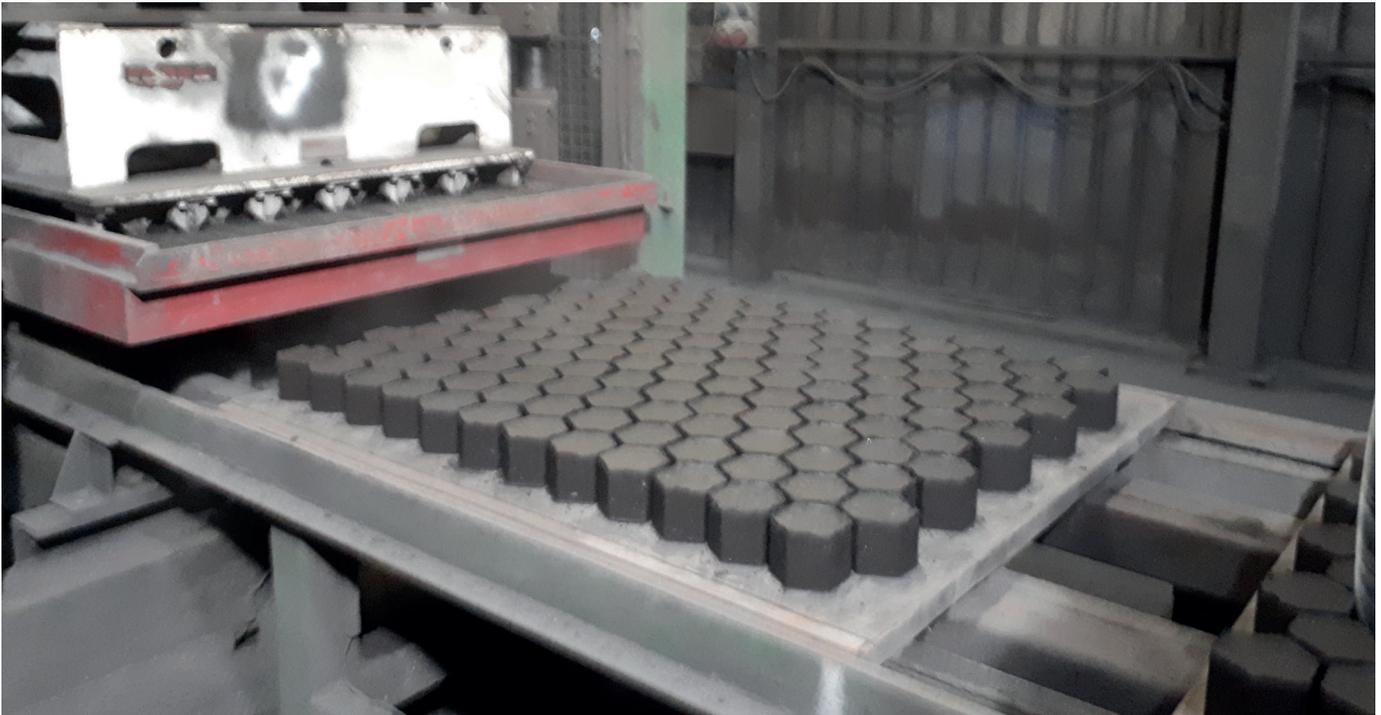


Figure 2: Agglomerate bricks from LD sludge after demoulding

The functions of the new control system have helped to optimize the production process and thus improve the quality of the agglomerate bricks produced from blast furnace gas and LD sludges with regard to uniform physical properties. The degree of filling of all individual moulds is standardized in particular by the variable timing of the pre-vibrations. The targeted control of the vibrating process optimizes compaction during the pressing process. The integration of the height measurement of the wooden boards largely avoids differences in the stone height.

In the production of agglomerate bricks with higher proportions of blast furnace gas and LD sludges, exceptionally high adhesion forces between the filling material and the side wall of the moulds can occur due to the fineness of the grains and the inhomogeneities, especial-

ly in the water content and water distribution. When the moulds are squeezed out, this creates a short pressure peak in the hydraulic system and, due to the sudden release of the moulded bodies from the moulds, an impact load in the frame or carrier structure of the presses. In order to avoid these load peaks, the opening angle of the moulds was increased downwards. In test series, this opening angle was optimized, since no homogeneous compaction is achieved with too large an opening angle, especially in the edge area of the agglomerate bricks.

The optimization measures have made it possible to process the blast furnace gas and LD sludges, which are difficult to process overall, into dimensionally stable agglomerate bricks with the existing plants as far as possible without complications (Figure 2).

Newer mixer types, which have a higher energy input than the planetary countercurrent mixers used here and thus better homogenization of even critical mixtures, should be able to compensate for some of the difficulties mentioned above. Within the framework of the project, an intensive mixer of this type was rented and comparative investigations of the existing technology were carried out. In campaigns with various formulations developed here, the intensive mixer showed advantages with regard to faster homogenization compared to the available, optimized plant technology. However, the target criteria, in particular the desired strength of the agglomerate bricks, could not be set reliably and did not justify the high investment costs.

## DEVELOPMENT OF FORMULATIONS FOR AGGLOMERATE BRICKS

In the development of formulations for agglomerate bricks from blast furnace gas and LD sludges, the focus was on the target criteria of dimensional stability after the pressing process as well as sufficient pressure and drop resistance to produce solid and thus manageable agglomerate bricks for recycling in metallurgical plants.

The results obtained in the previous project [1, 2] already showed that different formulations had to be developed for agglomerated bricks made from LD sludge or blast furnace sludge, since they differ fundamentally from each other with regard to zinc content, grain size distribution, grain shape, carbon content, moisture content and tendency to agglomerate.

## FORMULATION DEVELOPMENT FOR AGGLOMERATE BRICKS FROM LD SLUDGES

According to the laboratory experience with LD sludges [1] already gained in the past, the large-scale production of agglomerate bricks proved to be comparatively unproblematic (Figure 2).

On an industrial scale, mixtures of 70 % LD sludge, 20 % mill scale and 10 % Portland cement were initially processed. Due to the very good compressive strengths of > 8 MPa achieved after three days of storage, the proportions of mill scale and Portland cement were further reduced in favour of the proportion of LD sludge. A mixture of 82 % LD sludge, 11 % mill scale and 7 % Portland cement showed compressive strengths > 6 MPa after three days, which can be regarded as sufficient for transport and storage. The drop strength from a height of three metres also showed chipping of less than 10 % < 10 mm and less than 1 % < 1 mm. A further reduction of the cement content to 5 %, however, led to a significant drop in strength, as this quantity was obviously not sufficient for a complete coating of the individual grains of the fine-grained LD sludge.

Since the agglomerate bricks with LD sludge were to be fed onto the slag in the converter as a cooling scrap substitute and thus exposed to a minimum pressure load, a test of the hot compressive strength and the reduction behaviour, as with the use of agglomerate bricks in the shaft furnace or blast furnace, was dispensed with.

## FORMULATION DEVELOPMENT FOR AGGLOMERATE BRICKS FROM BLAST FURNACE GAS SLUDGE

The development of an optimal formulation for the industrial production of agglomerated bricks from blast furnace gas sludges was clearly more problematic than that for agglomerated bricks from LD sludges. In comparison to LD sludges, the reasons for this are the higher zinc content (see Table 1), which has a negative effect on the strength development of the agglomerated bricks, and in the higher moisture content of the blast furnace gas sludge. While the moisture content of the blast furnace gas sludge after removal from storage was approx. 40 to 50 %, that of the LD sludge was only 10 – 15 %. A targeted reduction of the zinc content was not feasible within the scope of this project. To improve the water balance, the mixture of blast furnace gas sludge and LD dust described above in a ratio of 1:1 in dry conditions was used as a basic mixture.

Based on this basic mixture, a total of 34 different formulations with different Portland cement qualities and contents as well as different types and quantities of additives were tested operationally in test series (Table 2), each with 25 t of agglomerated bricks. The achievement or failure to meet the above-mentioned target criteria was decisive for the further development of the formulations.

In all test series, dimensionally stable agglomerate bricks could always be produced on the stone press without complications.

Agglomerate bricks from the base mix with different Portland cement qualities (series 1) usually achieved only low compressive strengths in the range of the response threshold of the press. However, during prolonged storage, a slight increase in compressive strength was recorded. The drop strength was low.

In the following series, various additives were tested in order to quickly achieve the desired compressive strength and thus a faster handling of the agglomerate bricks. The additives were selected on the basis of their quantity and local availability. Mill scale, agglomerate quarry and pig iron desulphurisation slag, which essentially act as supporting grain, commercially available additives to improve compactability and materials changing the grading curve, such as fly ash,

Series:	Formulation:	Additives:	Remarks:
1	7	without	dimensionally stable, low compressive/drop strength
2	7	Mill scale, agglomerate quarry, LD-dust	dimensionally stable, low compressive/drop strength
3	8	Pig iron desulphurisation slag, commercial additives, fly ash	dimensionally stable, low compressive/drop strength
4	2	Pig iron desulphurisation slag, Micro-Silica	dimensionally stable, higher but still excessively low compressive strength
5	6	Fly ash or Micro-Silica	dimensionally stable, 4 MPa compressive strength, acceptable drop strength
6	2	Fly ash plus Micro-Silica	dimensionally stable, 4 MPa compressive strength, acceptable drop strength
7	2	Melt chamber granulate	dimensionally stable, 4 MPa compressive strength, good drop strength

Table 2: Test series for the production of agglomerate bricks from a basic mixture with blast furnace gas sludge

micro-silica and fines from the processing of melt chamber granulate to blasting agent, were tested.

Agglomerate bricks of series 2 to 4, which were essentially based on the use of supporting grains, showed significantly lower compressive strengths than the targeted 5 MPa after three days of storage. With fly ash or micro-silica (series 5 and 6), a significant improvement in compressive strength could already be achieved. The drop strength has also been improved. However, at a fall height of three metres, it was still close, and in some cases even above the target criteria of a chipping of less than 10 % < 10 mm and less than 1 % < 1 mm.

The agglomerate bricks produced in series 7 using 65 % and 75 % of the basic mixture of blast furnace gas sludge and LD dust, 20 % and 10 % melt chamber granules and 15 % Portland cement, respectively, showed similar compressive strengths after three days of storage to those using fly ash or micro-silica. Seven days storage always resulted in compressive strengths of  $\geq 4$  MPa. However, a significant improvement over all other test series was achieved at an early stage in the drop strength. Here, chippings < 10 mm of only 0.15 to 2.9 % and < 1 mm of 0.15 to 1.3 % were determined, thus ensuring good handling properties.

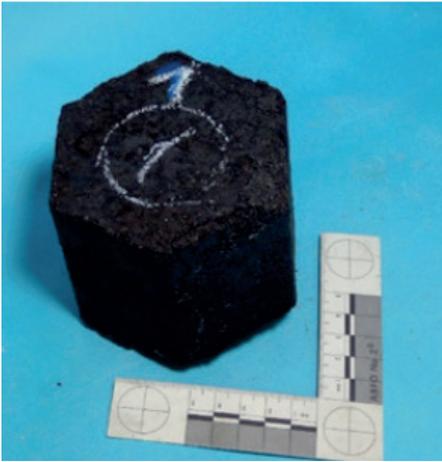
The low chippings are essential for internal recycling, as higher fines could impede through-gassing in the blast furnace or shaft furnace. In order to test the behaviour in such an application, the hot compressive strength and the reduction behaviour of agglomerate bricks of these test series were also tested in the modified RuL - test (Reduction under Load).

To test the hot compressive strength, cylindrical test specimens with a diameter of 30 mm had to be drilled out of the agglomerate bricks (Figure 3, left).

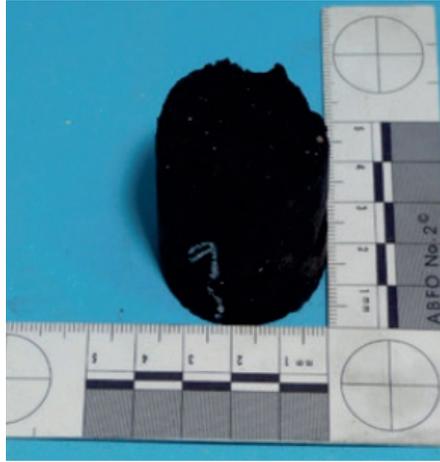
During this processing, which is actually designed for refractory bricks with significantly higher strengths, the structure of the agglomerate bricks was partially significantly damaged (Figure 3, middle) and consequently only hot compressive strengths of 1 MPa at 800° C were determined. However, the agglomerate bricks after the hot compression test (Figure 3, right) show no flour-like or grit-like decay, as would be expected with this low compressive strength. Rather, a sufficiently dimensionally stable „residual brick“ remains, the size of which corresponds perfectly to that of other materials used in blast furnaces or shaft furnaces.

The RuL test simulates the softening behaviour of materials containing iron oxide and carbon in the

Agglomerate brick



Test specimen



Test specimen after test

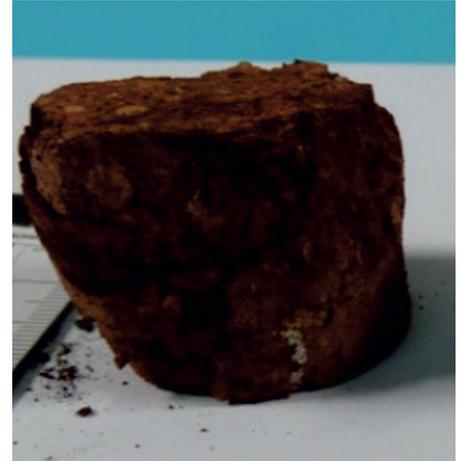


Figure 3: Determination of the hot compressive strength of agglomerate bricks, Series 7

blast furnace or shaft furnace under high temperatures and pressure of the burden column. This is to ensure that the charge materials do not negatively influence the gas flow through the burden column by premature softening. For the RuL test, the sample is heated in a furnace under load and subjected to defined reduction conditions (reduction gas from CO, H<sub>2</sub>, N<sub>2</sub>), whereby the weight and height decrease of the sample are determined. The more dimensionally stable the specimen, the more suitable the material is for use in the blast furnace.

The RuL test was carried out in the laboratory of an integrated steel plant with a Series 7 agglomerate stone. At the end of the test it showed a relative weight reduction of 40 % and a height reduction of 30 % (Figure 4) and met the experience-based requirements.

What is more, the stone structure remained completely preserved; cracks and inhomogeneities occurred only sporadically. Sudden, discontinuous height changes were not observed during the heating phase. Thus, the agglomerate stone showed a sufficiently positive softening behaviour and was classified as suitable for use, for example in a shaft furnace.

#### RECYCLING OF THE AGGLOMERATE BRICKS IN THE METALLURGICAL PLANT

With the successful development of a formulation for the large-scale production of agglomerate bricks from LD sludge, larger quantities of these bricks were

produced and delivered to a metallurgical plant as a cooling scrap substitute for the LD converter. The metallurgical plant did not provide any information on the influence of the charged agglomerate bricks on the metallurgical processes or on the cooling capacity. Since the metallurgical plant has repeatedly ordered and used these agglomerate bricks and no complaints have been made, it can be assumed that reuse was largely problem-free and that no metallurgical problems occurred.

