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# Influence of slag composition on the hydration of alkali-activated slags

Frank Winnefeld<sup>a\*</sup>, Mohsen Ben Haha<sup>a,1</sup>, Gwenn Le Saout<sup>a,2</sup>, Mercedes Costoya<sup>b</sup>, Suz-Chung Ko<sup>b</sup> and Barbara Lothenbach<sup>a</sup>

<sup>a</sup>*Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Concrete and Construction Chemistry, Überlandstrasse 129, 8600 Dübendorf, Switzerland;*

<sup>b</sup>*Holcim Technology Ltd, Innovation R&D, Im Schachen, 5113 Holderbank, Switzerland*

The hydration of different blast-furnace slags with sodium metasilicate or NaOH as activator was investigated. Sodium metasilicate shows poor strength after 1 day, but high strength after 7 days and beyond, whereas NaOH activation leads to high strength after 1 day, but only moderate strength development at later ages. At the same hydration degree, sodium metasilicate activation gives a much higher compressive strength than NaOH activation. This is due to the formation of a dense hydration product in the NaOH-activated system at the early age, which leads to a more porous microstructure than in the case of sodium metasilicate. A higher MgO content in the slags is beneficial with respect to faster hydration kinetics and a more rapid strength development. Increasing Al<sub>2</sub>O<sub>3</sub> contents lead to slightly slower hydration kinetics and slightly lower compressive strengths. The best correlation between compressive strength and slag composition was found using the extended basicity (CaO + MgO)/SiO<sub>2</sub> index.

**Keywords:** alkali-activated slag; activator; slag chemistry; hydration degree; compressive strength; porosity

## 1. Introduction

Due to the climate debate there is a need for using different types of cement, which produce less greenhouse gases during their manufacturing than ordinary Portland cement.[1–5] In Portland cement technology a wide variety of industrial by-products are used as supplementary cementitious materials, including fly ash from coal combustion, ground-granulated blast furnace slag from iron production, and silica fumes from ferrosilicon production.[6] However, these generally replace only a portion of the Portland cement in concrete, typically in the order

of 10–50% (and sometimes more like in the case of ground granulated blast-furnace slag), as higher replacements are often linked to a reduced performance and are usually not allowed in the cement and concrete standardization documents.

Thus, there is an increasing interest in the development, manufacturing, and applications of binders free of Portland cement and, when possible, made entirely or almost entirely from local secondary materials, with low-energy and low CO<sub>2</sub> emissions. Alkali-activated binders are, besides other cementitious materials like supersulfated slag cements or calcium

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\*Corresponding author. Email: [frank.winnefeld@empa.ch](mailto:frank.winnefeld@empa.ch)

<sup>1</sup>Now at Heidelberg Technology Center GmbH, Rohrbacher Str. 95, 69181 Leimen, Germany.

<sup>2</sup>Now at Ecole des Mines d'Alès, 6 avenue de Clavières, 30319 Alès cedex, France.

sulfoaluminate cements, one of such potential alternatives to Portland cement.[4,5,7–18] They combine high CO<sub>2</sub> savings and use of industrial by-products with good performance in engineering properties like high compressive strength and high durability e.g. with respect to acid attack or fire exposure.[5,14,15,18]

A possible Portland cement free binder can be obtained by the activation of ground-granulated blast-furnace slag by alkaline solutions, e.g. alkali silicates, hydroxides, or carbonates. Such alkali activated slags can have high-strength development and using the adequate activators can lead to rapid setting and hardening, good durability and high resistance to chemical attack.[5,14,15,18–21] The main hydration products are calcium silicate hydrates containing aluminum (C–A–S–H) with a low Ca/Si ratio ( $\approx 1$ ), a hydrotalcite-like phase, and in some

cases also an AFm phase, most likely strätlingite.[18,19,22–30] Many variables influence the reaction of alkali-activated slags such as slag fineness and chemical composition, type, and concentration of the alkaline activator, water/binder (w/b) ratio, temperature, or pH.[18–38]

The present paper is focused on one of these parameters, namely the chemical composition of the slag and its impact on hydration and strength development. The influence of the chemical composition of the blast-furnace slag on the properties of slag-blended Portland cements has been widely studied since decades, see [17,37–55] and references cited therein, and several characteristic values or moduli for suitable slags have been proposed (Table 1). Most of these values are focused on the basicity (ratio CaO/SiO<sub>2</sub> = ratio of network modifier to network former). In some of the characteristic values, this “simple basicity” is

Table 1. Moduli describing the reactivity of blast-furnace slags.

Formula	Comment
$K_1 = \frac{\text{CaO}}{\text{SiO}_2}$	Simple basicity, >1 for good (basic) slags, between 0.50 and 2.0 suitable for alkali activation [16]
$K_2 = \frac{\text{Al}_2\text{O}_3}{\text{SiO}_2}$	Modulus of activity, between 0.1 and 0.6 suitable for alkali activation [16]
$K_3 = \frac{\text{CaO} + \text{MgO}}{\text{SiO}_2}$	Extended basicity, European Standard EN 197-1 [56] requires a value of >1
$K_4 = \frac{\text{CaO} + \text{MgO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3}$	Extended basicity,[47] $\geq 1$ for good quality
$K_5 = \frac{\text{CaO} + \text{MgO} + 1/3\text{Al}_2\text{O}_3}{\text{SiO}_2 + 2/3\text{Al}_2\text{O}_3}$	Extended basicity,[45] $\geq 1$ for good quality
$K_6 = \frac{\text{CaO} + \text{Al}_2\text{O}_3 - 10}{\text{SiO}_2 + 10}$	Extended basicity according to [46]
$K_7 = \frac{\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3}{\text{SiO}_2}$	Extended basicity,[45] below 1.5 poor, between 1.5 and 1.9 good, above 1.9 very good quality
$K_8 = \frac{\text{CaO} \cdot \text{Al}_2\text{O}_3}{(\text{SiO}_2 + \text{Al}_2\text{O}_3)^2}$	Index of reactivity,[38] should be $\geq 0.18$ for good quality
$K_9 = \frac{\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3}{\text{SiO}_2 + \text{TiO}_2(+\text{P}_2\text{O}_5 + \text{F} + \text{MnO})}$	quality coefficient [17,36]
$K_{10} = \frac{\text{CaO} + \text{CaS} + 0.5 \cdot \text{MgO} + \text{Al}_2\text{O}_3}{\text{SiO}_2 + \text{MnO}}$	<i>F</i> -value according to [44], should be $\geq 1.5$ for good quality

