

Properties of iron and steel slags regarding their use

Jürgen Geiseler

Forschungsgemeinschaft Eisenhüttenschlacken e. V.
Bliersheimer Straße 62, 47229 Duisburg (Germany)

To use slags from iron and steelmaking it is essential to know the respective properties of these slags. Therefore a comprehensive characterisation of the slags is an important prerequisite to develop possibilities of their use.

During steel production there are generated different types of slags:

Using iron ore as the main iron bearing raw material in the Blast Furnace(BF)-Basic Oxygen Steelmaking (BOS)-route

Blast Furnace slag (BFs)

Basic Oxygen Steelmaking slag (BOSs)

Secondary Metallurgy slags (SMPs) are generated.

On the other hand Electric Arc Furnace (EAFs) and Secondary Metallurgy slags (SMPs) result from the scrap based steel production (**fig. 1**). **Figure 2** shows the usual chemical composition for slags from Blast Furnace (BFs), Basic Oxygen Steelmaking (BOSs), Electric Arc Furnace (EAFs) and Secondary Metallurgy Processes (SMPs).

These slags always result from lime silicatic melts. Blast Furnace slags additionally contain about 10 % MgO and Al₂O₃. The content of iron is usually lower than 0.5 wt.-% since they result from a reduction process. In contrary to Blast Furnace slags BOS- and EAF-slugs are generated in an oxidising process. Therefore their total iron contents are significantly higher. If dolomite is used as a flux the MgO-content of the respective BOS-slugs will be in the range of 5 to 10 %, while the CaO-content is about 45 % or even lower. The CaO/SiO₂ basicity of BOS slag is in the range of 3.5 and significantly higher than that of EAF slags with a basicity in the range of 2.0. Slugs from secondary steelmaking often have a CaO/SiO₂-basicity of about 4. But if Al₂O₃ is used for the formation of these slags the basicity will drop to about 2.

The mineral composition gives important informations with regard to the properties for the use. The vitreous solidification of Blast Furnace slags is the essential prerequisite for the latent hydraulic properties of granulated Blast Furnace slag. Though standards only require a glass content of more than 67 % usually 90 % and more are achieved operating the modern granulation systems. But also chemistry and other properties of the quenched Blast Furnace slag are important with regard to the hydraulicity of the vitrified Blast Furnace slag. There exist a lot of formulas which aim at in predicting the hydraulicity of a granulated Blast Furnace slag. It can be stated that all elements of the slag influence the hydraulicity. But as can be derived from results obtained by cooling melts with the same chemical composition there exist yet a lot of additional parameters like cooling rate, water/solid ratio etc. which influence the hydraulicity of Blast Furnace slags. Even investigations using Scanning Electron

Microscopy (SEM), Nuclear Magnetic Resonance Spectroscopy (NRM) and Atomic force Microscopy (AFM) until now do not allow to predict the hydraulicity of a slag. The most important reason is that hydraulicity is always the result of interactions of all components of a cement: clinker – granulated slag – sulphate and perhaps additions and admixtures. It is obvious that it is impossible to correlate the hydraulicity of a system of three or even five components with the chemical composition of only one component. This is the reason why it is necessary to consider always all components of this system and perform investigations regarding the hydraulicity which include all components forming this system.

By slow cooling Blast Furnace slags precipitate melilite and merwinite (**fig. 3**). Steelmaking slags mainly are formed by dicalciumsilicate (C_2S), dicalciumferrite and wustite. They usually contain free oxides, especially free lime. Steel slags with higher MgO-contents (≥ 3 wt-%) under special conditions may also contain free magnesia.

Both dicalciumsilicate and the free oxides may influence the volume stability of the respective slag.