It can therefore be stated that the production of agglomerate bricks from LD sludge can be controlled on a large scale and that the use in the converter as a cooling scrap substitute is technically and metallurgically feasible.

Since the agglomerated bricks with Series 7 blast furnace gas sludge had sufficient compressive and drop strengths for transport and handling and both the hot compressive strength and the RuL test showed positive results, 800 t of agglomerated bricks were produced according to this formulation in consultation with a metallurgical plant and used in the shaft furnace of the metallurgical plant. In a 5-day campaign, an agglomerate brick quantity of 10 % of the burden input was initially charged and increased to 50 % of the burden input of approx. 500 t/d.

The metallurgical plant evaluated the campaign for recycling the agglomerated bricks with blast furnace gas sludge as successful and target-oriented. Opera-

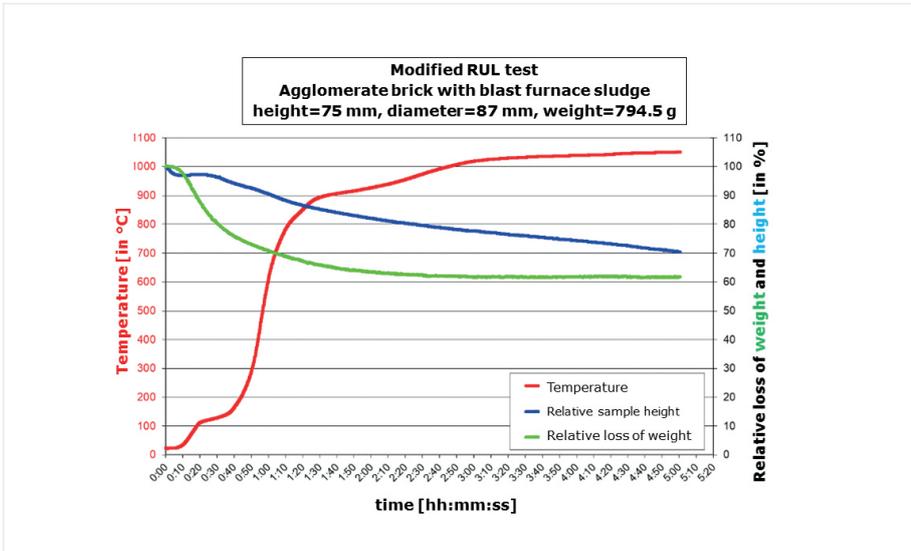


Figure 4: RuL test of an agglomerate stone with blast furnace gas sludge, Series 7

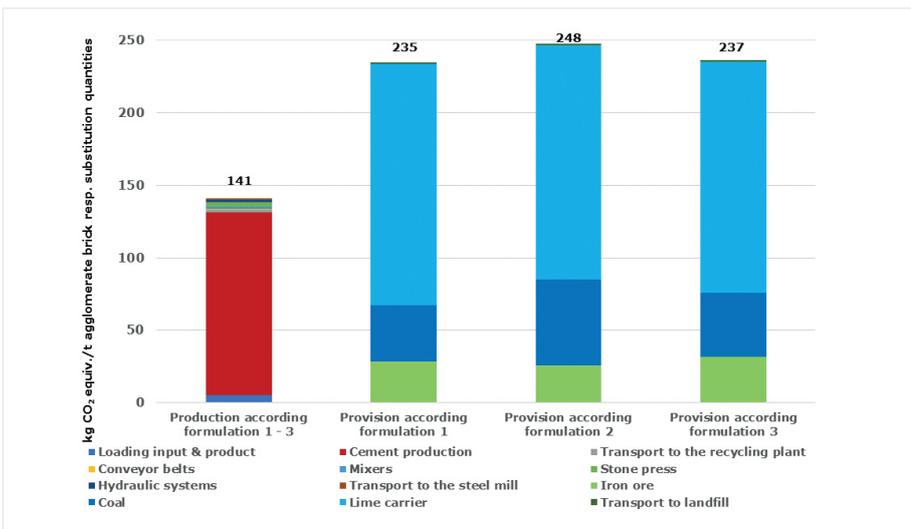


Figure 5: Ecological impact of the provision of agglomerate bricks and substitution quantities

tional handling and metallurgical process control were unproblematic. The objective of recovering iron from the agglomerate bricks without the need for additional reducing agents was achieved. This opens up the possibility of minimizing the amount of blast furnace gas sludge to be deposited. Further campaigns were expressly requested by the metallurgical plant. With a view to further op-

timization, the aim is to increase the proportion of blast furnace gas sludge in the agglomerated bricks.

### ECOLOGICAL BALANCE CONSIDERATIONS

From an ecological point of view, the production of agglomerate bricks from sludges and dusts from metallurgical plants is associated with some effort compared to landfilling. On the other hand,

these agglomerate bricks also provide certain substitution quantities for iron ore, coal and lime carriers. The ecological footprint for the production and supply of the agglomerated bricks compared to the equivalent substitution quantities from natural raw materials and the landfilling of the sludge was determined by the Fraunhofer Institute for Environmental, Safety and Energy Technology UMSICHT, Oberhausen, with the help of a life cycle assessment. The assessment was based on the process data elaborated in the project and life cycle assessment databases (ecoinvent, Ganzheitliche Bilanzierung [GaBi]). The balancing was carried out for three different formulations of agglomerate bricks that could be used in a blast furnace or shaft furnace. The formulations used and substitution quantities of iron ore, coal and lime carriers are listed in Table 3. A close geographical proximity of 12 km to the smelting works, the stone manufacturer and the landfill was assumed.

Figure 5 compares the ecological impact of providing one tonne of agglomerate bricks in kg CO<sub>2</sub> equivalent with the impact for providing corresponding substitution quantities of natural raw materials according to formulations 1 to 3 plus transport of dust and sludge to the landfill.

With 141 kg CO<sub>2</sub>-equivalent, the ecological effect of the production of 1 tonne of agglomerate bricks is largely independent of the formulation. The main carrier of the CO<sub>2</sub> balance with almost 90 % is the cement used. Since the formulations 1 to 3 differ in their proportions of substitution quantities for iron

Formulation	Composition	Percent age share	Substitution quantities per tonne of agglomerate bricks			
			Iron ore, 65% Fe [kg]	Coal [kg]	Lime carrier [kg]	Transport landfill [km]
1	Blast furnace sludge, LD dust/sludge, melt chamber granulate, cement	33 42 10 15	454	115	138	12
2	Blast furnace sludge, LD dust/sludge, cement	53 32 15	413	175	134	12
3	Blast furnace sludge, LD dust/sludge, mill scale, cement	38 42 5 15	509	130	133	12

Table 3: Formulations and substitution quantities for ecological balance consideration

ore, coal and lime carriers, values between 235 and 248 kg CO<sub>2</sub>-equivalent are calculated for this. Figure 5 shows that the supply of agglomerate bricks is associated with greenhouse gas savings of 93 to 106 kg CO<sub>2</sub>-equivalent compared with the supply from natural raw materials. In terms of figures, the CO<sub>2</sub> balance is positive up to 1,142 km transport distances between the smelting works and the stone manufacturer. Similar advantages result from an ecological point of view for the consumption of resources.

### SUMMARY

A large part of the sludge from the wet dedusting plants of the smelting works is currently landfilled. These sludges contain valuable materials, mainly iron and carbon, the reuse of which helps to conserve resources. In Germany alone, 300,000 t/a of sludge previously disposed of in landfills could be recycled by reuse, saving a calculated 110,000 t/a of iron and 30,000 t/a of carbon as well as the corresponding landfill space.

As part of the project, an industrially usable and environmentally friendly process to produce agglomerated bricks on stone presses was developed for the first time, which enables the operational recycling of these sludges in the metallurgical process. After the development of suitable formulations and technical process optimisations, larger quantities of the agglomerated bricks produced could be successfully used as a cooling scrap substitute in the LD converter or as an Fe carrier in a shaft furnace. Ecological balance considerations of this approach showed clear advantages in terms of greenhouse gas emissions and resource consumption compared to the provision of corresponding quantities of natural iron ore, coal and lime carriers.



The present investigations were funded by the Deutsche Bundesstiftung Umwelt under file numbers 32417/01 und /02.

### LITERATURE

- [1] Dislich, H.; Abel, R.; Drissen, P.; Algermissen, D.: Umweltentlastung durch Entwicklung eines Verfahrens zur Verfestigung und Rückführung von Schlamm aus Nassentstaubungsanlagen der Eisen- und Stahlindustrie; Aktenzeichen 32417/01 der Deutschen Bundesstiftung Umwelt, Abschlussbericht März 2016 (Bezug unter [www.dbu.de](http://www.dbu.de))
- [2] Drissen, P.; Algermissen, D.: Verfestigung von Schlamm aus Nassentstaubungsanlagen der Eisen- und Stahlindustrie; Report des FEhS – Instituts für Baustoff-Forschung 23 (2016) Heft 1, S. 1–8
- [3] Dislich, H.; Abel, R.; Drissen, P.; Algermissen, D.: Umweltentlastung durch Entwicklung eines industriellen Verfahrens zur Verfestigung und Rückführung von Schlamm aus Nassentstaubungsanlagen der Eisen- und Stahlindustrie; Aktenzeichen 32417/02 der Deutschen Bundesstiftung Umwelt, Abschlussbericht, März 2019 (Veröffentlichung demnächst)
- [4] Lieber, W.: Einfluss von Zinkoxid auf das Erstarren und Erhärten von Portlandzement; Zement-Kalk-Gips 20 (1967) Heft Nr. 3, S. 91–95
- [5] Rentz, O.; Spengler, T.; Häre, S.; Sieverdingbeck, A.: Prozessintegrierte Umweltschutzmaßnahmen der Eisen- u. Stahlindustrie (BMBF), Karlsruhe 1997
- [6] Gara, S.; Schrimpf, S.: Behandlung von Reststoffen und Abfällen in der Eisen- und Stahlindustrie, MONOGRAPHIEN Band 92 M-092, Wien, 1998 - BM für Umwelt, Jugend u. Familie – Austria
- [7] CIROVAL® Treatment of Blast Furnace Sludge, [http://brochures.paulwurth.com/recycling/brochures/\(Brochure\)-Ciroval-en.pdf](http://brochures.paulwurth.com/recycling/brochures/(Brochure)-Ciroval-en.pdf) (Stand: Juli 2019)

# OCCURRENCE AND UTILIZATION OF DUSTS, SLUDGES AND MILL SCALE FROM THE IRON AND STEEL INDUSTRY

Dr.-Ing. P. Drissen  
(FEhS – Building Materials Institute)

## INTRODUCTORY REMARKS

The production of steel is indispensable for a modern industrial society. Steel production is also inseparably linked to the production of by-products, which have long been used to a large extent in various fields of application.

After iron and steel slag, the fine-grained residual materials from the dust removal systems of the various production units and the scale from the rolling mills represent the second largest group of solid oxidic by-products in terms of volume. The production of the various iron and steel slags and their use as high-value, quality-monitored products has long been statistically recorded and documented [1]. On the other hand, for a long time there was no similar, comprehensive data collection for fine-grained dusts, sludges and mill scales, apart from non-public records of internal plant data or data records at specific points in time [2].

With the aim of collecting reliable data and analyzing the need for action and research, a survey on the occurrence and utilization of dusts, sludges and mill scale was therefore conducted among the

members of the FEhS Institute for the first time in 2000. Since then, this survey has been repeated every two years. While only a limited number of plants participated in the first surveys, a largely stable group of participants from about 28 plants has contributed to the collection of data since 2006.

With the exception of two electric steelworks, these are all iron and steelworks producing in Germany as well as two integrated steelworks and two electric steelworks from the Netherlands, Austria and Switzerland.

For the year 2018, 4 plants have not provided data. Data from 2016 were used for these plants. This relates to residual quantities generated in the production of around 6.9 million tonnes of LD steel and 1.5 million tonnes of electrical steel. This corresponds to approx. 16 % and 13 % of the recorded production. In percentage terms, these are relatively small quantities, so that a qualified estimate of the data for 2018 can be assumed here.

In 2018, therefore, the occurrence of fine-grained residual materials was recorded in the production of

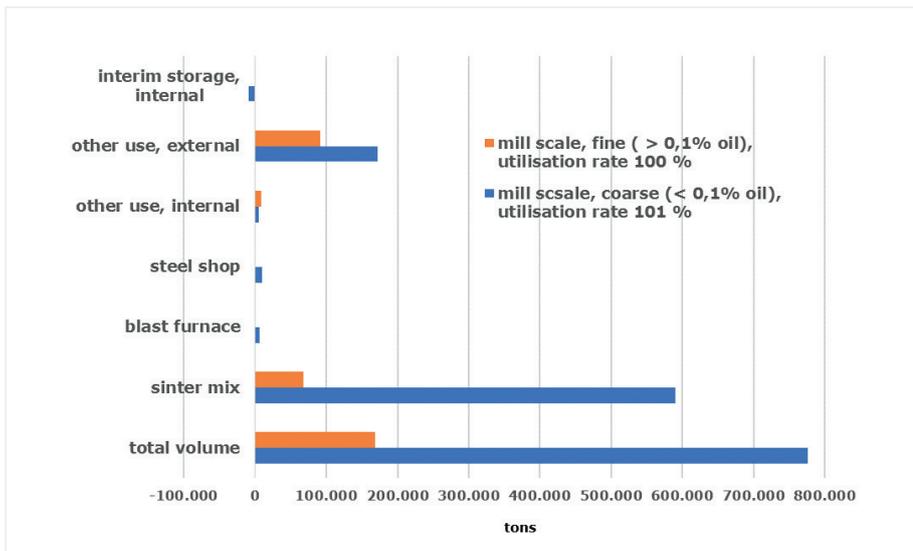


Figure 1: Occurrence and utilization of mill scale in 2018

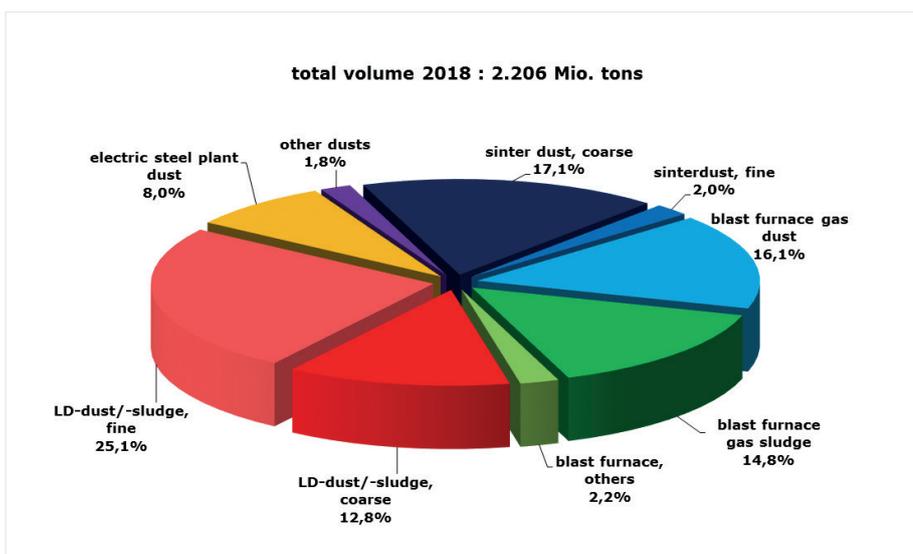


Figure 2: Occurrence of dusts and sludges by origin in 2018

37.8 million tonnes of pig iron and 53.9 million tonnes of crude steel from 27 mills. In total, this was 0.945 million tonnes of mill scale and 2.206 million tonnes of dust and sludge.