Source: Adapted from [39,40,43,53].

modified by the introduction of other oxides, like MgO, a network modifier (e.g. in the extended basicity according to EN 197-1 [56]). The role of  $\text{Al}_2\text{O}_3$  can be both network former and network modifier. This is considered in a different way by the various moduli, as  $\text{Al}_2\text{O}_3$  is sometimes added to CaO, sometimes added to  $\text{SiO}_2$  or distributed between both oxides. The last option is indirectly done by the simple basicity, as besides CaO and  $\text{SiO}_2$  generally mainly  $\text{Al}_2\text{O}_3$  is present in the slags. Also the ratio  $\text{Al}_2\text{O}_3/\text{SiO}_2$  is used as parameter to assess the reactivity of slag. Some other characteristic values also include minor oxides, like MnO or  $\text{P}_2\text{O}_5$ . In [40,41], the impact of the most important oxides on slag reactivity in blends with Portland cement is summarized: higher CaO and lower  $\text{SiO}_2$  contents improve reactivity of the slag, which refers to the simple basicity. Higher  $\text{Al}_2\text{O}_3$  contents have a positive impact on early strength (2 days), a moderate impact on 28 and 91 days strength, and in cases of high contents (>13 mass-%) a negative influence on long-term strength (>91 days). MgO does not seem to have the same positive impact as CaO, as some authors report a positive influence on strength, others observe a decrease in strength at high (>13 mass-%) concentrations.  $\text{TiO}_2$  amounts above a level of about 1 mass-% lead to strength decrease.

The above-mentioned moduli are based on the application of blast-furnace slags in blends with Portland cement. However, there is much less information in literature on the impact of slag composition on binder properties under conditions of alkaline activation. Probably most studies on alkali-activated slags are focusing on the activator and not on slag chemistry. Only few attempts have been made to correlate reactivity or (strength) performance with slag moduli, which is probably related to the wide range of possible activation conditions. Knowing that slags, which can easily activated in a cementitious environment,

are already largely used, a better understanding of the effects of the chemical composition of the slag could indicate ways to use less reactive slags efficiently. Slags with a CaO/ $\text{SiO}_2$  ratio between 0.50 and 2.0 and an  $\text{Al}_2\text{O}_3/\text{SiO}_2$  ratio between 0.1 and 0.6 are thought to be suitable for alkali activation.[16] These wide ranges are related probably as well to the different possibilities for alkaline activation, but may also be an indication of a certain insensitivity of slag chemistry towards alkaline activation conditions.

This paper assembles results from our previous studies, which have been focused on the influence of MgO and  $\text{Al}_2\text{O}_3$  contents in alkali activated blast-furnace slags on hydration kinetics, hydrate assemblage, microstructure, and compressive strength.[25–27,29] When replacing CaO by MgO and simultaneously increasing  $\text{Al}_2\text{O}_3$  content, the activity of the slag increases.[17] It has been shown that a small amount of crystalline phases in slags and/or the presence of minor elements such as MgO increase slag reactivity,[34,35,52,56] as observed by isothermal calorimetry and strength measurements on pastes. In a recent study [30], it is reported that with increasing MgO content the early hydration of a slag is decelerated, but the hydration degree at longer hydration times is increased. In addition, the authors found a decrease of carbonation depth with increasing slag MgO content.

In the case of  $\text{Al}_2\text{O}_3$ , a delay of the hydration reaction of alkali activated slags, which were mixed with externally added  $\text{Al}_2\text{O}_3$ , is reported.[57] The authors observed that the addition of a low amount of  $\text{Al}_2\text{O}_3$  (2 wt%) increased the 7 and 28 days compressive strength, while the addition of 15 wt% or more did not further improve the mechanical properties. An increase of early compressive strength with increasing  $\text{Al}_2\text{O}_3$  content in the slag is reported by [37]. The authors of [58] observed an increase in compressive

strength especially at early ages with higher  $\text{Al}_2\text{O}_3$  content in the case of NaOH activation, whereas with potassium silicate a decrease of compressive strength at all testing times was found.

## 2. Materials and methods

Eight different ground-granulated blast-furnace slags with different chemical compositions and ground to a comparable particle size using a laboratory ball mill were used in this study. The chemical composition of the slags was determined by X-ray fluorescence and X-ray diffraction (XRD) analyses (Rietveld method using  $\text{CaF}_2$  as internal standard). Particle size distribution and specific surface area were measured by laser diffraction and Blaine method, respectively.

The slags were activated either by NaOH or by sodium metasilicate (sodium silicate  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ ) using the same added  $\text{Na}_2\text{O}$ -equivalent of 2.9% referred to the slag in both cases and including the presence of additional 2.8 g  $\text{SiO}_2$  per 100 g slag in the sodium metasilicate system. All pastes were hydrated at a w/b ratio of 0.42 (slags HA, LA) or 0.40 (slags M8, M11, M13, A7, A14, A17) including the chemically combined water of the activators at 20 °C in sealed conditions. After different hydration times, compressive

strength measurements were performed as well as thermogravimetric analysis (TGA), XRD, and scanning electron microscopy (SEM) on crushed samples after stopping the hydration with isopropanol. Chemically bound water was determined from the TGA data as weight loss between 30 and 600 °C. For SEM analyses, the samples were impregnated in an epoxy resin, polished, and carbon-coated. Per sample and hydration time several hundred back-scattered electron images (BSE) were gathered and used for the quantitative determination of coarse capillary porosity and hydration degree by image analysis (IA).[59,60] The volume of coarser pores as determined by SEM-IA includes, depending on the magnification (2500×) used, pore sizes in the range of 0.05–5  $\mu\text{m}$ . The hydration degree determined by this method agrees very well with data obtained by  $^{29}\text{Si}$  nuclear magnetic resonance.[29] For more details of the experimental procedures, see [25–27,29]. Thermodynamic modeling was carried out using the geochemical software GEMS [61,62] in combination with the cemdata2007 database.[63,64]

## 3. Results and discussion

### 3.1. Characterization of the slags

The composition of the slags has been reported previously [25–27] and is here

Table 2. Chemical composition in mass-% of the investigated slags.