C_2S during cooling undergoes several transformations (**fig. 4**). If coarse crystals of $\alpha\frac{1}{L}-C_2S$ are being generated the further cooling leads to $\gamma-C_2S$ at temperatures below 500 °C which is connected with an increase in volume of about 10 %. If it is possible to generate fine crystals of $\alpha\frac{1}{L}-C_2S$ further cooling leads to $\beta\frac{1}{L}-C_2S$ preventing the volume increase. From these fundamental investigations can be derived that the falling of C_2S can be prevented by the following measures:

- 1) Preventing C_2S -precipitation
 - by precipitation of other mineral phases or
 - by vitreous solidification
- 2) Fine grained precipitations of $\alpha\frac{1}{L}-C_2S$
- 3) Stabilisation of C_2S

This stabilisation can be achieved by special amounts of different elements listed in **figure 5**.

With regard to free oxides we have to consider free lime and free magnesia. Though both react with water doubling their volume the essential difference is that free lime reacts rather quickly while the time for reaction of free magnesia is many times over.

Regarding free lime one has to distinguish precipitated free lime and residual free lime which has not been solved during melting. Both types can be further subdivided according to **figure 6**. But it is essential that all types of free lime will react with water.

Though there exist different methods to determine free lime no chemical analysis exists according to which it is possible to differentiate between free lime and the hydrated free lime Ca(OH)_2 . But this is of great importance since it is of interest whether a slag may yet hydrate or is already hydrated.

For this reason other possibilities to determine the reactivity with water have to be developed. This method should be applicable to free magnesia, too. But the question arises, what is free magnesia since there exists a solid solution between MgO and FeO . From very detailed investigations it has been derived that the expression free MgO covers both periclase and magnesio-wustite which contains more than 70 % MgO .

Since the chemical analysis of free lime does not distinguish between CaO_{free} and Ca(OH)_2 and there does not exist any method to analyse free magnesia it is necessary to develop a method to measure the volume stability which is the property of greatest interest for the use of slags.

In the meantime there has been developed a great number of different methods to measure the volume stability. Aggregates for road construction are tested according to the steam test which is part of prEN 1242. Slag which is filled into a cylindrical vessel is being passed by steam during a period of 24 or 168 hours. The resulting volume increase must not exceed the limit values of **figure 7**. From this figure can be seen that the permissible values for the use in asphalt layers are lower or in any case equal to the values which are allowed for unbound layers. Since there exist different methods of road construction in different European countries the respective country has to choose its class of requirement according to the national experiences.

For testing steel slags which shall be used in hydraulic constructions, especially for the protection of river banks steel slags have to be stored in water of room temperature for 20 days or – according to a draft for a European standard – in boiling water for 8 hours. The percentage of spillings during this time is a measure for the volume stability of the respective slag.

Intensive investigations have been performed to guarantee the necessary volume stability at the end of blowing in the BOS-process. There exists a correlation between different parameters of slag composition and free lime content. Therefore it is possible to calculate the probable free lime content of the tapped slag and to separate slag according to a free lime

content which guarantees the intended volume stability. But the disadvantage of this method is that one needs to double the number of slag pits as before.

Many investigations have been performed to decrease the free lime content of the slag after tapping

- by extension of the time until pouring the slag into the pit
- by additions to the liquid slag
 - a) without any addition of external energy
 - b) with addition of external energy
- by mixing liquid steel slag with liquid Blast Furnace slag

While the extension of time leads to no significant decrease of the free lime content the amount of additions to liquid slag is limited due to the limited heat reserve of the slag. The mixing of two liquid slags resulted in an effective decrease of the free lime content but causes problems to combine these slags which are tapped at different times and different places. Therefore weathering for a long time has been the only method to lower the free lime content as the essential force for the volume increase of BOS slag. The main disadvantages of this method are: it needs a long time of treatment which may last until 6 months and more and as a consequence of this treatment one will get more or less fines since the reaction of CaO_{free} with water is being performed in the storage.

From all investigations the treatment of liquid slag by oxygen and sand or comparable additions has been developed and introduced into operational scale (**fig. 8**). Using this process one can increase the volume stability to those values which are a prerequisite for the respective field of application.

Furthermore the essential advantage of this treatment is that the amount of fines can be limited to those values which are desired for the production of fertiliser or dense layers.