### OCCURRENCE AND UTILIZATION OF MILL SCALE

Figure 1 shows the occurrence and utilization of mill scale in 2018,

distinguishing between coarse, less oily and fine, more oily mill scale.

Of the 776,000 tonnes of coarse mill scale, 76 % was recycled internally via the sintering plants. Only a comparatively small quantity of 173,000 tonnes was used externally as Fe carrier in various applications, in particular in

the cement industry. 40 % of the significantly smaller quantity of 169,000 tonnes of fine mill scale was recycled in the sintering plant. 92,000 tonnes were put to external use. Other uses for mill scale play only a minor role. As in previous surveys, 100 % of the mill scale is used.

However, with the external use of 265,000 tonnes of mill scale, the iron and steel industry also loses considerable quantities of ferrous materials. With an approximate content of 65 % Fe, this corresponds to about 170,000 tonnes of Fe.

### OCCURRENCE OF DUSTS AND SLUDGES

The volume of 2.206 million tonnes of dusts and sludges in 2018 is shown in Figure 2, broken down according to the areas of origin.

The sinter plant segment is responsible for 19.1 %, the blast furnace segment for 33.1 % and the LD steelworks segment for 37.9 % of the dust and sludge. Compared with the data for 2016, this represents a decrease of 3.4 % in the sinter plant segment, a decrease of 0.2 % in the blast furnace segment and an increase of 1.3 % in the LD steelworks segment. The electric steel plant and other dusts areas are unchanged at 8.0 % and 1.8 % respectively.

The sintering plant and blast furnace segments together account for the largest volume of dusts and sludges at around 52 %. Compared to 2016, this is a decline of about 2 %, and in relation to 2014 even of 6 %. However, this decline is at least partly attributable to the fact that increasingly larger quantities of coarse sinter dust

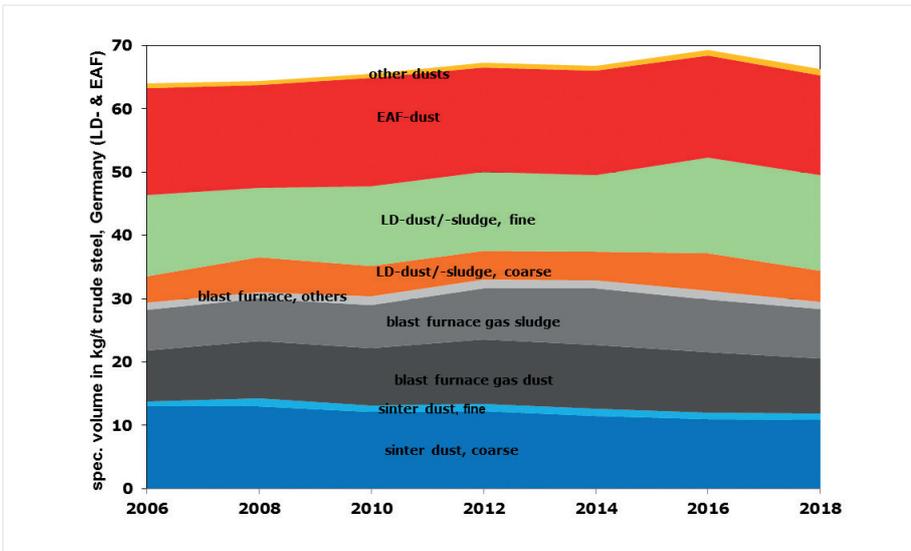


Figure 3: Specific occurrence of the various dusts and sludges in relation to the recorded quantities of LD and electrical steel for the years 2006 to 2018

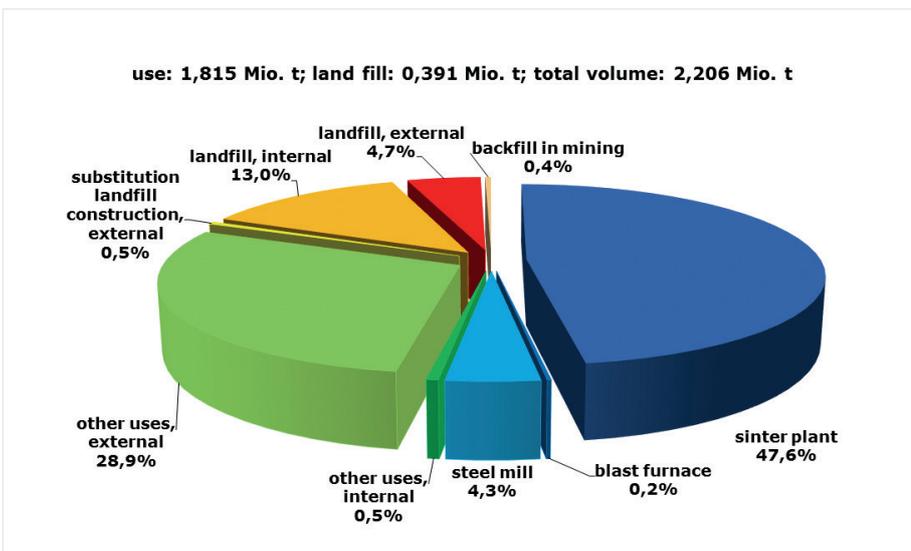


Figure 4: Utilization of dusts and sludges in 2018

are recycled internally without quantity recording.

In addition to the total volume, the specific volume is of greater interest for some issues. Figure 3 shows the specific volume of the various dusts and sludges in relation to the recorded quantities of LD and electrical steel in kg/t crude steel (CS) in Germany for the years 2006 to 2018.

For the sinter dusts, a downward trend from 13.7 kg/t CS in 2016 to 11.8 kg/t CS in 2018 can be seen here. As already explained, this is at least partly due to an increasing internal circulation without quantity recording. In the blast furnace segment, this value is currently 17.7 kg/t CS; however, in recent years, as in 2014 with 20.3 kg/t CS, higher values have also been determined. In the LD steel plant

area, a significant increase from around 17 kg/t CS to currently 20 kg/t CS has been observed in the period under review. This increase is clearly attributable to the fine LD dust/sludge, whereas the quantity of coarse LD dust/sludge has always been around 5 kg/t CS. For all other types of dust, there were at most marginal changes over the period considered.

### UTILIZATION OF DUSTS AND SLUDGES

Figure 4 shows the utilization of the 2.206 million tonnes of dust and sludge in 2018.

In 2018, 1.815 million tonnes were put to use, corresponding to about 82 % (2016: 83 %). As in the last surveys, the sintering plant is responsible for only a relatively small part of the dust volume (19 %), but processes more than twice as much as it generates (48 %). In addition to this 5 % of the materials are used for other ways of internal recycling.

At 28.9 %, the proportion of materials used externally is slightly higher than in the previous surveys (2016: 26.3 %; 2014: 24.3 %). 0.5 % (2014: 0.9 %) was used as a substitute for landfill construction material. 0.4 % is used for the backfill in mining, as in 2016. 17.7 % was disposed of in landfills. Compared to 2016, this is a slight increase of 0.9 %, but in the preceding years this share was in the same order of magnitude. Landfill accounts for 17.8 %, corresponding to 0.391 million tonnes.

Overall, the utilization rate for dusts and sludges is quite high at around 82 %. However, if one considers the different dust qualities

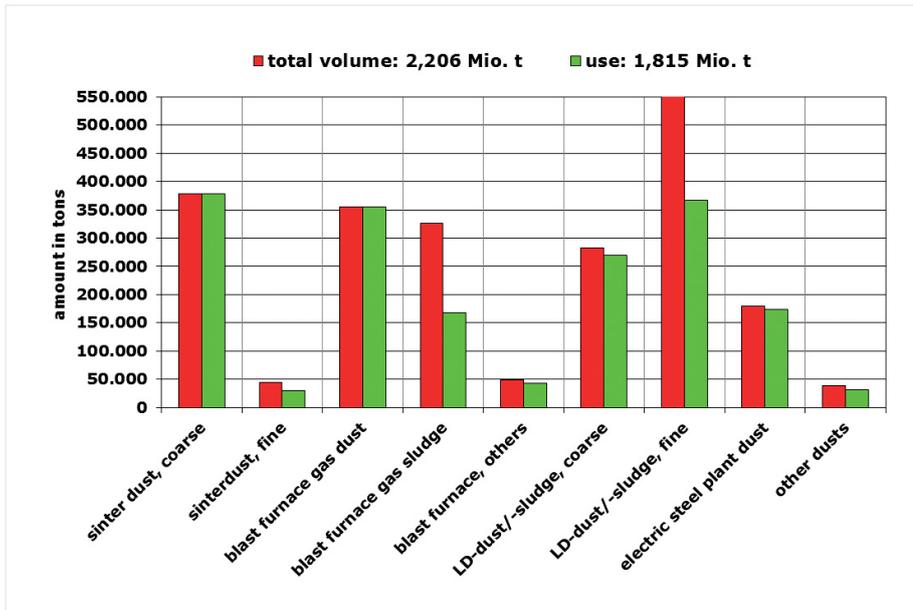


Figure 5: Utilization rate of dusts and sludges in 2018

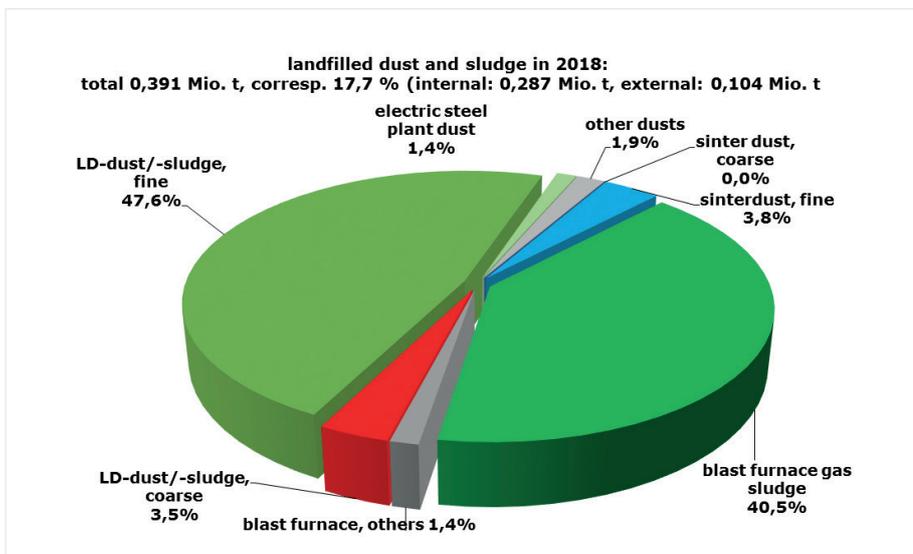


Figure 6: Landfill materials in 2018

and their utilization, clear differences become apparent (Figure 5). While for most dusts and sludges a utilization rate of or close to 100 % is achieved, this is only 51 % for blast furnace gas sludge and only 65 % for fine LD dust/sludge. This picture corresponds to the experience of all previous surveys.

The comparatively low utilization rate for blast furnace gas sludge and fine LD dust/sludge is primarily due to the fact that the zinc content of a few percent does not permit internal recycling via the sinter belt, as the zinc load for the blast furnace is limited. The blast furnace gas sludge is therefore mainly deposited in landfills

in some integrated steel mills. The zinc content is too low for economic recovery of the zinc, for example in the rotary kiln. At present, only part of the blast furnace gas sludge and the fine-grained LD dust/sludge can be processed together with other by-products of iron and steel production in suitably specialised processes such as the shaft furnace and the DK process. A further complication is that, at least with blast furnace gas sludges, handling is made more difficult by high and strongly fluctuating moisture contents, even though some R&D work has recently been completed on this subject [3, 4].

The low utilization rate of blast furnace gas sludge and fine LD dust/sludge is also reflected in the composition of the deposited fine-grained materials (Figure 6). Of the total of 0.391 million tonnes deposited in landfill, the share of these two materials amounts to 88.1 %.

Here, too, it should be noted that the quantities of dusts and sludges deposited in landfills, as well as those that are not used internally, i.e. metallurgical recycling, within the metallurgical plants, add up to 1 million tonnes, or about 47 %. Assuming an average  $Fe_2O_3$  content of 40 %, this corresponds to around 0.4 million tonnes of  $Fe_2O_3$  or 0.28 million tonnes of Fe, which are lost to the steel industry.

#### LONG-TERM DEVELOPMENTS

Looking at the utilization rates in an overview of the years 2006 to 2018 (Figure 7), a very constant utilization rate at a high level over the years can be seen, irrespec-

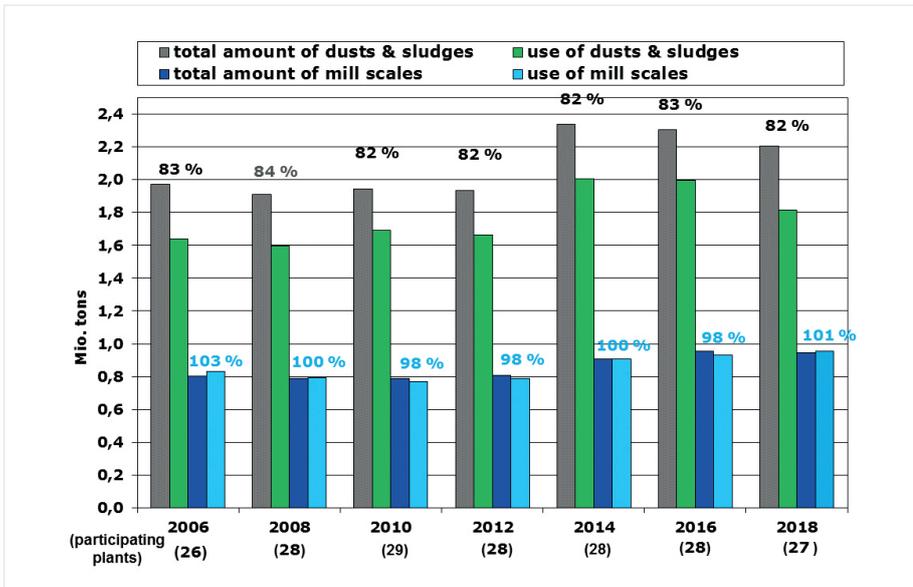


Figure 7: Utilization rates in the years 2006 to 2018 (deviations of 100 % for mill scale result from additions and disposals in interim storage)

tive of the group of participants or steel production. For dusts and sludges this is largely constant at 82 +/- 1 %. For mill scale, the utilization rate is a constant 100 %, which is only influenced by minor changes in intermediate stocks.