	HA	LA	M8	M11	M13	A7	A14	A17
CaO	36.5	39.4	35.8	34.6	33.4	39.1	36.0	35.0
$\text{SiO}_2$	37.4	41.2	38.2	37.1	36.4	41.6	38.2	37.2
$\text{Al}_2\text{O}_3$	12.0	7.1	12.0	11.5	11.3	7.0	14.1	16.7
$\text{Fe}_2\text{O}_3$	0.58	1.0	1.6	1.8	1.4	1.3	1.4	1.4
MgO	8.0	7.4	7.7	10.5	13.2	7.2	6.6	6.4
$\text{Na}_2\text{O}$	0.40	0.57	0.41	0.40	0.52	0.49	0.49	0.48
$\text{K}_2\text{O}$	1.2	0.70	1.2	1.1	1.0	0.63	0.58	0.54
$\text{TiO}_2$	0.50	0.26	0.50	0.48	0.47	0.28	0.25	0.24
$\text{Mn}_2\text{O}_3$	1.6	1.1	1.5	1.5	1.4	1.1	1.0	1.0
$\text{P}_2\text{O}_5$	0.03	<0.01	0.03	0.03	0.02	0.01	0.01	0.01
$\text{SO}_3^{\text{a}}$	2.4	1.6	1.4	1.2	0.36	1.3	1.2	1.0
L.O.I. <sup>a</sup>	-0.41	-0.98	-0.80	-0.86	-0.40	-0.91	-0.50	-0.49

<sup>a</sup>Usually approximately 90% of the sulfur present in the slags occurs as sulfide.[65] Thus also a negative loss on ignition is measured due to oxidation of the sulfide.

repeated for the convenience of the reader. The chemical composition of the slags (Table 2) varies between a CaO content of 33.4 and 39.4 mass-%, a SiO<sub>2</sub> content of 36.4 and 41.6 mass-%, an Al<sub>2</sub>O<sub>3</sub> content of 7.0 and 16.7 mass-%, and an MgO content of 6.4 and 13.2 mass-%. Glass content is high, between 94.2 and 99.0 mass-% (Table 3). Among the various minor crystalline phases are merwinite and melilite. Simple basicity (Table 1) is between 0.91 and 0.96, when calculated using the average glass composition, which can be derived from the bulk oxide composition and the contents of the crystalline phases. All slags can be considered as slightly acidic ( $K_1 < 1$ ); however when taking into account also the MgO content (extended basicity according to EN 197-1 [56]) the slags are slightly basic with  $K_3$  between 1.10 and 1.27 and fulfill the requirements according to the aforementioned standard ( $K_3 > 1$ ). The ratio of Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> ( $K_2$ ) varies between 0.17 and 0.45. Both  $K_1$  and  $K_2$  are within the limits defined by [16] for slags suitable for alkali activation.

When taking into account the Al<sub>2</sub>O<sub>3</sub> in the basicity according to the different formulas  $K_4$ – $K_7$ , the quality assessment changes, e.g. all slags were classified as poor when using  $K_4$ , but mainly as good when using criteria  $K_5$  and  $K_7$ . Except for two samples (LA and A7 with the lowest Al<sub>2</sub>O<sub>3</sub> contents) the slags fulfill the requirement according to [39], but do not fulfill the  $F$ -value according to [45]. Thus, in agreement with [53], it can be stated that there is probably no simple formula to assess the reactivity of blast furnace slags.

The particle size distribution and the specific surface of the eight investigated slags (Table 4) are very similar, which makes the slags very suitable to study the effect of their chemical composition on hydration kinetics and strength development.

### 3.2. Influence of the activator

Figure 1 gives the compressive strength development of the slag pastes activated with sodium metasilicate and NaOH.

Table 3. Phase composition in mass-% of the investigated slags.

	HA	LA	M8	M11	M13	A7	A14	A17
Akermanite	0.9	5.0				3.1		
Anhydrite						0.3	0.4	0.3
Calcite	1.3							
Larnite	3.7							
Melilite			0.2	0.7	0.2			
Merwinite				0.5	1.3			
Iron						0.6	0.6	0.6
Amorphous	94.2	95.0	99.8	98.9	98.5	96.0	99.0	99.0

Table 4. Granular properties of the investigated slags.

	HA	LA	M8	M11	M13	A7	A14	A17
Density (g/cm <sup>3</sup> )	2.88	2.92	2.92	2.93	2.94	2.90	2.88	2.87
Blaine value (cm <sup>2</sup> /g)	5020	5030	4990	5070	5010	5020	4960	4990
R <sub>63</sub> μm (Vol.-%) <sup>a</sup>	0.0	0.0	0.0	0.0	0.0	0.2	0.4	0.1
R <sub>45</sub> μm (Vol.-%) <sup>a</sup>	0.8	0.9	0.5	0.0	0.0	1.0	1.3	1.1
R <sub>18</sub> μm (Vol.-%) <sup>a</sup>	21.3	24.9	23.0	18.7	21.8	21.6	22.4	22.4
R <sub>3</sub> μm (Vol.-%) <sup>a</sup>	71.7	78.4	76.9	74.7	76.9	74.9	76.5	75.6
D <sub>50</sub> (μm) <sup>b</sup>	7.4	9.0	8.3	7.3	8.1	7.9	8.3	8.2

<sup>a</sup>Laser diffraction, fractions above 63, 45, 18, and 3 μm, respectively.

<sup>b</sup>Laser diffraction, mean particle diameter.