While for steel slags the volume stability is the most important property regarding their use for air cooled Blast Furnace slag the porosity is of similar importance. The porosity influences the resistance to impact significantly. A dense slag has a high impact strength which is an important prerequisite for the use as aggregate in road construction. For the use as aggregate for concrete a porous slag has a high demand of binding agents. Therefore since long times it has been investigated how to guarantee a low porosity of slags.

The porosity is being caused by the release of gases from the liquid Blast Furnace slag during cooling. The solubility of nitrogen, hydrogen and oxygen is decreasing with lower

temperatures. Therefore they are released as gas. But since the viscosity of slag is increasing with lower temperatures more and more of the gas bubbles may not escape. During solidification of the slag these entrapped gas bubbles form pores which decrease the impact strength of the cooled slag. Sometimes oxidised sulphur may act in the same way.

It is well known that the release of gases may be suppressed or intensified by oxidising or reducing additions to the liquid slag. Consequently the impact strength will be influenced accordingly. But both the handling to introduce the additions into the liquid slag and the fact that the viscosity of the slag will be decreased by the additions sometimes led to unsatisfactory results. Therefore we have performed further tests regarding the correlation of impact strength and viscosity of the liquid slag. For this purpose it has been necessary to develop a method to calculate the viscosity of any Blast Furnace slag composition dependent on chemical composition and temperature. First results led to the conclusion that it will be possible to guarantee a low porosity sufficient for a slag with a good impact strength if the calculated viscosity of the slag fulfils a given value. Further investigations will be performed in order to state these results.

The environmental compatibility has been investigated since decades. From these investigations it is known that the environmental compatibility has to be judged by the contents which will be leached from the respective material but not by the total content of any element.

Since most of the mineral phases listed in figure 3 have no or only a very poor solubility in water and due to the low porosity the leached values of different kinds of slags using the German leaching method DIN 38 414 - S4 are low compared with the German drinking water regulation (**fig. 9**). The higher pH-values and the electrical conductivity result from leaching of free lime and/or calcium silicates. These results show that Blast Furnace and steel slags do not affect the environment if they are used in an appropriate way. From investigations under practical conditions it can be derived that Blast Furnace and steel slags can be used on a lot of fields of application. But in standing and not flowing water Blast Furnace slags should not be used.

Due to their chemical and mineral composition Blast Furnace and steel slags have a similarity to natural stones. Therefore most fields of application are the same as for natural stones. Blast Furnace slags in Germany can be divided by increasing porosity into the grades A, B and C. The main technical properties are listed in **figure 10**. Both Blast Furnace slags and steel slags show comparable properties like basalt and granite or other natural stones. A speciality of steel slags is their high density. This has to be considered for transportation but also for the necessary amount of bitumen when using these slags as an aggregate in bituminous bound layers.

In summary we can state that Blast Furnace and steel slags usually are being generated with a chemical composition which by applying a suitable heat treatment allows to produce a great variety of different products.

By quenching the Blast Furnace slag a vitreous solidification can be achieved. By slow cooling Blast Furnace and steel slags precipitate mineral phases which enable the production of aggregates for concrete and for the bituminous bound and unbound layers of the roads or for hydraulic structures with good impact strength, resistance against abrasion and low leachability. Furthermore air cooled and granulated Blast Furnace slag and BOS slag can be mixed to form various selfhardening slag bound mixtures. Last but not least both Blast Furnace and steel slags can be used to produce lime fertiliser which are being used since decades.

Using the results from the investigations reported above regarding volume stability and porosity it is possible

1. to decrease the porosity and increase the impact strength
or
to increase the porosity to produce foamed slags
2. to force the C_2S falling to produce slags suitable for fertiliser
or
to suppress the C_2S falling to produce strong aggregates
3. to use the hydration of free lime and free magnesia to produce fertiliser
or
to avoid free lime in order to produce dense aggregates suitable for road and waterway construction and concrete structures as well.

Thus these results offer instruments for the generation of slags suitable for many fields of application.

Similar to steel which according to variations of chemical composition and heat treatment can be produced to steel products with different properties also slags by variation of their chemical analysis and/or heat treatment can be processed to products with different properties.