However, it can also be seen from the available data that there is still considerable potential for optimization due to landfilling and exter-

nal use, as a total of 0.45 million tonnes of Fe, corresponding to around 0.65 million tonnes of iron ore, are lost to the iron and steel industry on these routes. In the interests of better raw material efficiency, measures to remove oil from the fine-grained mill scale and to improve recycling of the blast furnace sludge and the fine LD dust/sludge would therefore be expedient.

#### LITERATURE

- [1] Merkel, Th.: Daten zur Erzeugung und Nutzung von Eisenhüttenschlacken 2018; Report des FEhS – Institut für Baustoff-Forschung e.V., 26 (2019) Nr. 1, S. 25–26
- [2] Unveröffentlichte Mitteilung des VDEh (1980), zitiert in Grade, K.; Geiseler, J.: Verwertung von Stäuben und Schlämmen aus der Abgasreinigung in Hüttenwerken; Fachberichte Hüttenpraxis Metallverarbeitung, 20 (1982) Nr. 10, S. 748–756
- [3] Dislich, H.; Abel, R.; Drissen, P.; Algermissen, D.: Umweltentlastung durch Entwicklung eines Verfahrens zur Verfestigung und Rückführung von Schlämmen aus Nassentstaubungsanlagen der Eisen- und Stahlindustrie; Abschlussbericht März 2016, Aktenzeichen 32417/01 der Deutschen Bundesstiftung Umwelt (Bezug unter [www.dbu.de](http://www.dbu.de))
- [4] Dislich, H.; Abel, R.; Drissen, P.; Algermissen, D.: Umweltentlastung durch Entwicklung eines industriellen Verfahrens zur Verfestigung und Rückführung von Schlämmen aus Nassentstaubungsanlagen der Eisen- und Stahlindustrie; Abschlussbericht März 2019 (Veröffentlichung demnächst), Aktenzeichen 32417/02 der Deutschen Bundesstiftung Umwelt

# OPTIMIZING THE ACID RESISTANCE OF CONCRETE WITH GRANULATED BLAST FURNACE SLAG

C. Gerten, M. Sc., Dr.-Ing. A. Ehrenberg  
(FEhS – Building Materials Institute)

## INTRODUCTION

In principle, concrete has a high resistance to many media [1]. As a rule, buildings subject to high chemical stress, such as wastewater engineering plants, cooling towers or collecting trays (Figure 1), are made of concrete, as many of the properties of this building material are initially advantageous. However, a considerable disadvantage is the limited resistance of concrete to acid attacks. Concrete corrosion caused by aggressive stress depends on the one hand on the composition and concentration of the corrosive medium and on the other hand on various binder and concrete technology parameters and their interaction [1]. If one assumes acid-resistant aggregates, which are generally regarded as advantageous, then in the event of acid attack, mainly portlandite ( $\text{Ca}(\text{OH})_2$ ) and calcium carbonate

( $\text{CaCO}_3$ ) of the cement stone react to easily soluble compounds and are progressively dissolved out from the outside to the inside, which ultimately leads to the destruction of the concrete structure (Figure 1).

The structure or morphological and chemical composition of the concrete is changed within the damage depth. As a result, mass losses and cross-sectional weaknesses occur, which significantly impair the durability, serviceability



Figure 1: Concrete exposed to acid attack  
(source: FEhS-Institute)

and stability of the structures. The repair of such stressed and damaged concrete structures is associated with high costs and downtimes for the operators. Thus, increased resistance of concrete to acid attacks offers significant technical and economic advantages, as the damage to concrete structures caused by a wide variety of acid attacks is considerable.

The acid resistance of concrete is determined by the packing density of the aggregates, water/bin-

GGBS		(C+M)/S	Target surface	Specific surface	Description	Position Parameter	Rosin Rammler Slope
			[cm <sup>2</sup> /g]	[cm <sup>2</sup> /g]	[-]	$d'_{RRSB}$ [μm]	$n_{RRSB}$ [-]
	A	1.18	4,200	4,090	A4.2	16.3	0.97
			7,000	6,670	A7	7.5	1.40
			10,000	8,970	A10	5.4	1.54
			13,000	12,200	A13	3.4	1.59
	B	1.32	4,200	4,300	B4.2	16.7	0.97
			7,000	7,050	B7	7.4	1.49
			10,000	9,670	B10	5.0	1.51
			13,000	12,600	B13	4.0	1.55
	C	1.45	4,200	4,100	C4.2	15.3	0.99
			7,000	6,540	C7	7.7	1.45
			10,000	9,220	C10	5.8	1.56
			13,000	12,900	C13	3.4	1.60

Table 1: Key parameters of GGBS

der (w/b) ratio, cement content and proper installation. Besides the type of aggregate, the binding agent-dependent properties of the cement stone greatly influence the acid resistance of concretes. The content and distribution of calcium hydroxide, the density of the cement stone structure, i.e. porosity and pore distribution, and the hydration level determine the acid resistance of the binder matrix and also of the concrete.

It is already known that the use of ground granulated blast furnace slag (GGBS) instead of ordinary Portland cement (OPC), which releases  $\text{Ca(OH)}_2$  during hydration, offers technical advantages for increasing acid resistance. From the chemical point of view, the potential weak point of the cement stone structure, i.e. the easily soluble large portlandite crystals, is

reduced. Another essential advantage is a lower capillary porosity of the blast furnace cement stone at a constant w/b ratio [2-8], which makes access by harmful media more difficult. The hydration products of cements containing GGBS are basically comparable to those produced during the hydration of OPC [9-12]. However, they have finer particles and less calcium, which leads to advantageous technical properties, such as the capillary/gel pore ratio in the cement stone, which is more favourable at a constant w/b ratio and constant total porosity compared to OPC. An optimized particle size distribution (PSD) of the binder, which on the one hand aims at the greatest possible space filling and on the other hand must also guarantee sufficient particle mobility in order to achieve this space filling, has a decisive influ-

ence both on the water demand and the workability of mortar- and concrete-systems as well as on the strength development and, via the capillary porosity of the cement stone, also on the chemical resistance [13]. An optimization of the PSD using fine materials must also take into account that excessively high contents are more likely to loosen the microstructure rather than to compress it. The hydration level of the binder constituents is also positively changed by a narrower PSD with a constant specific surface area of the binder constituents [14].

## OBJECTIVES

Within the framework of the research project carried out in cooperation with the Ruhr University Bochum, the aim was to exploit the known advantages of OPC substitution by GGBS and to optimize

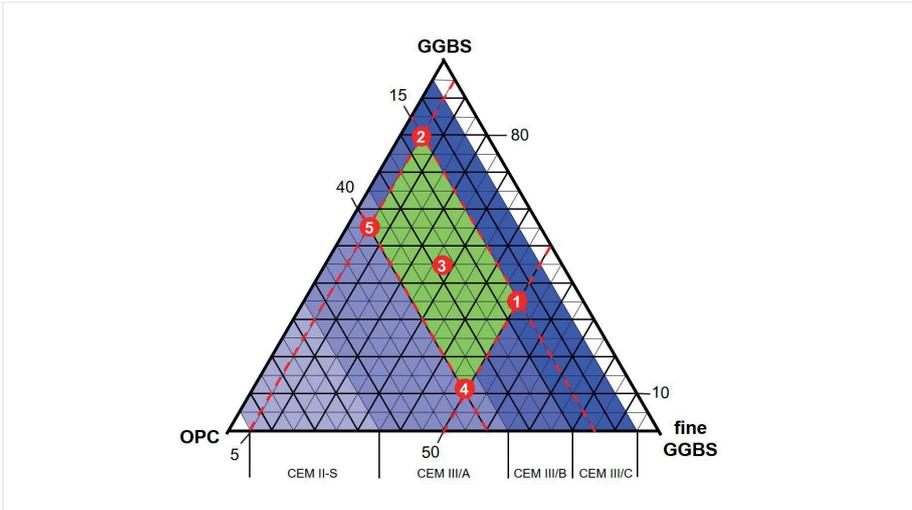


Figure 2: Testing area, based on DoE

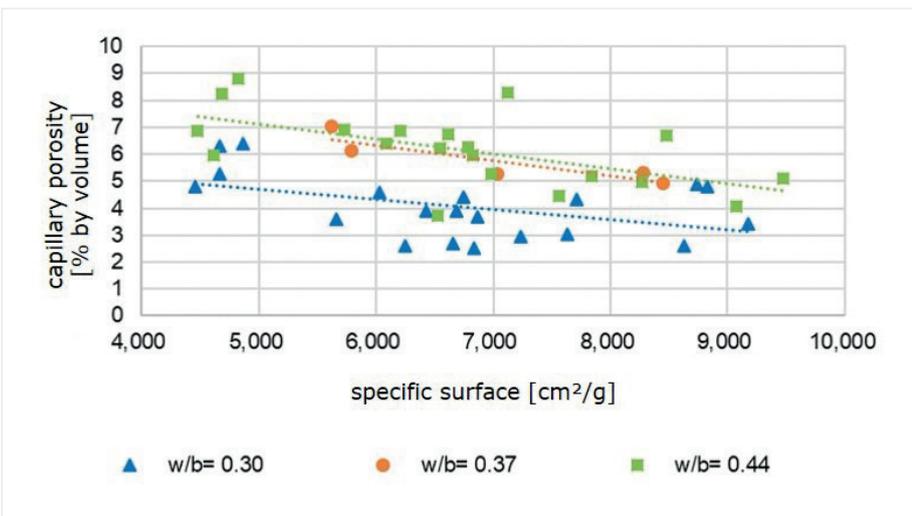


Figure 3: Capillary porosity after 28 days depending on binder fineness and w/b ratio

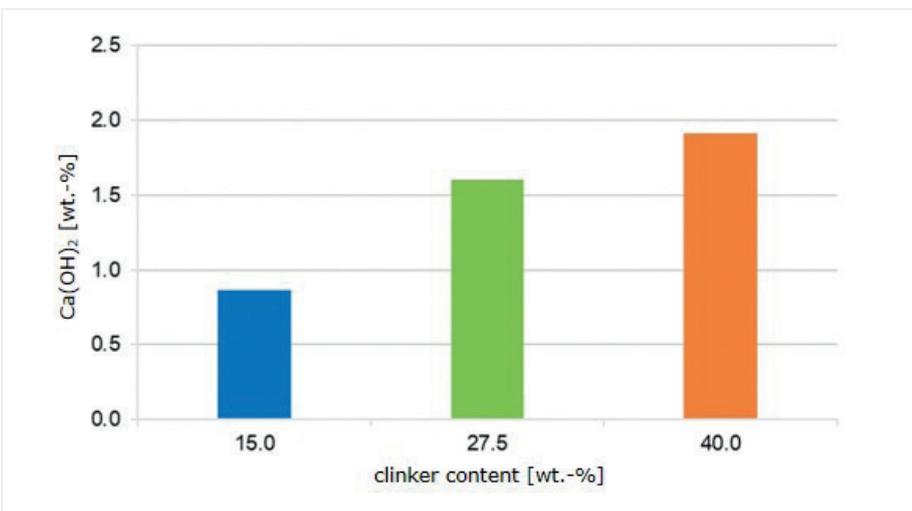


Figure 4: Calcium hydroxide content after 28 days depending on the clinker content in the cement stone of the mortar samples

these advantages with regard to acid resistance [15-17]. Concretes based on GGBS-rich binders were to be optimized chemically, granulometrically and by means of concrete technology in order to provide increased resistance to acid chemical attack. Within the normatively regulated range, additional protective measures were not to be used for exposure class XA3 and the durability of the components was to be ensured solely by the increased resistance of the concrete.

**MATERIALS**

The materials required for the planned experiments were procured in sufficient quantities so that the same materials could always be used for the entire project. In addition to three industrial GGBS of different reactivity (A-C), an OPC (CEM I 52.5 R) was also selected. An OPC (CEM I 42.5 R) and a blast furnace cement (CEM III/B 42.5 N-LH/SR/NA) were selected as reference samples.

The GGBS were prepared in a grinding and classifying system. The fine GGBS (10,000 and 13,000 cm<sup>2</sup>/g according to Blaine) were obtained by optimized sifting processes. The granulometric characteristics of the GGBS are listed in Table 1.

**BINDER AND MORTAR TECHNICAL INVESTIGATIONS**

Since the binder matrix is of great importance with regard to the acid resistance of a concrete, tests were first carried out on samples on a mortar scale. Statistical methods were used to design the experiments in order to produce a number of binder combinations that could be controlled in the la-