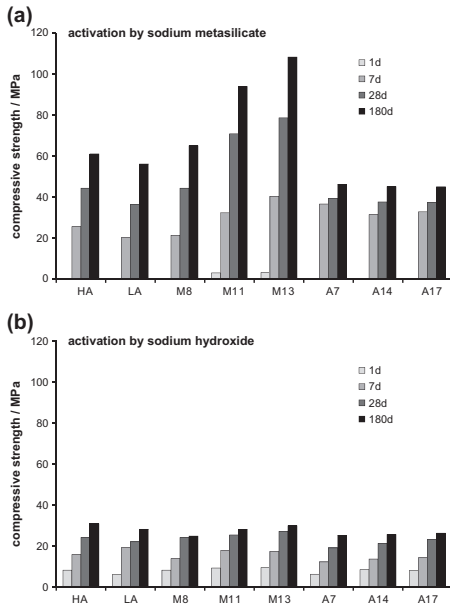


Figure 1. Compressive strength of the slag pastes activated with (a) sodium metasilicate and (b) sodium hydroxide. Data taken from [25–27]. Values after 90 and 360 days were omitted.

With sodium metasilicate activation, compressive strength after 1 day could not be measured with the exception of slags M11 and M13 with the highest MgO content. Between 1 and 7 days a rapid strength development occurs, reaching values between 20 and close to 40 MPa. After 180 days, compressive strength is between 45 and 110 MPa. Strength development is strongly depending on the slag composition (see below).

Pastes activated with NaOH show a compressive strength of maximum 10 MPa after 1 day. Beyond 1 day, strength development is moderate; reaching about 30 MPa after 180 days. Strength development is almost independent from slag composition.

The relation between compressive strength and hydration degree is given in Figure 2. The samples with NaOH reach after 1 day (17–31%) and 7 days (23–37%) higher hydration degrees than

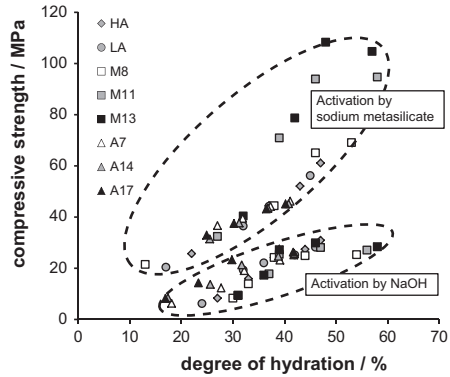


Figure 2. Compressive strength of the slag pastes vs. degree of hydration. Data taken from [25–27].

the pastes with sodium metasilicate (not measurable by SEM/BSE after 1 day, 13–32% after 7 days). The faster hydration kinetics with NaOH compared to sodium metasilicate can also be seen by conduction calorimetry.[26,27] Similar hydration degrees result for both activators after 180 days (sodium metasilicate 40–48%, NaOH 42–47%). From Figure 2, it can be derived that at the same hydration degree a higher compressive strength is reached with sodium metasilicate than with NaOH. Within one activation system approximately, a linear relation between hydration degree and compressive strength is observed.

The amount of bound water is a parameter which can be potentially used monitoring the progress of hydration for a given activator. Its correlation with compressive strength is shown in Figure 3. The NaOH activated pastes show lower compressive strengths than those activated with sodium metasilicate at the same content of bound water, while within an activation system roughly a linear correlation between both parameters can be observed.

In all systems, C–A–S–H incorporating aluminium and a hydrotalcite-like phase are the main hydration products.[25–27] The initial rate of reaction is

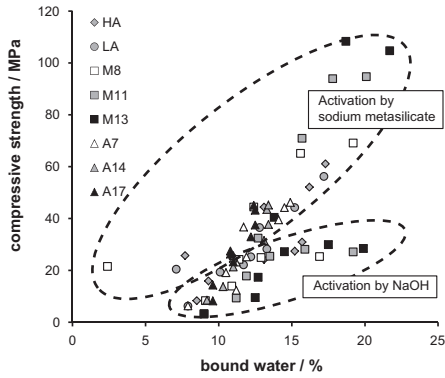


Figure 3. Compressive strength of the slag pastes vs. bound water. Data taken from [25–27].

higher using NaOH. During the fast initial hydration in the case of NaOH activation reaction a dense C–A–S–H with, compared to the sodium metasilicate activated system, less chemically bound water is formed, the microstructure is coarser with a higher porosity, and the hydration products appear not well distributed throughout the matrix. This is evident from Figure 4 showing the microstructure of slag M13 with sodium metasilicate and NaOH activation, respectively, after 7 days of hydration.

Figure 5 shows the compressive strength vs. coarse capillary porosity. Both correlate very well, independently of the activator system used. From this, it can be

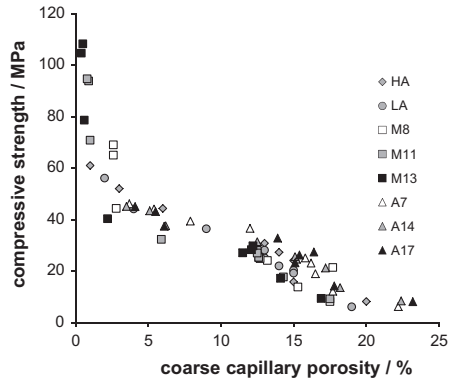


Figure 5. Compressive strength of the slag pastes vs. coarse capillary porosity. Data taken from [25–27].

concluded that the porosity of the system governs compressive strength. In the system activated with sodium metasilicate, the slag hydrates slowly and there is enough time for the hydration products to precipitate relatively uniformly throughout the interstitial space between the slag grains. This results in a lower porosity and much higher compressive strength at the same degree of slag reaction compared to the NaOH activated system. In the case of NaOH, despite the continuous reaction, the increase in compressive strength and the decrease of coarse porosity is limited due to the formation of a very dense hydration product.

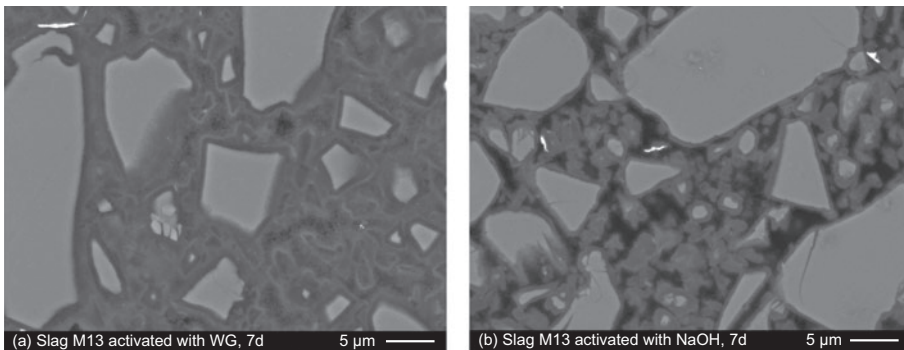


Figure 4. SEM images of slag M13 activated by (a) sodium metasilicate (WG) and (b) NaOH, hydration time 7 days.