But this goal cannot be reached if slags are discriminated as "wastes". Everybody who honestly will contribute to the protection of natural resources and the minimisation of energy consumption and CO_2 -emissions should use the approved slag products from iron and steel making. At any time steel industry has been a pioneer for the recycling. Recycling of scrap and the early use of slag products on a high level are two splendid examples. Recycling has to

be further extended but not impeded. To name slag products as "wastes" leads to disadvantages in competition with products from natural resources and therefore impedes or prevents the use of slag products and to intensify the recycling rate.

The discrimination of slag products as wastes causes great disadvantages for the ecology: quarrying of natural stone and increasing CO₂-emissions.

Therefore we should use the high potential which the slags offer to produce those products from slags which are most interesting and important for the market in the respective area.

Fig. 1 Steel routes

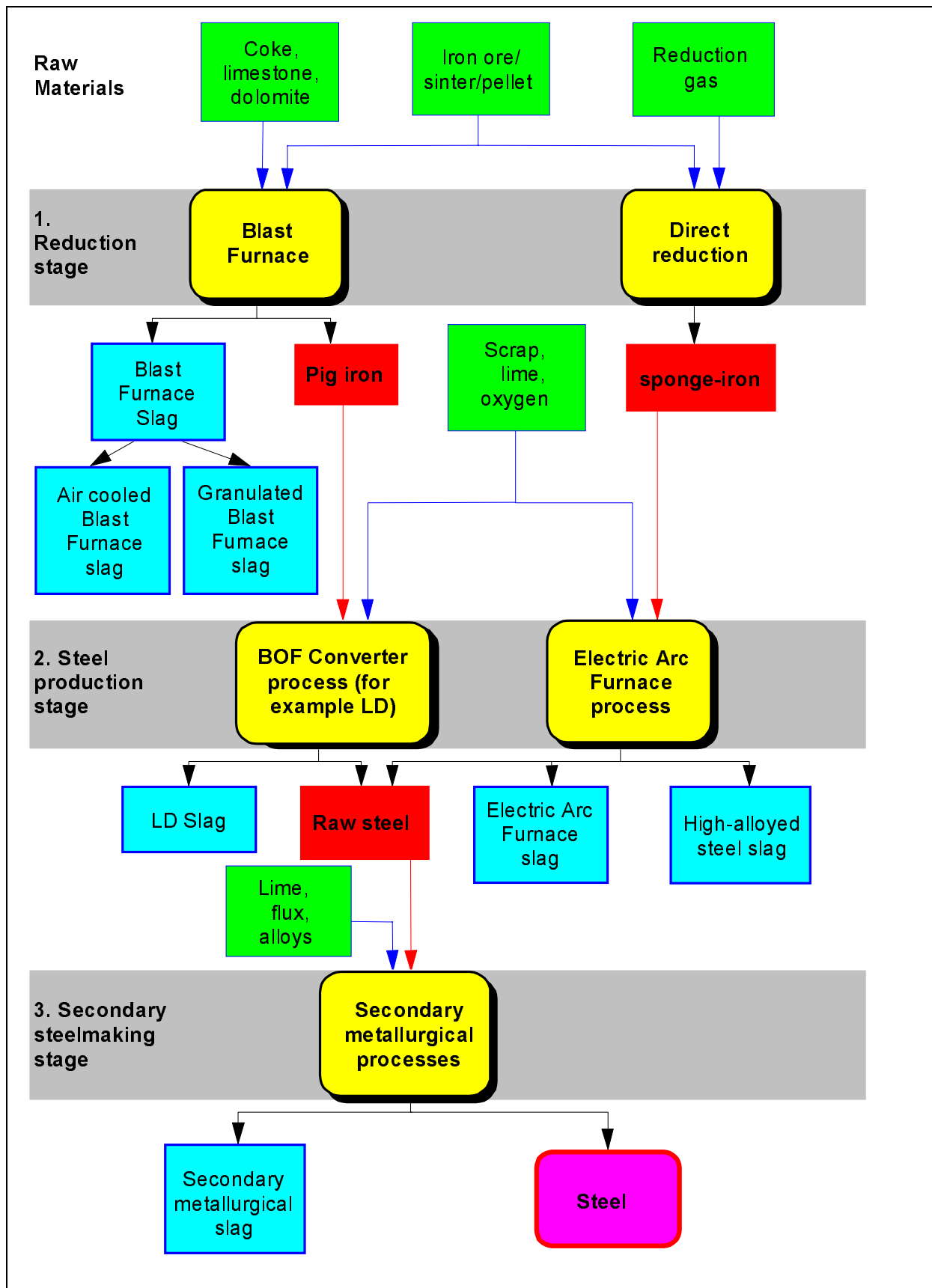


Fig. 2 Usual chemical composition of slags in wt.-%

| Constituent | Slag type | | | |
|--------------------------------|-----------|-----------|-----------|-----------|