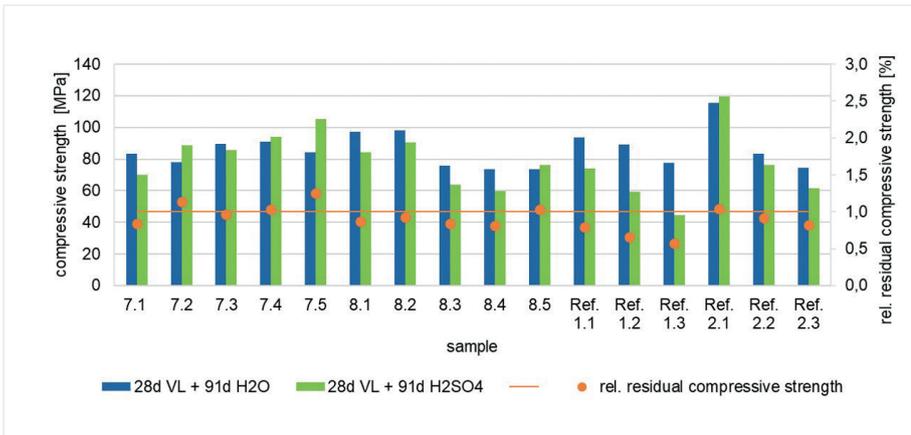


Figure 5: Compressive strength of mortar prisms at the age of 119 days

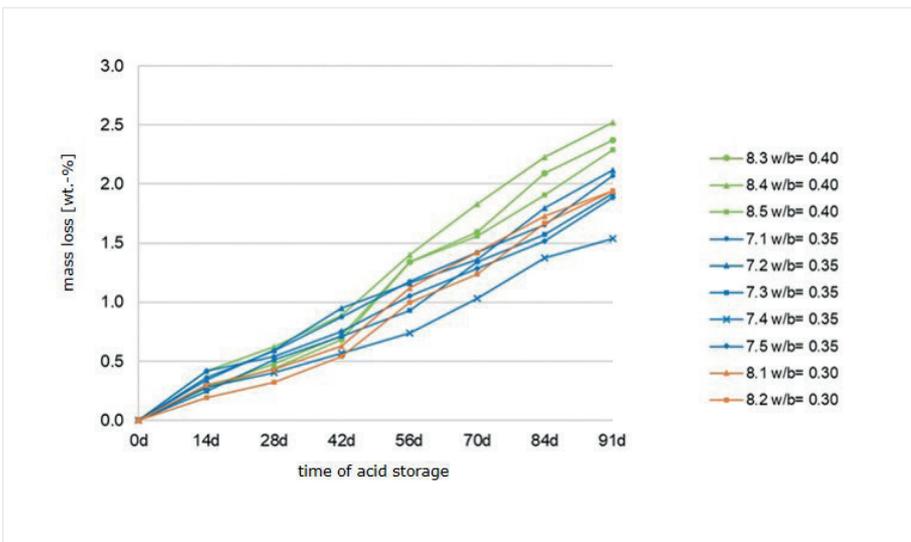


Figure 6: Mass loss of mortar prisms after 91 days storage in  $H_2SO_4$

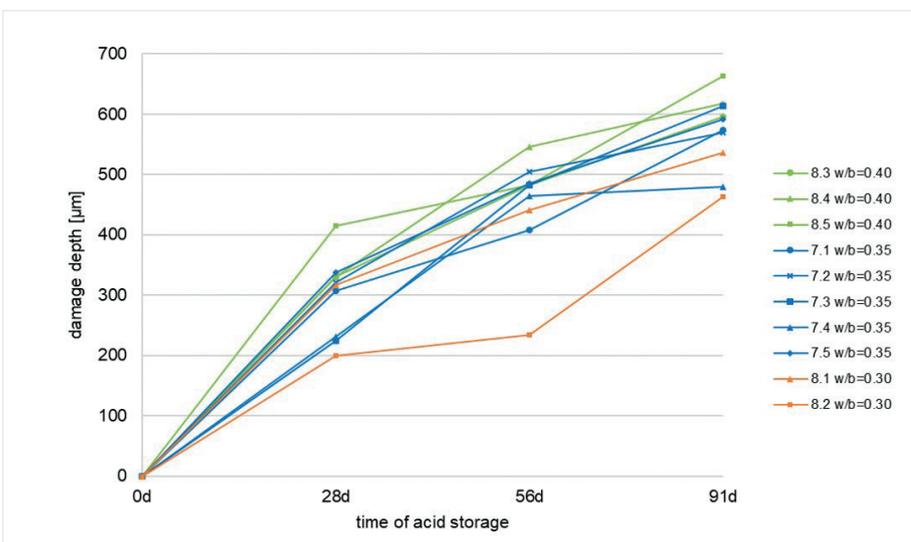


Figure 7: Damage depth of mortar prisms after 91 days of storage in  $H_2SO_4$

laboratory. The testing area of OPC, GGBS and fine GGBS, which is generated by limiting factors, is shown in Figure 2. Based on the design of experiments (DoE), a total of 45 binder compositions were generated for the mortar technical investigations of the characteristic values, i.e. strength, porosity and  $Ca(OH)_2$  content.

The capillary porosity determined by mercury pressure porosimetry (Figure 3) is primarily determined by the w/b ratio, but also by the fineness of the binder. The proportion of capillary pores decreases both with a lower w/b ratio and with a higher specific surface area of the binder.

At 0.9 wt.-% to 1.9 wt.-%, the calcium hydroxide content was low at the age of 28 days (Figure 4). The content of  $Ca(OH)_2$  increased as the GGBS decreased. At a w/b ratio of 0.44, the  $Ca(OH)_2$  content was higher than at a w/b ratio of 0.30. This is due to the fact that at a low w/b ratio of 0.30, the OPC clinker phases do not hydrate completely so that less  $Ca(OH)_2$  is formed. There were no significant differences between the binder compositions with GGBS A, B or C.

#### ACID-RESISTANCE TESTS ON MORTAR SAMPLES

Those binder compositions were selected which promised a potentially increased acid resistance on the basis of the mortar-technical investigation results. From a total of 15 binder compositions, 7 prism sets (315 prisms) were produced to investigate their acid resistance. The compositions differed in their w/b ratio, the amount of OPC (CEM I 52.5 R), GGBS and fine

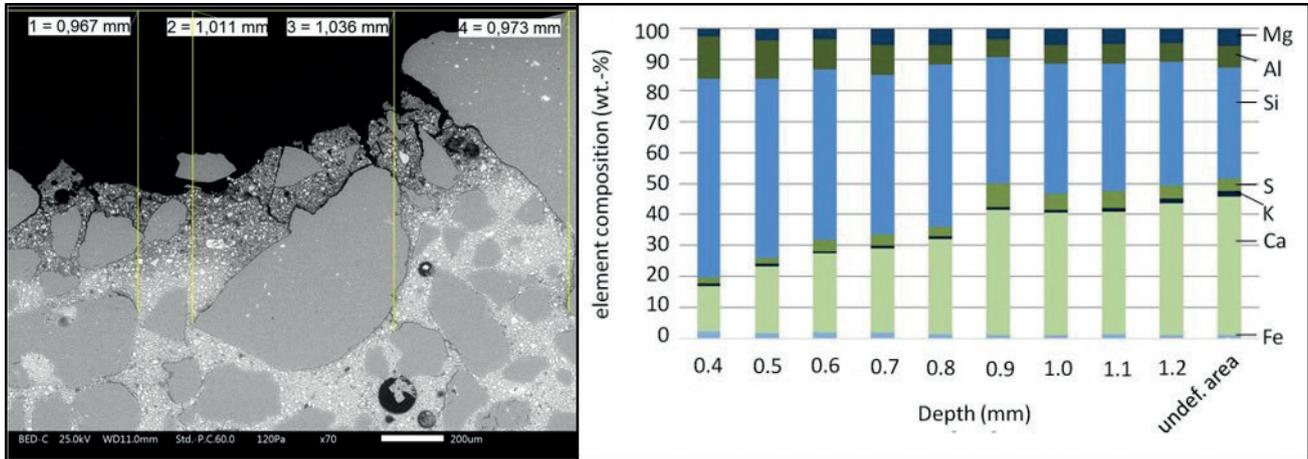


Figure 8: SEM picture and distribution of elements (binder composition 8.4) at the age of 91 days

GGBS as well as in the reactivity of the GGBS. In addition, reference mixtures of OPC (CEM I 42.5 R) and blast furnace cement (CEM III/B 42.5 N) with different w/b ratios were produced.

The acid-resistance test was carried out in an acid test rig consisting of several storage tanks connected to a reservoir with automatic titration (pH static test). The pH value of the test medium, i.e. sulphuric acid ( $H_2SO_4$ ), was permanently  $3.5 \pm 0.05$ .

The determination of the strength values showed no significant differences between the acid-storage samples and the water-storage samples. With the exception of the OPC reference samples, the compressive strength tests showed only minor deviations (Figure 5). The compressive strength losses of the reference samples made with OPC (Ref. 1.1 to Ref. 1.3) of 20 to 33 MPa are striking, corresponding to a relative residual compressive strength of only 58 % to 79 %. The main results of the acid-resistance tests (mass loss and damage depth) are shown in Figure 6 and Figure 7.

The w/b ratio is of great importance for the mass loss. The lower the w/b ratio, the lower the mass loss. In addition to the w/b ratio, mixtures 8.2 and 8.5 also differed in the fineness of the binder. For 8.2 it was coarser with a specific surface of  $4,740 \text{ cm}^2/\text{g}$  than for 8.5 with a specific surface of  $6,670 \text{ cm}^2/\text{g}$ , but had a lower w/b ratio (0.30 to 0.40). While mixture 8.2 had a mass loss of about 1.9 wt.-%, mixture 8.5 lost almost 2.3 wt.-%.

The damage depths were determined microscopically after 28, 56 and 91 days of acid storage using the indicator phenolphthalein. The results correlate with the results of the mass losses. Again, the w/b ratio has the greatest influence, while the average fineness of the binder and the reactivity of the GGBS are of secondary importance.

Thin sections were prepared from selected mortars in order to examine the damage depth under the scanning electron microscope (SEM). On the basis of the energy dispersive X-ray spectroscopy (EDX), the optically determined damage depths were confirmed

Description	OPC	GGBS	Fine GGBS	(C+M)/S	Specific surface GGBS	Specific surface fine GGBS	Binder content	w/b ratio
	[%]	[%]	[%]	[-]	[cm <sup>2</sup> /g]	[cm <sup>2</sup> /g]	[kg/m <sup>3</sup> ]	[-]
BE1	30	63	7	1.45	6,540	9,220	350	0.30
BE2	20	68	12	1.18	4,090	8,970	350	0.30
BE3	20	68	12	1.45	4,100	9,220	350	0.30
BE4	25	68	8	1.45	4,100	9,220	350	0.32
BE5	25	68	8	1.45	4,100	12,900	350	0.32
BE6	26	67	7	1.18	6,670	8,970	350	0.35
BE6.1	26	67	7	1.18	6,670	8,970	300	0.35
BE6.2	26	67	7	1.18	6,670	8,970	400	0.35
BE6.3	26	67	7	1.18	6,670	8,970	350	0.30
BE6.4	26	67	7	1.18	6,670	8,970	350	0.40
BE6.5	26	67	7	1.18	6,670	8,970	280+70 kg fly ash	0.35
BE7	27	62	11	1.18	4,090	12,200	350	0.35
BE8	27	62	11	1.45	4,100	12,900	350	0.35
BE9	27	62	11	1.32	4,300	12,600	350	0.35
Ref. BE1	CEM I 42,5 R						350	0.35
Ref. BE2	CEM III/B 42,5 N-LH/SR/NA						350	0.35

Table 2: Concrete compositions

by the element composition of the binder stone. The calcium compounds are first dissolved out by sulphuric acid attack. If no significant change can be detected between the near-surface area and the core area, the undamaged area is present and the damage front is reached (Figure 8).

#### ACID-RESISTANCE TESTS ON CONCRETE SAMPLES

For the concrete tests, potential concrete compositions were derived from the results of the statistical evaluation of the binder and mortar tests. Due to the large number of possible combinations, a statistical DoE was used again to limit the laboratory work. By varying concrete technological parameters, such as binder content and w/b ratio, concretes were produced from the compositions listed in Table 2. A total of 6 samples of each composition was prepared to test the acid resistance.

The quartzite aggregate used is inert to the acid. The binder stone is therefore the main weak point of the concrete. In the mortar tests, the proportion of

binder paste was around 40 % by volume, whereas that of an optimized concrete was reduced to around 24 % by volume by using coarse aggregate with an optimal packing density.

Concrete BE 6.3 with a low w/b ratio of 0.30 has the lowest mass loss of approx. 95 g/m<sup>2</sup>. This is due to the lower capillary porosity and therefore finer pore structure compared to concrete BE 6.4 with a w/b ratio of 0.40. As expected, the highest mass loss of 142 g/m<sup>2</sup> was determined for concrete BE 6.4. The influence of the binder content is very low, which can probably be attributed to the optimization of the binder. The BE 6.1 series with a binder content of 300 kg/m<sup>3</sup> and the BE 6.2 series with a binder content of 400 kg/m<sup>3</sup> showed no significant differences with regard to their mass losses. A proportional substitution of the binder by fly ash did not lead to an improvement of the acid resistance of the concrete. The mass loss of the BE 6.5 series was in the same size range as that of the original BE 6 concrete (132 g/m<sup>2</sup>). Although the reference concrete Ref. BE 2 with a commercial blast furnace cement had a



Figure 9: Mass loss of concretes BE 6 after 91 days of storage in  $H_2SO_4$

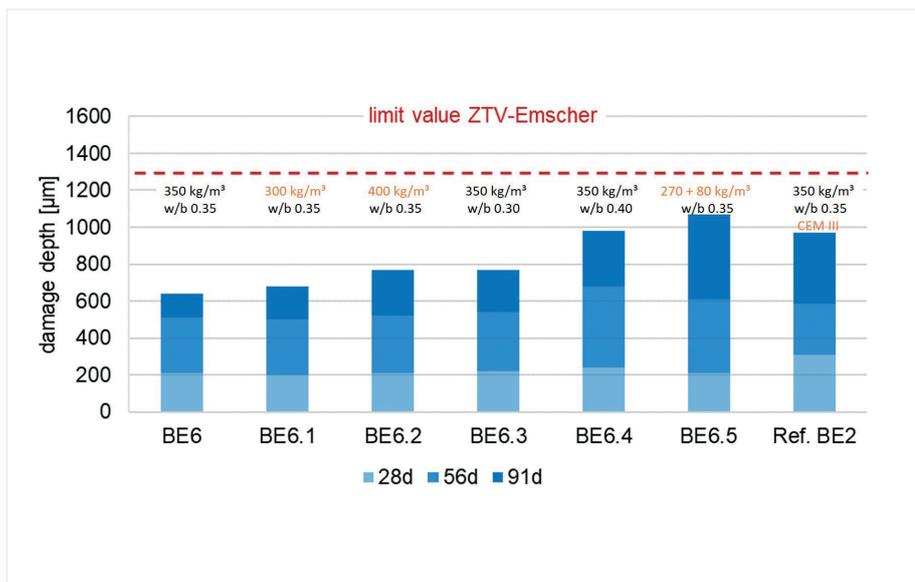


Figure 10: Damage depth of concretes BE 6 after 91 days of storage in  $H_2SO_4$

w/b ratio of 0.35, it had a mass loss of  $140 \text{ g/m}^2$ , which corresponds to that of the concrete BE 6.4 (w/b = 0.40). This is probably due to the fact that the binder in the commercial cement was not optimized.

In addition to the regular determination of the mass loss (Figure 9), two fragments of the test samples

were taken and after application of phenolphthalein they were examined light microscopically for their depth of damage after 28 days, 56 days and after 91 days at the end of acid storage. While the damage depths of the initial concrete BE 6 and the concretes BE 6.1 to BE 6.3 were at almost the same low level, the highest

damage depths of  $980 \text{ }\mu\text{m}$  and  $1070 \text{ }\mu\text{m}$  respectively were measured for concrete BE 6.4 with a higher w/b ratio of 0.40 and for concrete BE 6.5 with a proportionate substitution of the binder by fly ash. For concrete BE 6.4, this is due to the increase in capillary porosity associated with the higher w/b ratio. The proportionate substitution of the binder by the fly ash of BE 6.5 concrete also had an unfavourable effect on the damage depth. A higher binder content of  $400 \text{ kg/m}^3$  (BE 6.2) resulted in greater damage depths ( $770 \text{ }\mu\text{m}$ ), while a reduction of the binder content to  $300 \text{ kg/m}^3$  (BE 6.1) had no appreciable effect. The lowest damage depth of  $640 \text{ }\mu\text{m}$  was determined on the initial concrete BE 6 with a binder content of  $350 \text{ kg/m}^3$ . To evaluate the damage depths, the limit value for acid-resistant concretes according to ZTV-Emscher [18] of  $1,300 \text{ }\mu\text{m}$  (12 weeks  $H_2SO_4$  pH 3.5) was used in Figure 10.