### 3.3. Influence of MgO content

The slags M8, M11, and M13 show an increasing MgO content, while the contents of the other oxides differ only slightly.

In the case of sodium metasilicate activation, an increase of both early (1 and 7 days) and late strength (28 and 180 days) can be observed with increasing MgO content (Figure 1(a)). M11 and M13, show the by far highest compressive strengths among all slags. The increase of early hydration kinetics could also be observed by conduction calorimetry.[26] An increase of MgO content of the slag increases the hydration degrees determined by SEM (Figure 2) and decreases the coarse porosity (Figure 5). For M11 and M13 a very low coarse capillary porosity of <1 Vol.-% already at a sample age of 28 days was determined. It has to be kept in mind that pores with smaller diameter than 0.05  $\mu\text{m}$  cannot be detected by SEM-IA using the chosen experimental setup. Nevertheless, those two slags develop a very dense microstructure with low capillary porosity and a high compressive strength when activated with sodium metasilicate.

Experimental observations by XRD and energy disperse X-ray spectroscopy (EDX) analyses [26] show the same phase assemblage for slags M8, M11, M13 with the main hydration products C–A–S–H and hydrotalcite-like phase, and in the case of the low MgO slag M8 also possibly traces of strätlingite.

Thermodynamic calculations indicate that the amount of hydrotalcite-like phase increases with increasing MgO content as shown on the example of NaOH-activated slag (Figure 6(a)).

With sodium metasilicate the formation of a C–A–S–H with a lower Ca/Si ratio and 5% more C–A–S–H is calculated when compared to NaOH-activated systems.[26] The calculated Ca/Si ratio in the C–A–S–H is 1.05 for the NaOH-

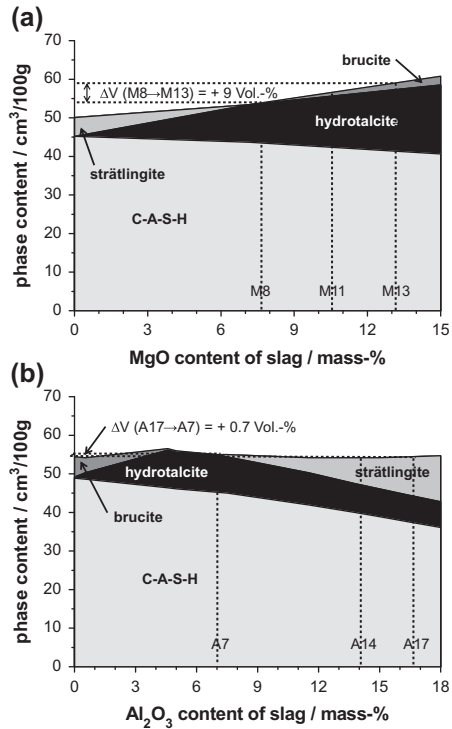


Figure 6. Thermodynamic modeling – influence of (a) MgO and (b) Al<sub>2</sub>O<sub>3</sub> content on the calculated volume of the hydrates present in NaOH activated slag. Adapted from [26,27].

activated slags and 0.94 for the system activated with sodium metasilicate (due to the introduction of SiO<sub>2</sub> with the activator) independent of the MgO content.[26] At high MgO content, a higher fraction of the available aluminum is bound by the hydrotalcite-like phase (Mg<sub>4</sub>Al<sub>2</sub>O<sub>7</sub>·10H<sub>2</sub>O). The remaining aluminum is incorporated in C–A–S–H. EDX analyses show that the Al uptake by C–A–S–H decreases with increasing MgO content, which was taken into account by the GEMS model.[26] A higher hydrate volume is predicted with increasing MgO content due to the formation of more hydrotalcite and thus a lower porosity. Calculations indicate a 9% higher volume of the hydrates for M13 compared to M8, which could explain the higher strength with increasing MgO content in the slag.

In the NaOH-activated system, the higher MgO content leads to a slightly higher degree of reaction and thus to a slightly increased compressive strength at all ages (Figure 1(b)). The increase of the amount of hydrotalcite-like phase and thus the higher calculated volume at higher MgO contents has no significant effect on the compressive strength of the NaOH activated slags. Also the measured coarse porosity is not decreased in the presence of more hydrotalcite-like phase (Figure 5). Obviously in the case of NaOH, the high content of coarse capillary porosity is the determining parameter regarding compressive strength, and the chemistry plays only a minor role.

### 3.4. Influence of $Al_2O_3$ content

The slags A7, A14, and A17 represent a series of slags with increasing  $Al_2O_3$  contents, while the contents of the other oxides are comparable among the slags.

In the case of sodium metasilicate activation, a slightly decreasing strength after 7 and 28 days can be observed with increasing  $Al_2O_3$  content, whereas all three slags reach a similar compressive strength after 180 days (Figure 1(a)). The faster early kinetics with lower  $Al_2O_3$  content could also be confirmed by conduction calorimetry [27] and SEM (Figure 2). After 28 and 180 days similar hydration degrees are reached for all three slags. At these ages, the coarse porosities are very small and independent of the amount of  $Al_2O_3$  present in the slag (Figure 5).