| | BFs | BOSs | EAfs | SMPs |
| CaO | 36 - 42 | 48 - 54 | 25 - 35 | 30 - 52 |
| CaO _{free} | – | 1 - 10 | 0 - 4 | 1 - 10 |
| SiO ₂ | 35 - 39 | 11 - 18 | 8 - 18 | 8 - 23 |
| Al ₂ O ₃ | 8 - 12 | 1 - 4 | 3 - 10 | 3 - 20 |
| MgO | 4 - 12 | 1 - 4 | 3 - 9 | 6 - 12 |
| Fe _{tot} | < 0.5 | 14 - 19 | 20 - 30 | 0.5 - 12 |
| Mn _{tot} | < 0.5 | 1 - 4 | 2 - 5 | 0.5 - 3 |
| Na ₂ O | < 0.5 | - | - | - |
| K ₂ O | < 0.7 | - | - | - |
| S | 1.2 - 1.6 | - | - | - |
| CaO/SiO ₂ | 1.0 - 1.2 | 2.8 - 4.4 | 1.7 - 4.0 | 1.4 - 5.5 |

Fig. 3 Mineral composition of slags from iron- and steelmaking

| | | | | |
|--------------------|--------------------|---------|--|--------------|
| Blast Furnace Slag | | | | |
| | melilite | | | |
| | solid solution | between | 2CaO • Al ₂ O ₃ • SiO ₂ | (gehlenite) |
| | | and | 2CaO • MgO • 2SiO ₂ | (akermanite) |
| " | merwinite | | 3CaO • MgO • 2SiO ₂ | |
| NO FREE OXIDES | | | | |
| Steelmaking Slag: | | | | |
| " | dicalciumsilicate | | 2CaO • SiO ₂ | |
| " | tricalciumsilicate | | 3CaO • SiO ₂ | |
| " | dicalcium ferrite | | 2CaO • Fe ₂ O ₃ | |
| " | wustite | | Fe(Ca, Mn, Mg)O | |
| " | free lime | | CaO _{free} | |
| | | | MgO _{frei} | |

Fig. 4 Modifications of dicalciumsilicate (C_2S)