## CONCLUSION AND OUTLOOK

The first investigations already showed that the w/b ratio has a superior influence on the characteristic parameters (porosity,  $Ca(OH)_2$  content). Although a composition with a w/b ratio of 0.30 can be produced on a laboratory scale using highly effective superplasticizers (PCE), it will lead to difficulties in production and processing in practice according to the current state of the art. For this reason, the w/b ratio for the concrete compositions that may be suitable for practical use has therefore been limited to a minimum of 0.35. Even then, it is still difficult to adjust the fresh concrete workability, but with a certain amount of experience it is quite feasible.

It became clear that a high (fine) GGBS content had a positive effect both on the capillary/gel pore ratio and on the calcium hydroxide content in the cement stone. However, the addition of fine GGBS with very high finenesses ( $> 10,000 \text{ cm}^2/\text{g}$ ) did not necessarily lead to a higher acid resistance. Rather, it is important to note that a wide PSD in the range up to  $63 \mu\text{m}$  generally led to higher resistance. The wide PSD of the binder resulted in a higher packing density and thus a higher acid resistance.

Overall, the results of the concrete tests showed that the optimized composition led to very low damage depths and very low mass loss.

It was possible to achieve an increased resistance of the GGBS-rich concretes against acid chemical attack in comparison to concretes with commercially available (blast furnace) cements.

#### ACKNOWLEDGEMENT

The research project IGF 18949 of the Forschungsvereinigung VDEh-Gesellschaft zur Förderung der Eisenforschung mbH was supported by the German Federal Ministry for Economic Affairs and Energy through the AiF based on a decision of the German Bundestag. The financial help is gratefully acknowledged by the research partners FEhS Institute and Ruhr University Bochum, chair for building materials technology.

#### LITERATURE

- [1] Grün, R.: Einwirkung von Salzlösungen auf Zement und Beton, Mitteilung aus dem Forschungsinstitut der Hüttenzementindustrie Nr. 188, Berlin, 1938
- [2] Grün, R.: Der Beton, Berlin, 2. Auflage 1937
- [3] Hecker, E.: Verhalten von Beton bei Sulfat-, Chlorid- und Säureangriffen, Zement-Kalk-Gips 15 (1962) Nr. 12, S. 513–521
- [4] Weber, R. et al.: Hochofenzement, 2. Auflage, Düsseldorf, 1998
- [5] Rendchen, K.: Hüttsandhaltiger Zement – Verkehrsbau, Wasserbau, Kanalisation, Düsseldorf, 2002
- [6] Smolczyk, H.-G.: Die Hydratationsprodukte hüttsandreicher Zemente, Zement-Kalk-Gips 18 (1965) Nr. 5, S. 238–246
- [7] Romberg, H.: Einfluß der Zementart auf die Porengrößenverteilung im Zementstein, Tonindustriezeitung 95 (1971) Nr. 4, S. 105–115
- [8] Romberg, H.: Zementsteinporen und Betoneigenschaften, Beton-Informationen 18 (1978) Nr. 5, S. 50–55
- [9] Ehrenberg, A.: Hüttsand – Ein leistungsfähiger Baustoff mit Tradition und Zukunft, Beton-Informationen 46 (2006) Nr. 4, S. 35–63, Nr. 5, S. 67–95
- [10] Ehrenberg, A. et al.: Hüttsand-Reaktionspotential und Herstellung optimierter Zemente, Cement International 6 (2008) Nr. 2, S. 90–96, Nr. 3, S. 82–92
- [11] Schmidt, M.; Bornemann, R.; Bilgeri, P.: Entwicklung optimierter hüttsandhaltiger Zemente für den Einsatz in der Betonwarenindustrie, BWI – BetonWerk International, Heft 3, Juni 2005
- [12] Bijen, J.: Blast furnace slag cement, 's-Hertogenbosch, 1996
- [13] Palm, S.; Wolter, A.: Determining and optimizing the void filling of dry particle systems, Cement International 7 (2009) Nr. 1, S. 96–102
- [14] Ehrenberg, A.: Zur Optimierung der Korngrößenverteilung hüttsandhaltiger Zemente, Dissertation TU Clausthal, Schriftenreihe des FEhS (2001) Heft 10
- [15] Gerten, C.; Ehrenberg, A.; Breitenbücher, R.: Optimierung des Säurewiderstands von hüttsandreichem Beton, 20. ibausil 2018, Band 1, S. 1015–1023
- [16] Gerten, C.: Optimization of acid resistance in granulated blast furnace slag-rich concrete, 15. ICCI 2019, Proceedings, ID:567
- [17] Abschlussbericht Optimierung des Säurewiderstands von hüttsandreichem Beton, Schlussbericht zum AiF-Forschungsvorhaben 18949
- [18] ZTV der Herstellung und Lieferung von Abwasserrohren aus Beton und Stahlbeton, Anlage 10.2, Anhang 2, Emschergenossenschaft (Stand: 05.01.2011)

# GLASS FORMATION OF GRANULATED BLAST FURNACE SLAG AND ITS INFLUENCE ON SLAG REACTIVITY

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

Dr. phil. N. Romero Sarcos, D. Hart, M. Sc., Dr.-Ing. H. Bornhöft,  
Prof. Dr. J. Deubener (Clausthal University of Technology, Institute for  
Non-Metallic Materials, Clausthal)

## INTRODUCTION

Approximately 280 million tonnes of granulated blast furnace slag (GBS) are produced worldwide every year and it is used as a cementitious material for more than 130 years. Many approaches exist to evaluate the reactivity of glassy GBS in cementitious systems, whereby glass content, chemical composition and fineness are taken into consideration. However, all approaches have failed to define a suitable tool for judging an unknown GBS so as to be able to predict its contribution to strength, for example. This is because the thermal history of the slag resulting both from the blast furnace and from the granulation process, which for a long time has been generally considered to be very important [1], is unknown. The question to be answered is whether any correlation actually exists between thermal history, „enthalpy content“ and technical properties.

From 2017 to 2019, the FEhS Institute and the Technical University of Clausthal conducted an AiF research project designed to answer this question [2]. The basic idea of the project was to use analytical techniques which had already been established for several years for lime-soda-silica glasses, for example. Differential scanning calorimetry and viscosity measurements were combined for GBS characterization in order to measure the fictive temperature  $T_f$  (glass transition temperature on cooling during industrial quenching process) and to retrospectively

calculate the unknown cooling rates of the liquid blast furnace slags. One topic of the project was to modify the enthalpy content of the GBS by annealing tests below the glass transition temperature  $T_g$ . In addition, the cementitious properties were characterized in order to be able to correlate GBS glass properties and GBS reactivity.

This paper describes only some of the main important results regarding both the glass transformation temperature  $T_g$  and the fictive temperature  $T_f$  as well as the general impact of the thermal history on reactivity. Additional publications on further topics such as properties of slags generated in dry cooling processes are in progress.

## GLASS PROPERTIES

It is impossible to directly measure the cooling rate. However, a glassy material (GBS in our case) stores the information about the prior cooling process (so-called thermal history) in its structure, and a common way to define it is based on determining the fictive temperature ( $T_f$ ). Figure 1 shows that when the slag melt cools from the equilibrium liquid state, the fictive temperature  $T_f$  is equal to the physical temperature  $T$  ( $T_f = T$ ) and the system is in equilibrium. With decreasing temperature, however, the molecular mobility decreases while the viscosity of the melt increases. As from a certain temperature, the time required for structural rearrangement (re-

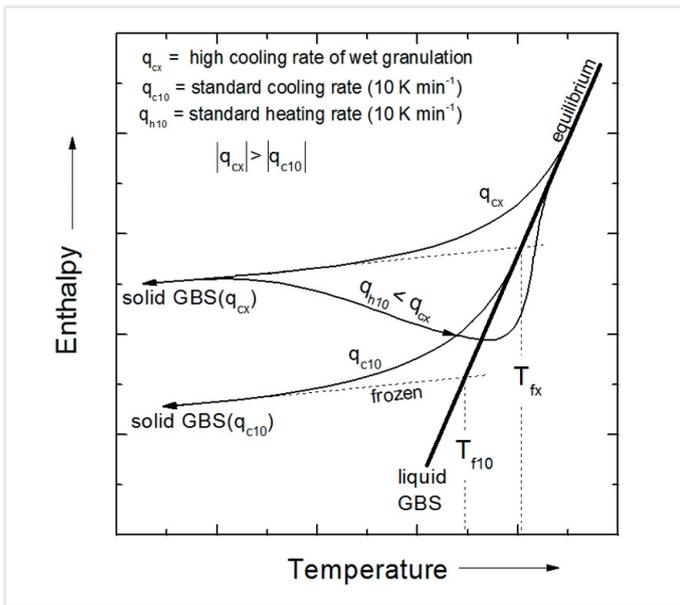


Figure 1: Schematic dependence of glass enthalpy on cooling and heating conditions [3]

Parameter	GBS 3	GBS 13b	GBS 14	
SiO <sub>2</sub>	37.6	38.0	34.6	wt.-%
Al <sub>2</sub> O <sub>3</sub>	9.8	12.4	13.7	
CaO	40.9	33.7	38.9	
MgO	6.4	11.3	8.4	
TiO <sub>2</sub>	0.61	0.61	1.16	
Na <sub>2</sub> O-equivalent	0.62	1.74	0.68	
S <sup>2-</sup>	0.58	0.61	0.79	
SO <sub>3</sub>	0.20	< 0.07	0.14	
CO <sub>2</sub>	0.14	0.05	0.11	
H <sub>2</sub> O	0.14	0.16	0.23	
(CaO+MgO)/SiO <sub>2</sub>	1.26	1.18	1.44	-
Glass	100	99	98	vol.-%

Table 1: Chemical composition and glass content of the original GBS

laxation) is longer than the time that the melt spends at that exact temperature. The structure then freezes in and the material deviates from the equilibrium and begins to form a solid glass ( $T < T_f$ ). The fictive temperature depends on the cooling rate of the melt: faster cooling leads to higher fictive temperature and higher enthalpy. Therefore, the higher the  $T_{f1}$ , the more the system has departed from equilibrium. The glass transition temperature  $T_g$  on the other hand is a particular case of the fictive temperature  $T_f$ . It is de-

termined for the defined thermal history at a cooling rate of 10 K/min ( $T_g = T_{f10}$  in Figure 1). Of course,  $T_g$  also depends greatly on the glass composition.

Relaxation of the GBS glass is a spontaneous process that would occur constantly in nature. However, at room temperature relaxation takes geological periods. Therefore, annealing at temperature  $T_a$  below the glass transition temperature  $T_g$  is necessary to decrease the fictive temperature  $T_f$  towards its physical temperature  $T$  on a reasonable time scale and to decrease the enthalpy content of the glass.

## MATERIALS AND METHODS

### Investigated granulated blast furnace slags

The research project investigated 16 industrial granulated (water-quenched) blast furnace slags. For the annealing tests, 3 GBS were selected: GBS 3, GBS 13 b and GBS 14. Table 1 summarizes their chemical composition and glass content. The chemical composition was measured by XRF (main and minor constituents), wet chemistry ( $S^{2-}$ ,  $SO_3$ ) and IR spectroscopy ( $CO_2$ ,  $H_2O$ ). The glass content was measured by transition light microscopy.

### Annealing procedure and glass analysis

The 3 selected GBS were investigated both in their original state with higher  $T_f$  and in their annealed state with lower  $T_f$ . The GBS were annealed in air at

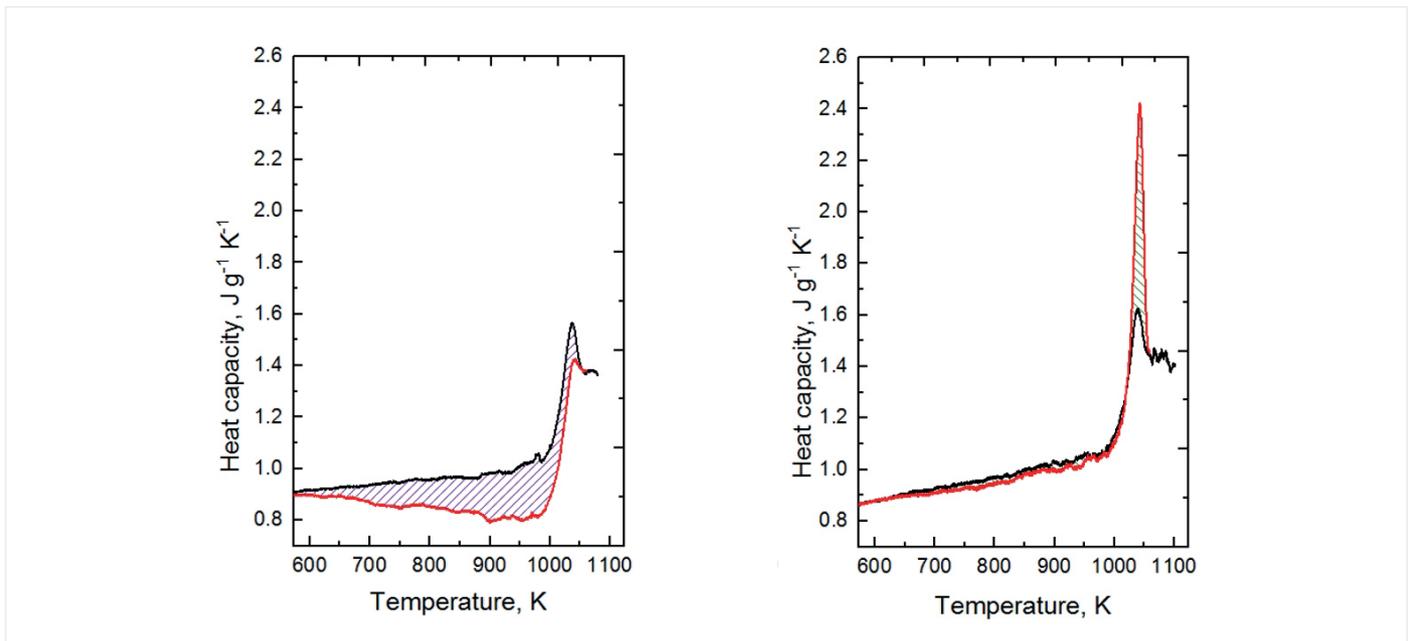


Figure 2: Heat capacity curves of GBS 14 after wet granulation (left) and after annealing at  $0.93 \times T_g$  for 24 h (right). The red curve represents the heat capacity of the first upscan ( $c_{p1}$ ), while the black line represents the heat capacity of the second upscan ( $c_{p2}$ ) after previous standard cooling at 10 K/min

$0.93 \times T_g$  for 1.5 h, 24 h and 96 h. This allowed the relaxation of the glass, modified the thermal history derived from quenching during granulation and also lowered  $T_f$  and enthalpy content.