C–A–S–H, hydrotalcite-like phases as well as strätlingite for the slags with high  $Al_2O_3$  content are observed by XRD and EDX analyses.[27] The Al uptake by C–A–S–H increases and the Mg/Al ratio of the hydrotalcite decrease with increasing  $Al_2O_3$  content in the slag based on EDX analyses.[27] Thermodynamic calculations as shown in Figure 6(b) on the system with NaOH activation agree well

with the experiments and predict the presence of C–A–S–H and hydrotalcite, and at higher  $Al_2O_3$  contents also the formation of strätlingite. Al intake into C–A–S–H was modeled by GEMS based on EDX data. For both activators, the same hydrate assemblage is calculated, with the only difference that a slightly lower Ca/Si ratio (Ca/Si = 0.9) in the C–S–H and 5% more C–A–S–H is calculated in the presence of sodium metasilicate compared to NaOH activated systems (Ca/Si = 1.0).[27] With increasing  $Al_2O_3$  content in the slag, the total amount of C–A–S–H and hydrotalcite decreases, as the presence of more  $Al_2O_3$  lowers the concentrations of the other oxides present in the slag. No relevant effect of  $Al_2O_3$  content on the volume of the hydrates is predicted in case of both activators, and thus no significant changes in the coarse porosity at the same degree of hydration are expected and observed also experimentally.

The activation with NaOH leads as in the case of varying MgO contents to only minor changes in strength development with varying  $Al_2O_3$  contents. Slightly faster early hydration kinetics up to sample age of 7 days with decreasing  $Al_2O_3$  content could be observed by conduction calorimetry and SEM,[27] whereas after 180 days the same reaction degrees and coarse capillary porosities are reached for all three slags.

### 3.5. Correlation between slag composition and compressive strength

The various moduli describing the reactivity of blast-furnace slags were tested upon correlation with compressive strength, degree of hydration, bound water, and capillary porosity. It was found, as also stated already by [53] that most of the moduli do not show a good correlation with the properties mentioned above. The best correlation for the investigated samples is found for the extended

basicity  $K_3 = (\text{CaO} + \text{MgO})/\text{SiO}_2$ , which is used in European Standard EN 197-1 [56] to assess slag reactivity. This parameter takes into account MgO as strength contributing component. In the formula,  $\text{Al}_2\text{O}_3$  is not present and thus it seems not to be considered at all. However, besides CaO,  $\text{SiO}_2$ , and MgO, it is the main component of the slag, and one can argue that the equation for  $K_3$  distributes  $\text{Al}_2\text{O}_3$  between numerator and denominator and thus takes the amphoteric nature of  $\text{Al}_2\text{O}_3$  into account.

Figure 7(a) shows that an increase of compressive strength with increasing  $K_3$  can be observed in case of activation with sodium metasilicate, especially regarding the longer hydration times. After 7 days, there seems to be a minimum around  $K_3 = 1.13$ . This is mainly a kinetic effect, as those samples also show a minimum in the determined hydration degree (Figure 9(a)). Slags HA, M8, and A14 show a quite similar composition (see Table 2), but their compressive strength is quite different. The correlation between their  $K_3$  and compressive strength is only good after 180 days. Thus, it seems to be a kinetic effect as well, as some minor components present in the slags like  $\text{TiO}_2$  or sulfide as well

as the temperature history during slag formation and cooling,[41,42] which may lead to phase separation in the order of between 50 and 400 nm might influence slag dissolution kinetics.[41,42]

This correlation between  $K_3$  and compressive strength is also valid in the case of NaOH activation. A slight increase of compressive strength with increasing  $K_3$  is observed (Figure 7(b)), however the strength values are much lower in this case. Here, kinetic effects are not visible, which is due to the – compared to sodium metasilicate – harsher activation conditions in the case of NaOH, providing a more rapid dissolution (see Figure 9(b) compared to Figure 9(a)).

The correlations with  $K_4 = (\text{CaO} + \text{MgO})/(\text{SiO}_2 + \text{Al}_2\text{O}_3)$ ,  $K_5 = (\text{CaO} + \text{MgO} + 1/3\text{Al}_2\text{O}_3)/(\text{SiO}_2 + 2/3\text{Al}_2\text{O}_3)$ ,  $K_7 = (\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3)/(\text{SiO}_2)$  and  $K_8 = (\text{CaO} \cdot \text{Al}_2\text{O}_3)/(\text{SiO}_2 + \text{Al}_2\text{O}_3)^2$  for the slags activated with sodium metasilicate are shown in Figure 8. All four moduli are taking the effect of  $\text{Al}_2\text{O}_3$  into account, but differently.

With increasing  $K_4$ ,  $K_5$  and  $K_7$  an increase of compressive strength can be observed as a general trend. In the case of  $K_4$  and  $K_5$  (total  $\text{Al}_2\text{O}_3$  assigned to the network formers in case of  $K_4$ , 2/3 of the

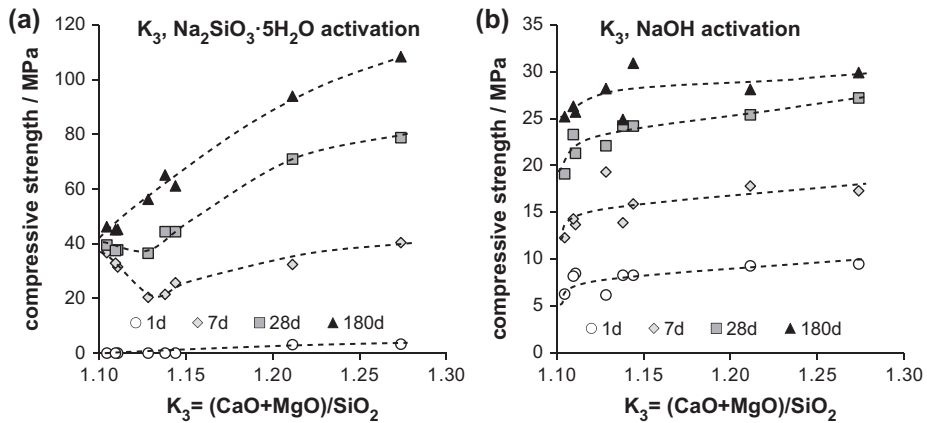


Figure 7. Correlation of  $K_3 = (\text{CaO} + \text{MgO})/\text{SiO}_2$ , with compressive strength for slags activated with (a) sodium metasilicate and (b) sodium hydroxide. Note that the scales for compressive strength are chosen differently. Data taken from [25–27]. Lines are for eye-guide only.