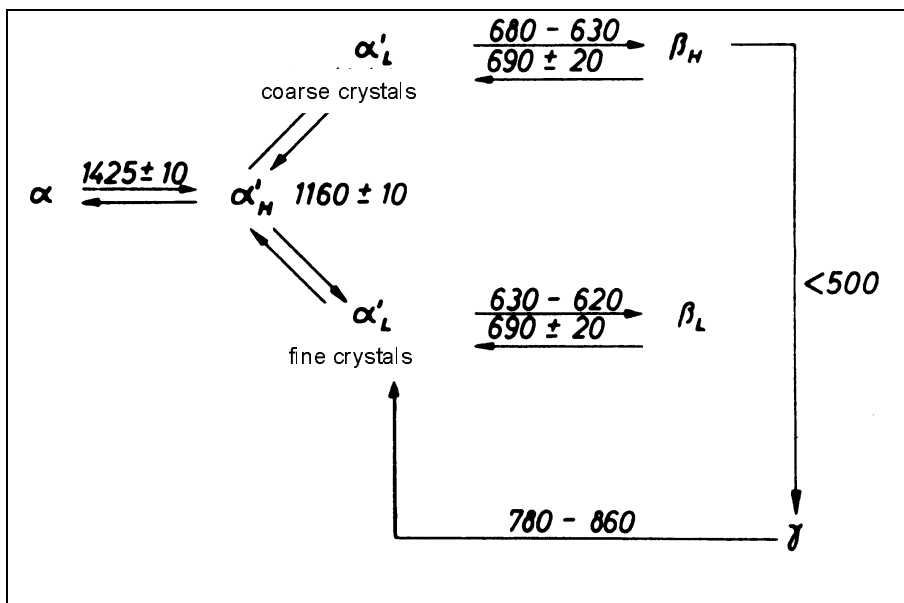


Fig. 5 C_2S -stabilisation by different ions

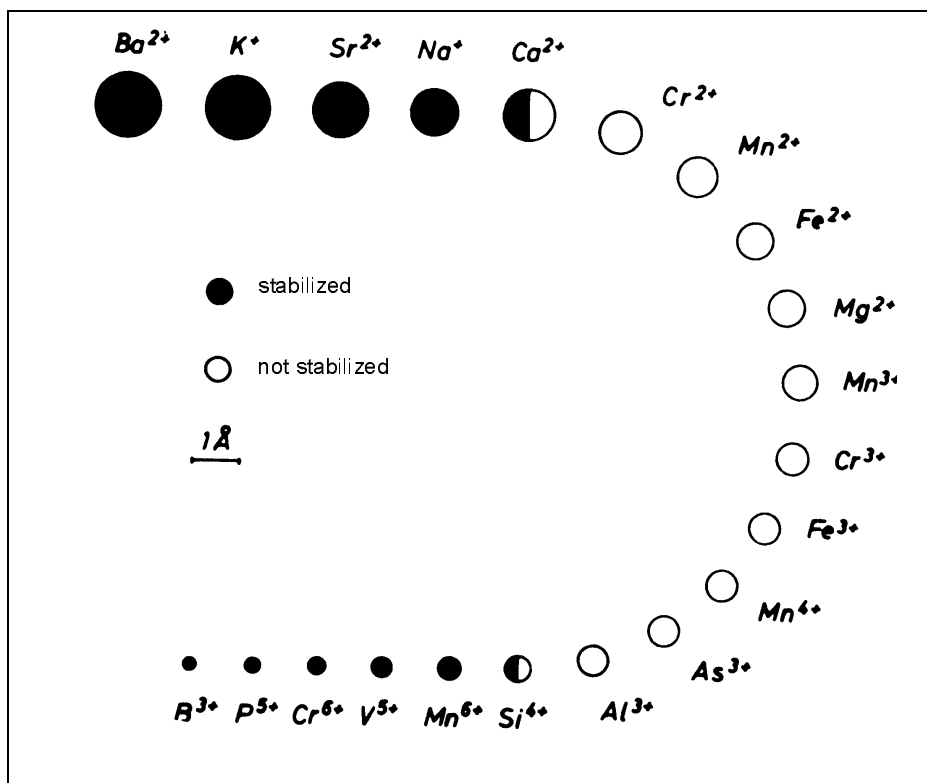


Fig. 6 Different kinds of free lime

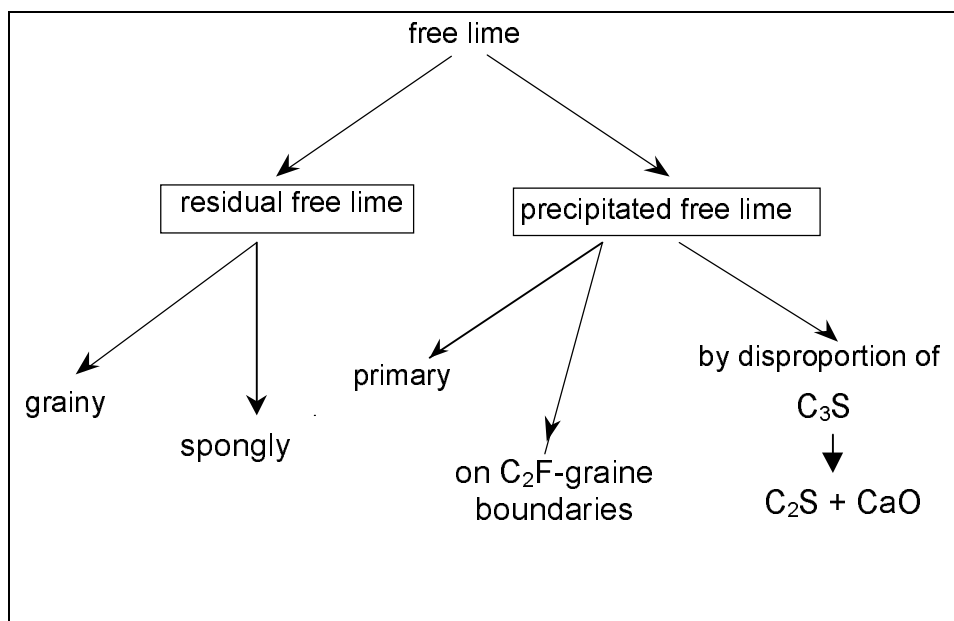


Fig. 7 Maximum expansion values for steel slag aggregates (prEN 1342, prEN 13043)

| Type of steel slag | Maximum expansion | | Testing time (hours) | Category |
|--|--|---------------------------------|----------------------|----------------|
| | aggregates for bituminous bound mixtures | aggregates for unbound mixtures | | |
| BOS slag/ EAF slag (MgO ≤ 5.0%) | 3.5 | 5 | 24 | V _A |
| BOS slag/ EAF slag (MgO > 5.0%) | 3.5 | 5 | 168 | |
| BOS slag/ EAF slag (MgO ≤ 5.0%) | 6.5 | 7.5 | 24 | V _B |
| BOS slag/ EAF slag (MgO > 5.0%) | 6.5 | 7.5 | 168 | |
| BOS slag/ EAF slag (MgO ≤ 5.0%) | 10 | 10 | 24 | V _C |
| BOS slag/ EAF slag (MgO > 5.0%) | 10 | 10 | 168 | |
| Note: tests for volume stability of steel slag aggregates with a satisfactory performance record are not necessary | | | | |
| | | | | |