For the calorimetric analyses, the GBS were sieved to a fraction of 355-500  $\mu\text{m}$  to minimize the grain size effect on fictive temperature. The sieved samples were then analyzed calorimetrically and  $T_g$  and  $T_f$  were determined as described in detail in [5]. The only difference was that the fictive temperature was calculated using a unified approach which is applicable both to  $T_f > T_g$  as well as  $T_f < T_g$  [4]. The calorimetric measurements were carried out in lidded PtRh (80/20) crucibles in a nitrogen environment. The samples were subjected to the sequence of heating to 771  $^{\circ}\text{C}$  (GBS

13b) and 794  $^{\circ}\text{C}$  (GBS 3 and GBS 14) with subsequent cooling to 40  $^{\circ}\text{C}$  followed by reheating to 815  $^{\circ}\text{C}$ . The heating, cooling and reheating were performed at 10 K/min. The first upscan was carried out on the original sample (unknown thermal history), whereas the second upscan was done on the sample with equilibrated thermal history created beforehand with standard cooling of 10 K/min. For the conversion of the DSC signal to heat capacity values, both the baseline and the sapphire standard were also measured. To compensate for possible inhomogeneities, the samples were measured at least twice. The glass transition temperature  $T_g$  was evaluated graphically by determining the crossover temperature of two tangents aligned to the base and the decreasing flank of the endotherm of  $c_{p2}$ .

Equation (1) was used to calculate the original cooling rate  $q$ .

$$\log \eta(T_f) = K - \log q \quad (1)$$

A critical point here is the prior determination of the viscosity  $\eta$  at  $T_f$ . In contrast to the viscosity at liquid state or around  $T_g$ , it cannot be measured. It can only be calculated based on different model approaches [5].

### Cementitious analyses

To evaluate the cementitious properties of original and annealed GBS, the slag was firstly ground in a 10 kg ball mill to approximately 4200  $\text{cm}^2/\text{g}$  (Blaine). To stress the influence of GBS properties on the cementitious properties, blast furnace cements CEM III/B with 75 wt.-% ground GBS and 25 wt.-% clinker were investigated

GBS	Status	$T_g$	$T_f$	Log viscosity at $T_f$	Calculated cooling rate	
		°C		Pa s	K s <sup>-1</sup>	
3	Original	742	826	7.22	12160	
	annealed $T_a = 668$ °C		90 min	756	10.56	3
			24 h	728	12.38	$4 \times 10^{-2}$
			96 h	716	13.26	$4 \times 10^{-3}$
13b	Original	720	828	6.38	86439	
	annealed $T_a = 650$ °C		90 min	720	12.06	$2 \times 10^{-1}$
			24 h	703	13.41	$8 \times 10^{-3}$
			96 h	686	14.94	$2 \times 10^{-4}$
14	Original	734	838	7.46	91300	
	annealed $T_a = 666$ °C		90 min	744	11.67	$6 \times 10^{-1}$
			24 h	709	13.88	$5 \times 10^{-4}$
			96 h	699	14.60	$4 \times 10^{-5}$

Table 2: Glass transition temperatures and cooling rates of original and annealed GBS

according to the GBS data base of FEhS [6]. The total SO<sub>3</sub> content of the cements was 4.5 wt.-% adjusted by adding anhydrite and gypsum. The strength development has been tested according to DIN EN 196-1 (mortar prisms 40 x 40 x 160 mm, w/c = 0.50). The heat of hydration development was measured for 7 days using an isothermal calorimeter according to DIN EN 196-11 (cement lime, w/c = 0.50).

## RESULTS

### Glass transition temperatures and cooling rates

By way of example, Figure 2 shows the heat capacity curves as a function of temperature obtained from DSC measurements of two upscans for GBS 14. For the quenched GBS sample (Figure 2, left), the 1st upscan (red) reveals the broad exothermic effect that is

attributed to the release of the enthalpy enclosed in the GBS during the wet granulation process. The 2nd upscan (black) of the standard cooled GBS exhibits no exothermic effects (since the cooling rate equals the heating rate). In the case of the annealed GBS 14 (Figure 2, right), the 1st and the 2nd upscan match in the sub- $T_g$  range ( $T_g$  equals 1007 K or 734 °C), but a larger overshoot for the  $c_{p1}$  curve at  $T > T_g$  is evident, which indicates a somewhat lower fictive temperature  $T_f$  than that of the standard cooling.

The determined temperatures  $T_g$  and  $T_f$  and the cooling rates are summarized in Table 2. As can be seen in the table, the highest  $T_f$  was measured for the industrially quenched GBS. Annealing lowered the fictive temperature towards the annealing temperature  $T_a$ . The

cooling rates for the industrial slags are very high. With respect to the absolute values, it must be pointed out that calculating the viscosity at  $T_f$  (equation 1) is unavoidably associated with uncertainty [5]. The very low cooling rates for the annealed samples are only theoretical values. If a real blast furnace slag were cooled down so slowly and if a glassy state nevertheless were still guaranteed, then it would have the same fictive temperature as the annealed GBS. However, in practice a blast furnace slag that is not quenched solidifies as a crystalline material.

### Chemical and physical properties

Data on different chemical and physical properties of the original and annealed slags GBS 3, 13b and 14 are summarised in Table 3. The data show that there is no ch-

GBS	Status	CO <sub>2</sub>	H <sub>2</sub> O	Glass	True density	Vickers	
		M,-%		Vol,-%	g/cm <sup>3</sup>	HV <sub>0.1</sub>	
3	Original	0.14	0.14	100	2.913	-	
	annealed T <sub>a</sub> = 668 °C	90 min	0.11	0.05	100	2.957	-
		24 h	-	-	-	-	-
		96 h	0.11	0.12	100	2.969	-
13b	Original	0.05	0.16	99	2.895	606	
	annealed T <sub>a</sub> = 650 °C	90 min	0.13	0.06	100	2.932	-
		24 h	0.09	0.18	95	2.943	648
		96 h	0.11	0.08	99	2.946	-
14	Original	0.11	0.23	98	2.910	599	
	annealed T <sub>a</sub> = 666 °C	90 min	0.14	0.09	99	2.952	-
		24 h	0.12	0.22	99	2.958	633
		96 h	0.13	0.11	99	2.949	-

Table 3: Properties of original and annealed GBS

ange in chemical composition, neither in chemically bound CO<sub>2</sub> and H<sub>2</sub>O, as is typical for GBS stored in a humid atmosphere for a longer period of time, nor in sulphate, as it might occur if sulphide is transformed to sulphate. What is more, the glass content is virtually unchanged if the variation of the analytical method (transition light microscopy, Figure 4) is considered. The increase in true density (measured by He pycnometry) during annealing indicates that the structure of the annealed slag glass is denser. The Vickers hardness also increased. Both correspond with the thermodynamic expectation (lower enthalpy = lower volume = denser structure = higher density) and with experiences for other glass systems.

XRD and microscopic tests confirm that the annealing at < T<sub>g</sub> did not cause crystallisation, as Figure 3 shows for GBS 13b by

way of example. Only after 96 h could first traces of gehlenite be detected. Figure 4 illustrates the glassy appearance both of the original and of the annealed slags. The coloured zones in some grains to be observed in scattered cases indicate very few crystalline parts.

### Cementitious properties

The mortar compressive strength between 2 and 91 days is shown in Figure 5. The black lines indicate the typical small standard deviation for each strength test. It is obvious that between 2 and 28 days all cements with annealed GBS result in a significant lower compressive strength. After 91 days the annealing influence seems to be lower. This is also the case, however, for the influence of the chemical composition. For GBS 13b, the effect after 2 days is very limited due to the general lower reactivity resulting from the lower basicity (see Table 1). However,

for GBS 14 with its higher basicity and higher alumina content, the negative impact of the annealing procedure was considerable after only 2 days.

Figure 6 shows that the influence of the fictive temperature on the compressive strength is not linear within the investigated T<sub>f</sub> range. The dependence is positive: a higher fictive T<sub>f</sub> corresponds to a higher compressive strength. However, the strong influence of the chemical composition must also be taken into consideration.

The results of heat of hydration measurements are shown for GBS 14 by way of example in Figure 7. In all cases, the 2nd peak of the specific heat flow typical for the GBS reaction was significantly lower for cements with annealed GBS compared with the original slags, whereas after about 12 hours the 1st peak resulting from

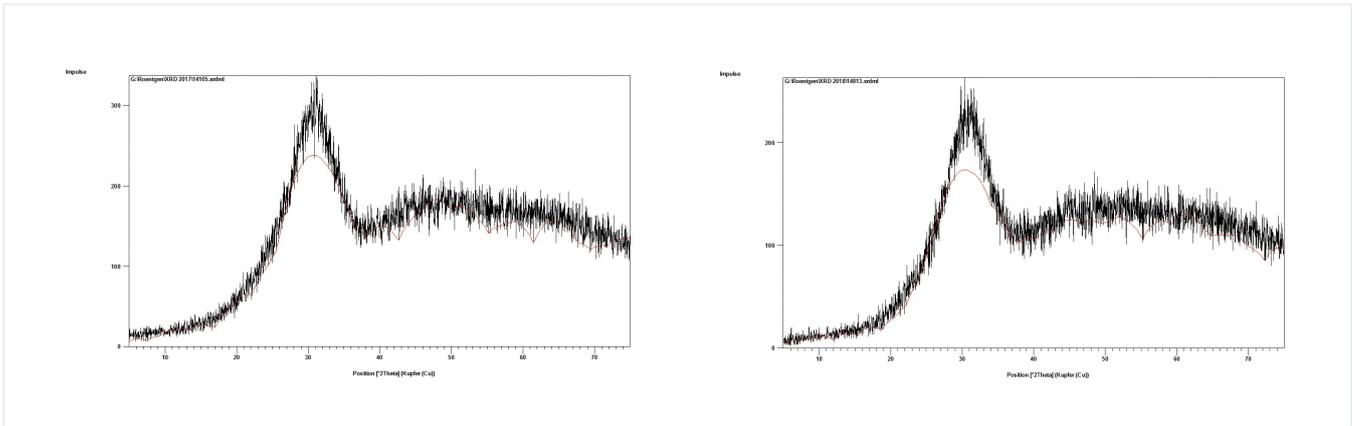


Figure 3: XRD of GBS 13b before (left) and after (right) 24 h annealing procedure

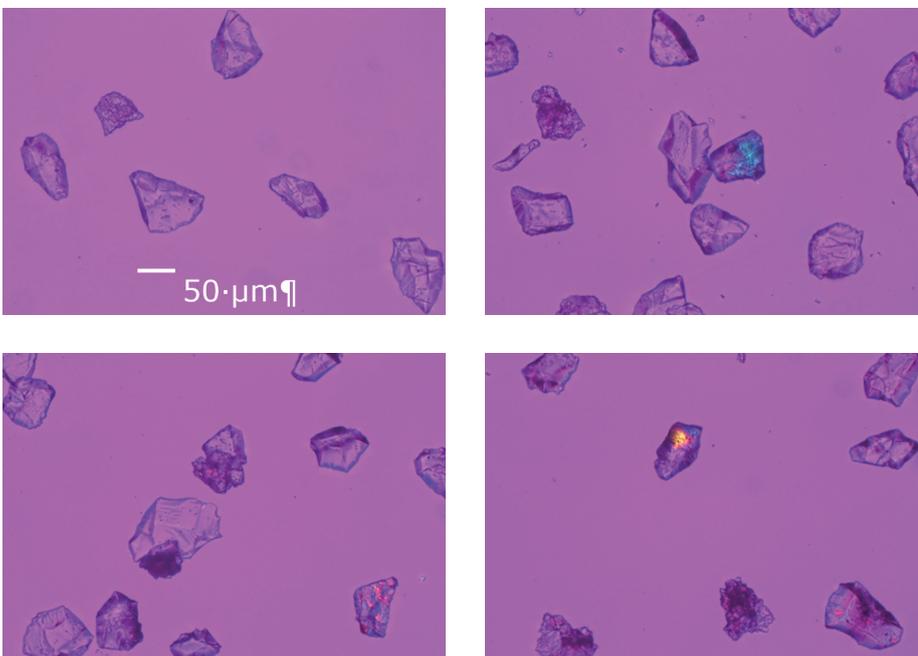


Figure 4: Fraction 40-63 µm of crushed GBS 13b (above) and GBS 14 (below) before (left) and after (right) 24 h annealing procedure (transition light microscopy)

the clinker reaction was virtually unchanged. The effect is more pronounced if the annealing time was longer and therefore the enthalpy content was lower. It was shown that 90 min annealing time was already sufficient for a significant loss in reactivity. However, the total hydration heat after 7 days varied only to a limited extent.

**SUMMARY**

It was possible for the first time to verify that the thermal history of a granulated blast furnace slag has a significant impact on the technical properties of slag-containing cements. As can be expected from a thermodynamic perspective, an annealed GBS with a lower enthalpy (= lower fictive temperature  $T_f$ ) has a lower reactivity in terms of heat of hydration or strength development of a slag cement compared to an industrial GBS.