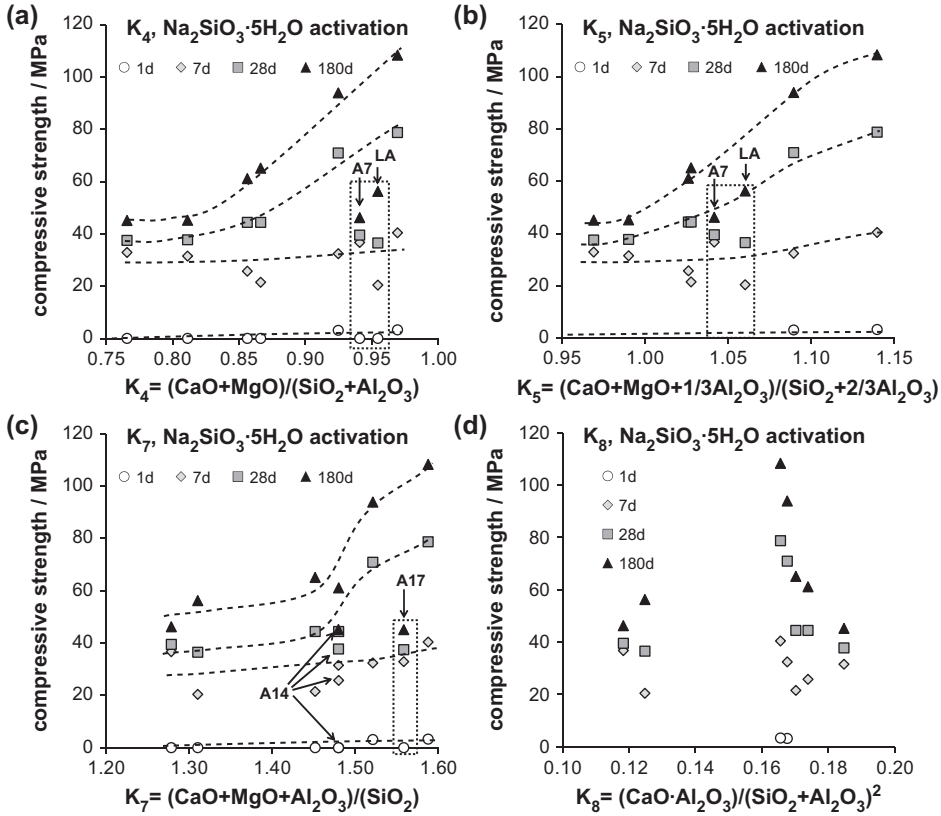


Figure 8. Correlation of (a)  $K_4 = (\text{CaO} + \text{MgO}) / (\text{SiO}_2 + \text{Al}_2\text{O}_3)$ , (b)  $K_5 = (\text{CaO} + \text{MgO} + 1/3\text{Al}_2\text{O}_3) / (\text{SiO}_2 + 1/3\text{Al}_2\text{O}_3)$ , (c)  $K_7 = (\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3) / \text{SiO}_2$  and (d)  $K_8 = (\text{CaO} \cdot \text{Al}_2\text{O}_3) / (\text{SiO}_2 + \text{Al}_2\text{O}_3)^2$  with compressive strength for slags activated with sodium metasilicate. Data taken from [25–27]. Lines are for eye-guide only.

$\text{Al}_2\text{O}_3$  in case of  $K_5$ , the slags with both low  $\text{Al}_2\text{O}_3$  and low MgO content (A7, LA) do not correlate well as they show a too low compressive strength. This is probably related to the fact that in such slags not much of the hydrotalcite-like phase can be formed, which seems to show also some strength contribution. In the case of  $K_7$  ( $\text{Al}_2\text{O}_3$  assigned to the network modifiers) the slags with both high  $\text{Al}_2\text{O}_3$  and low MgO content (A14, A17) do not correlate well showing a too low compressive strength. In this case, the role of  $\text{Al}_2\text{O}_3$  concerning strength is overestimated.

Thus, the amphoteric nature of the  $\text{Al}_2\text{O}_3$  needs to be taken into account and can be represented well by  $K_3 =$

$(\text{CaO} + \text{MgO}) / \text{SiO}_2$  in an indirect way. From this a general version of the equations  $K_4, K_5, K_7$  can be derived as follows:

$$K'_3 = \frac{\text{CaO} + \text{MgO} + x \cdot \text{Al}_2\text{O}_3}{\text{SiO}_2 + (1 - x) \cdot \text{Al}_2\text{O}_3}$$

with  $x = 0 \dots 1$

The parameter  $x$  describes the distribution of  $\text{Al}_2\text{O}_3$  between network modifier and network formers. In case of the slags investigated in this study the parameter  $x$  is 0.5 for both activation systems, when  $x$  is fixed in a way that the values of  $K_3$  and  $K'_3$  are the same (which works pretty well for all eight slags at  $x = 0.5$ ) and thus show the same correlations with compressive strength.

The use of  $K_8$  (Figure 9(d)) as parameter to relate compressive strength to slag composition did not yield any correlation for the investigated systems.

The correlation of hydration degree, bound water content and coarse capillary porosity with  $K_3$  (or  $K'_3$ ) is shown in Figure 9 for the slags activated with