Fig. 8 Liquid Slag Treatment Guarantees High Product Quality of Steel Slags

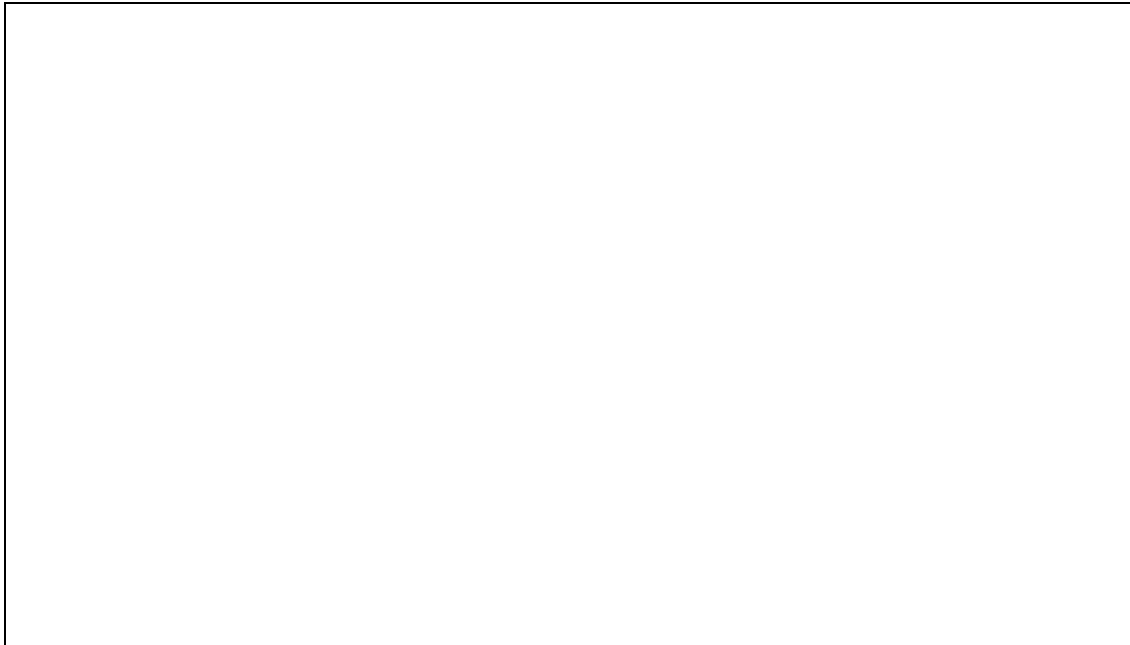


Fig. 9 Leached values of different kinds of slags in mg/l using the German leaching method DIN 38 414 - S4 in comparison with the German drinking water regulation

| Constituent | Slag type | | | | | German drinking water regulation |
|-----------------|-----------|----------|----------|----------|----------|----------------------------------|
| | BFs | GBs | BOSs | EAfs | SMPs | |
| AS | 0.002 | < 0.001 | < 0.001 | < 0.01 | 0.001 | 0.01 |
| Cd | < 0.0001 | < 0.0005 | < 0.0001 | < 0.0005 | 0.0002 | 0.005 |
| Cr | < 0.002 | 0.001 | 0.006 | < 0.01 | 0.002 | 0.05 |
| Cu | < 0.001 | 0.001 | 0.001 | < 0.002 | < 0.001 | 3* |
| F | 0.47 | 0.2 | 2.0 | < 0.5 | 2.0 | 1.5 |
| Hg | < 0.0005 | < 0.0005 | 0.0006 | < 0.0005 | < 0.0005 | 0.001 |
| Ni | < 0.002 | < 0.002 | < 0.002 | 0.005 | 0.003 | 0.05 |
| Pb | < 0.001 | < 0.001 | 0.001 | < 0.002 | 0.02 | 0.04 |
| SO ₄ | 168 | 30 | < 20 | < 15 | 70 | 240 |
| Zn | < 0.01 | < 0.002 | 0.01 | < 0.01 | 0.01 | 5* |
| pH | 11.0 | 10.0 | 12.1 | 11.5 | 12.0 | 6.5 – 9.5 |

Fig. 10 Main technical properties of iron and steel making slags

| Property | Aggregate type | | | | | | | German regulation for aggregates |
|---|----------------|-------|-------|---------|---------|---------|---------|--|
| | BFs-A | BFs-B | BFs-C | BOFs | EAfs | Basalt | Granite | |
| bulk density (g/cm ³) | > 2.4 | > 2.1 | > 2.1 | 3.0-3.7 | 3.2-3.8 | 2.8-3.1 | 2.6-2.8 | |
| resistance to impact SZ _{8/12} (wt.-%) | 48-25 | 55-34 | - | 10-26 | 10-26 | 9-20 | 12-27 | |
| strength (N/mm ²) | - | - | - | > 100 | > 100 | 250-400 | 160-240 | |
| resistance to weathering ↓ water absorption (wt.-%) ↓ resistance to freeze thaw change < 5mm (wt.-%) | < 4.0 | < 6.0 | < 8.0 | 0.3-1.0 | 0.3-1.0 | 0.3-1.0 | 0.3-1.1 | < 0.5 |
| | 0.5-2 | 1-3 | - | ≤ 1.0 | ≤ 1.0 | ≤ 1.0 | 0.8-2.0 | < 3.0 |
| resistance to polishing (PSV) | 50-60 | 45-56 | - | 48-60 | 50-62 | 45-56 | 45-58 | - |