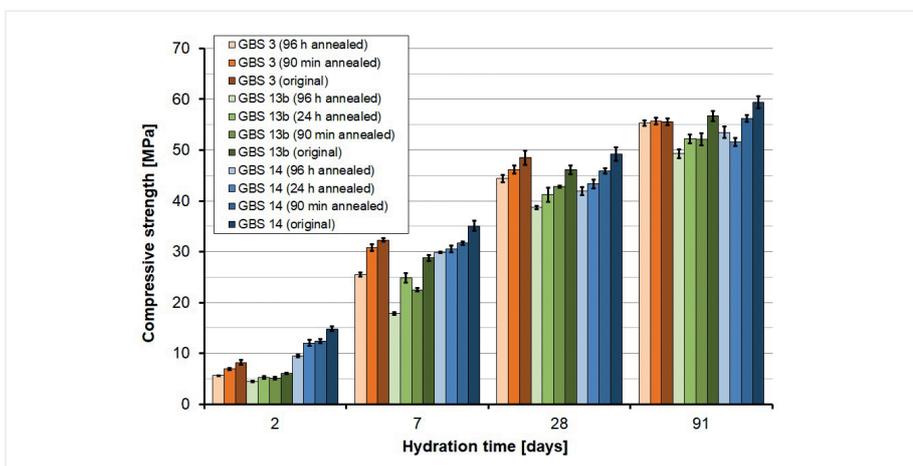


Figure 5: Mortar strengths for blast furnace cements (75 wt.-% GBS) with original and annealed GBS

This relationship is of great importance. It explains very well why attempts to explain the latent hydraulic property of GBS and to predict the strength development of slag cements based only on chemistry and glass content fail. It must now be investigated whether a standardized annealing

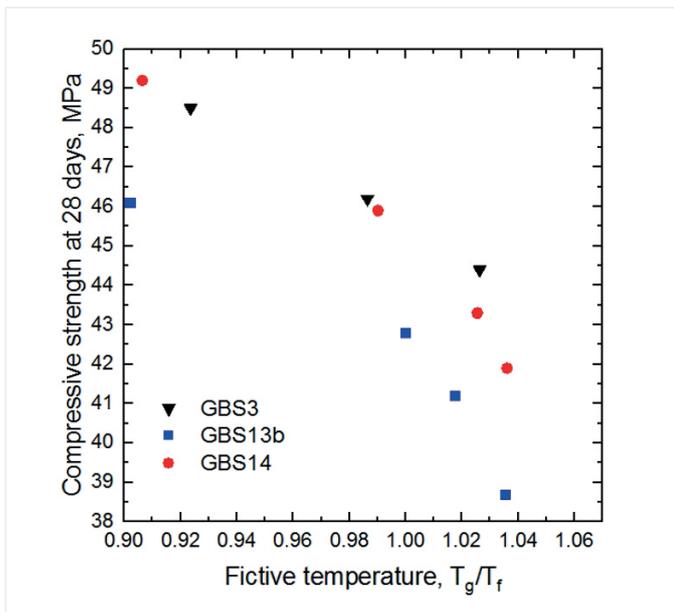


Figure 6: Dependence of the 28 days mortar strength of blast furnace cements on the fictive temperature of the GBS

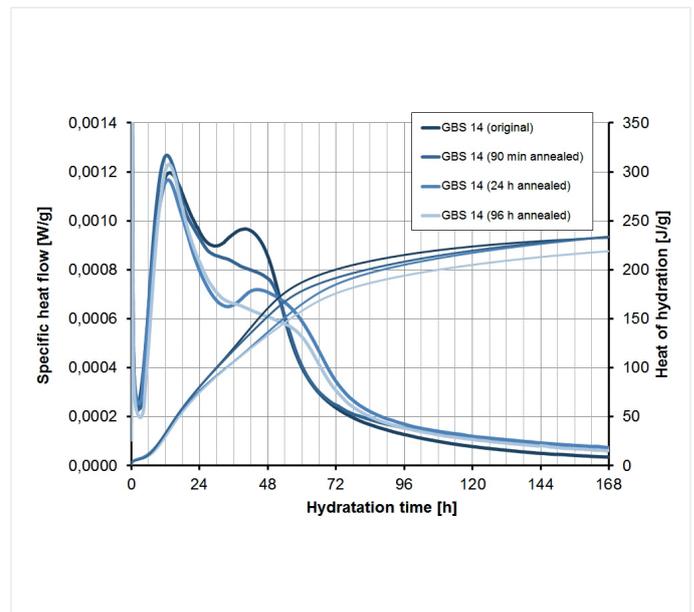


Figure 7: Heat of hydration for blast furnace cements (75 wt.-% GBS) with original and annealed GBS

procedure can be used to equalize each thermal history of a GBS in order to allow to achieve a better correlation between chemical composition and reactivity while all other framework conditions (glass content, fineness, mixture etc.) are kept constant. The relationship allows also the conclusion that a higher cooling rate during the wet or dry granulation process or a higher temperature of the liquid blast furnace slag should result in a higher GBS reactivity.

The results described above also explain very well why the reactivity of dry „granulated“ blast furnace slag was found to be lower compared to the same slag quenched with water. Cooling with enormous air-

flows is slower compared to the classical water granulation process even if it results in a glassy slag. These specific results will be published soon.

#### ACKNOWLEDGEMENT

The IGF project No. 19416 of the VDEh-Gesellschaft zur Förderung der Eisenforschung mbH has been funded by the AiF as part of the funding programme of the Industrial Joint Research (IGF) of the German Federal Ministry of Economic Affairs and Energy based on an enactment of the German Parliament. The authors are grateful for the support.

#### LITERATURE

- [1] Schröder, F.: Blastfurnace slags and slag cements. Proceedings of the 5th International Congress on the Chemistry of Cement, Tokyo, Japan, 1968
- [2] Ehrenberg, A.; Romero Sarcos, N.; Bornhöft, H.; Deubener, J.: AiF-Forschungsvorhaben 19416, Faktoren der Glasbildung von Hüttensand und deren Einfluss auf Glasstruktur und Reaktivität unter Berücksichtigung verschiedener Granulationsverfahren. 01.04.2017–31.10.2019
- [3] Moynihan, C.T.; Easteal, A.J.; De Bolt, M.A.; Tucker, J.: Dependence of the fictive temperature of glass on cooling rate. J Am Ceram Soc 59 (1976) pp. 12–16
- [4] Guo, X.; Potuzak, M.; Mauro, J.C.; Allan, D.C.; Kiczanski, T.J.; Yue, Y.: Unified approach for determining the enthalpic fictive temperature of glasses with arbitrary thermal history. J Non-Cryst Solids 357 (2011) pp. 3230–3236
- [5] Pronina, N.; Krüger, S.; Bornhöft, H.; Deubener, J.; Ehrenberg, A.: Cooling history of a wet-granulated blast furnace slag. J Non-Cryst Solids 499 (2018) pp. 344–349
- [6] Ehrenberg, A.: Granulated blast furnace slag – From laboratory into practice. Proceedings of the 14th International Congress on the Chemistry of Cement, Beijing, China, 2015

# TOXICOLOGICAL INVESTIGATIONS OF FERROUS SLAG IN THE CONTEXT OF THE REACH REGISTRATION

Dr. K. Jochims (IASON consulting, Niederzier)  
Dr.-Ing. R. Bialucha (FEhS – Building Materials Institute)

## INITIAL SITUATION

Ferrous slag was registered in 2010 on the basis of extensive investigations, which included testing for possible toxicological and ecotoxicological effects. As a result, it could be shown that ferrous slag behaves in a similar way to natural rocks. Therefore, it was not necessary to classify it as hazardous. However, at the time of registration in 2010 there were no investigations concerning the effect of inhaling respirable dust particles from ferrous slag [1]. These very time-consuming tests (in vivo and in vitro) have since been performed by specialised institutes [2], supported by a consultant (IASON consulting). The in vivo tests were performed in Edinburgh with ground granulated blast furnace slag (GGBS) which had been ground to a fineness of 4230 cm<sup>2</sup>/g according to Blaine. The in vitro tests were performed in Düsseldorf with every sort of registered ferrous slag, natural rocks and standard reference materials which served as positive or negative control, respectively. The most important results of the studies, which are summarised in executive summa-

ries on the ECHA website [3], are presented below. More detailed descriptions will be published in a medical journal soon.

## CHARACTERIZATION OF REGISTERED FERROUS SLAG

Ferrous slag is a solid UVCB substance (substance of Unknown or Variable composition, Complex reaction products or Biological materials) that resembles natural rocks - especially those of volcanic origin. The physicochemical properties are almost identical among all sorts of ferrous slag, and their benign toxicological and ecotoxicological profiles are very similar. Similarities also comprise the mineralogical composition of the ferrous slag. Importantly, all mineral components of ferrous slag are present in natural rocks; no new component is introduced during steel processing. Ferrous slag demonstrates low leachability in water as metals in slag are firmly bound in minerals, making them generally resistant to leaching. Ferrous slag is virtually free from hazardous fibres [4]. Overall, ferrous slag can be considered as artificial volcanic rock. The 'Ferrous Slag Category' comprises the

following 5 slag types: (1) ABS/GBS i.e. slag, ferrous metal, blast furnace (air cooled or granulated), (2) BOS i.e. slag, steelmaking, converter (converter slag), (3) EAF C i.e. slag, steelmaking, elec. furnace (carbon steel production), (4) EAF S i.e. slag, steelmaking, elec. furnace (stainless/high alloy steel production), and (5) SMS i.e. slag, steelmaking.

## EXECUTION AND EVALUATION OF TOXICOLOGICAL STUDIES ON FERROUS SLAG

Several studies were conducted regarding potential pathways of exposure such as inhalation of suspended airborne ferrous slag particulates, ingestion of ferrous slag, and dermal contact with ferrous slag.

It can be concluded from single-dose toxicity testing in animals via the oral, dermal and inhalation routes that ferrous slag is not acutely toxic. It does not need to be classified as oral, dermal and inhalation toxicant; neither a signal word nor hazard statement is required. Furthermore, ferrous slag exhibits no relevant irritant or sensitising potential, and does

not show any mutagenic potential. Extensive testing in rat inhalation studies (in vivo tests) revealed that the biological responses to inhaled ferrous slag show no correlation to the course of pulmonary toxicity reported for amorphous silica (quartz); quartz dust served as positive control as it is well known to produce irreversible lung damage. Overall, ferrous slag in vivo data differ markedly from those reported for quartz in rats exposed at similar doses.

Supplemental in vitro testing also shows that ferrous slag, in the same way as natural mineral samples, does not cause significant toxicity in cultured alveolar macrophages, nor does the slag induce major reactive oxygen species (ROS) formation and oxidative stress or trigger any inflammation in a biological system. On the contrary, the positive assay control quartz consistently provided evidence for an inflammation response in vitro associated with a significant secretion of the mature forms of pro-inflammatory cytokines from the cells, strong activation of the inflammasome pathway, and impaired phagocytosis functionality of alveolar macrophages.

Taken together, the data generated in vivo and in vitro for ferrous slag indicate that ferrous slag behaves like natural rock, representing an inert category of UVCB substances. Biokinetic investigations in rats suggest that the rat lung was able to rid itself of the inhaled solid aerosol via physiological clearance mechanisms.

The toxicology programme for ferrous slag, as documented in the Chemical Safety Report (CSR) as

part of the registration dossier of ferrous slag, can be considered to fulfil the information requirements for REACH (Registration, Evaluation, Authorisation and Restriction of Chemical substances) registration at the European Chemicals Agency (ECHA). There is sufficient, adequate and reliable information on hazardous properties for classification and risk assessment of ferrous slag.

The registrants make use of Annex XI criteria regarding the scientific necessity for information, the technical possibility for testing, and exposure-based waiving to adapt the standard information requirements under REACH. Data waiving is justified for repeated oral dose toxicity testing and studies for toxicity to reproduction or developmental toxicity / teratogenicity in order to avoid unnecessary testing in vertebrate animals. These non-clinical studies are waived based on physicochemical properties of ferrous slag that resemble natural rocks, mimicking the natural concentration of an element in the environment, and the low solubility in water, low extractability of components from ferrous slag, and lack of toxicological bioavailable fraction / systemic bioavailability of metals. Ferrous slag has been utilized in road construction for more than two centuries so that long-standing experience on the possible effects on human health is available. Furthermore, ferrous slag has no PBT (persistent, bioaccumulative and toxic) or vPvB (very persistent and very bioaccumulative) properties. It is also of note that no toxicity effects of particular concern were observed in animal inhalation studies, inhalation being the

likely route of human exposure, and results obtained from suitable in vitro studies demonstrate no certain dangerous property of ferrous slag. Finally, previous risk assessments of slag provide sufficient supporting evidence that toxicity can reliably be excluded.

There is no need to perform additional animal studies because from a toxicological point of view, ferrous slag behaves in a similar way to natural mineral samples; no further action is required.

In conclusion, the experimental data demonstrate that there is no likely hazard to humans from ferrous slag.

---

#### LITERATURE

- [1] Sokol, A.; Bialucha, R.: REACH-Registrierung von Eisenhüttenschlacken – aktueller Stand. Report des FEhS – Institut für Baustoff-Forschung e.V., 25 (2018) Nr. 2, S. 21–23
- [2] Testing Institutes: Charles River Laboratories Preclinical Services, Tranent (PCS-EDI) Edinburgh, EH33 2NE, UK  
IUF – Leibniz Research Institute for Environmental Medicine, Auf'm Hennekamp 50, D-40225, Düsseldorf, Germany
- [3] "executive summaries" on the ECHA website: <https://echa.europa.eu/de/information-on-chemicals/registered-substances>
- [4] Drissen, P.: Art und Kornform staubförmiger Partikel aus der Aufbereitung von Eisenhüttenschlacken. Report des FEhS – Institut für Baustoff-Forschung e.V., 16 (2009) Nr. 2, S. 5–8

# 10<sup>TH</sup> EUROSLAG CONFERENCE CALLS FOR FAIR TREATMENT OF FERROUS SLAG

## Secondary raw materials conserve natural resources

Th. Reiche (FEhS – Building Materials Institute)

The 10<sup>th</sup> conference of the European Slag Association EUROSLAG took place from 8<sup>th</sup> to 11<sup>th</sup> October in Thessaloniki, Greece. The conference was jointly organized by the Aristotle University, the Greece Slag Association AEI-FOROS and EUROSLAG. About 140 attendees from 29 countries, amongst them manufacturers and marketers of ferrous slag, representatives from politics, administrative bodies and associations, as well as scientists, demonstrated the global relevance of this event. The main message of the conference was already clear from the title “slag-based products – best practices for circular economy”: slag-based products have long been best practice examples of a circular economy and the preservation of natural resources – aims that both the UN and the EU are promoting. It also became clear during the conference that there is still room for improvement in this respect. To further increase their contribution to the circular economy, the framework conditions for secondary raw materials from the steel and slag value chain must be substantially improved both at European and at Member State level.

In order to be able to implement the findings from theory into practice as effectively as possible, EUROSLAG continued the format of the panel discussion with political decision-makers that had been introduced at the last conference in Metz in 2017. The key concerns of the organizers were the restoration of the balance between the justified needs for soil and water protection on the one hand and the promotion of the circular economy and resource conservation through the use of ferrous slag on the other. The preferential treatment of secondary raw materials in public construction measures was also a topic of discussion. A fundamental prerequisite for this would be an amendment to the European Waste Framework Directive. In Germany, the demands of the manufacturers of ferrous slag have already been included in the draft amendment to the Closed Substance Cycle Waste Management Act.

In the second session of the conference on “Utilization and best practices”, ten presentations and discussions focused on the processing and the specific properties of ferrous slag, as well as experience

with the use of building materials and fertilizers in practice. Finally, in the third session, ten experts presented current projects on the topic of “Research and innovation”, including the further optimization of slag-based products.

### The 11<sup>th</sup> EUROSLAG conference

will take place from  
5<sup>th</sup> – 8<sup>th</sup> October 2021 in  
Cologne, Germany.

The event will be jointly  
organized by the  
FEhS-Institute and  
EUROSLAG.

[www.euroslag.com](http://www.euroslag.com)  
[www.fehs.de](http://www.fehs.de)  
[www.rohstoff-schlacke.de](http://www.rohstoff-schlacke.de)



**Imprint // Editor:** FEHS – Building Materials Institute // **Responsible:** Thomas Reiche, Managing Director // **Layout:** del din design

FEHS – Building Materials Institute  
Bliersheimer Straße 62  
47229 Duisburg  
Germany

Telephone: +49 2065 9945-0  
Fax: +49 2065 9945-10  
E-Mail: [fehs@fehs.de](mailto:fehs@fehs.de)  
[www.fehs.de](http://www.fehs.de)



INSTITUT FÜR  
BAUSTOFF  
FORSCHUNG

FEHS