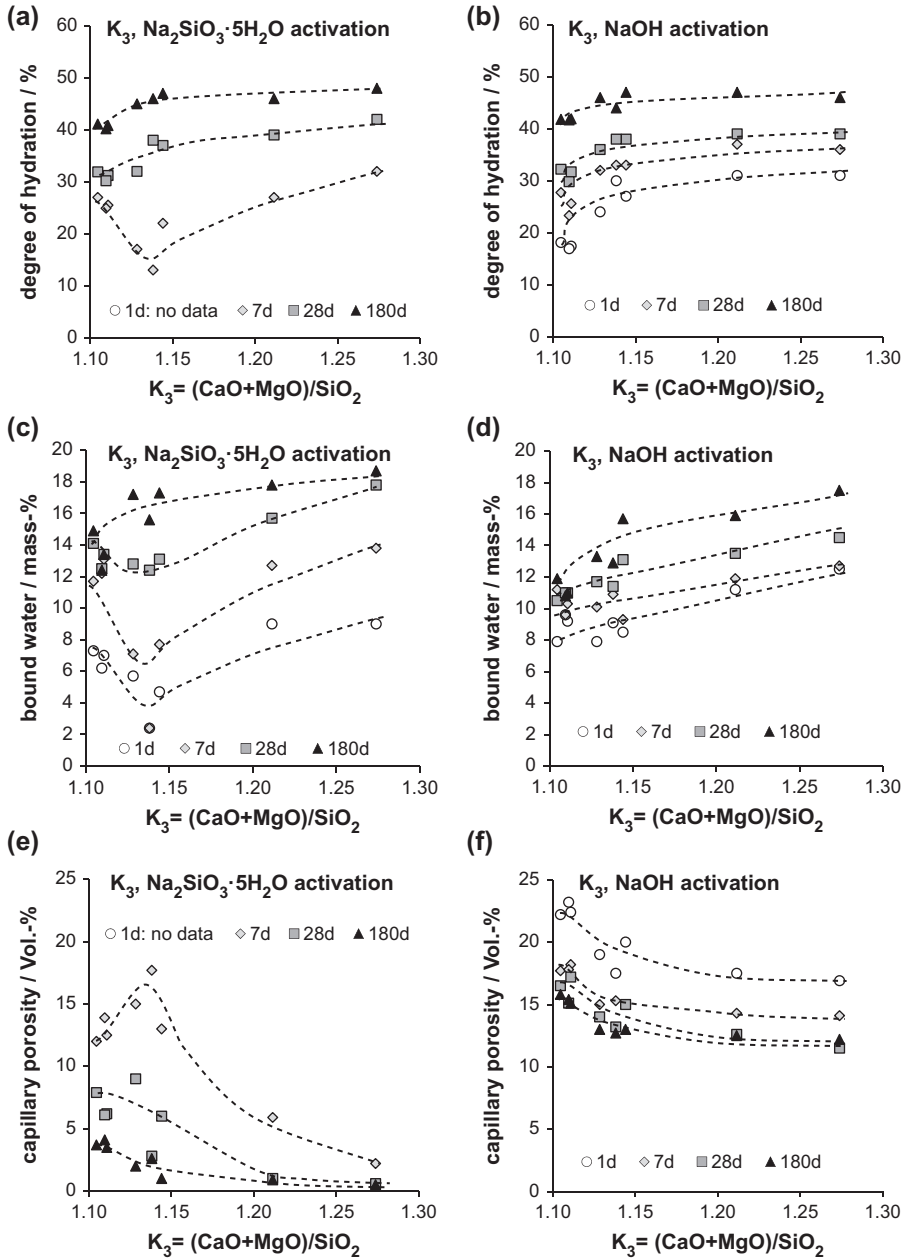


Figure 9. Correlation of  $K_3 = (\text{CaO} + \text{MgO}) / \text{SiO}_2$  with (a) & (b) degree of hydration, (c) & (d) bound water and (e) & (f) coarse capillary porosity for slags activated with sodium metasilicate and sodium hydroxide, respectively. Data taken from [25–27]. Degree of hydration was not measured after 1 day due to low strength. Lines are for eye-guide only.

sodium metasilicate (Figure 9(a), (c), and (e)) and with sodium hydroxide (Figure 9(b), (d), and (f)). The degree of hydration is correlated positively with  $K_3$  in case of both activators (Figure 9(a) and (b)). Also chemically bound water increases with increasing  $K_3$  (Figure 9(c) and (d)) in both cases, with the exception of the sodium metasilicate activated slags at early hydration times (1 and 7 days). Those systems show a slow early kinetics as mentioned previously. As a consequence of the positive correlation of the parameters described above, coarse capillary porosity is negatively correlated with  $K_3$  (Figure 9(e) and (f)) for both activation systems.

#### 4. Conclusions

Eight different blast-furnace slags with varying chemical compositions, but very similar particle size distributions were investigated. The slags vary mainly in their MgO and Al<sub>2</sub>O<sub>3</sub> contents. They were activated either by sodium silicate (sodium metasilicate) or by sodium hydroxide using the same Na<sub>2</sub>O-equivalent added.

Independent of slag composition, it was found that sodium metasilicate activation gives slow early hydration kinetics during the first days, and strength after 1 day could not be measured for most of the samples. After 7 days and beyond a high compressive strength can be measured. When activated with NaOH the slags show a moderate compressive strength after 1 day, but strength after 180 days is much lower than in the case of sodium metasilicate. At the same hydration degree, a higher compressive strength is reached with sodium metasilicate than with NaOH. During the fast initial hydration in the case of NaOH activation, a dense C–A–S–H with less chemically bound water than in the sodium metasilicate activated system is formed. Thus the microstructure is coarser with a higher porosity. Compressive strength and coarse capillary

porosity correlate very well, independently of the activator system used.

In the case of sodium metasilicate activation, an increase of both early and late strength can be observed with increasing MgO content, which is related to an increase of the hydration degree determined and a decrease of the coarse porosity. In addition, a higher hydrate volume is predicted by thermodynamic modeling with increasing MgO content and thus a lower porosity. In the NaOH-activated system, the higher MgO content leads to a slightly higher degree of reaction and thus to only a slightly higher compressive strength at all ages.

In the case of sodium metasilicate activation slightly slower early hydration kinetics and a slight reduction of strength after 7 and 28 days can be observed with increasing Al<sub>2</sub>O<sub>3</sub> content. This is confirmed by thermodynamic modeling, which predicts no relevant effect of Al<sub>2</sub>O<sub>3</sub> on the volume of the hydrates. Thus no significant changes in the coarse porosity at the same degree of hydration are expected as observed also experimentally. The activation with NaOH leads to only minor changes in strength development with varying Al<sub>2</sub>O<sub>3</sub> contents. Slightly faster early hydration kinetics up to a sample age of 7 days with decreasing Al<sub>2</sub>O<sub>3</sub> content could be observed.

Correlations between different “slag moduli” used to assess slag reactivity and compressive strength, chemically bound water, hydration degree, and coarse capillary porosity were tested. It was found that the ratio  $K_3 = (\text{CaO} + \text{MgO})/\text{SiO}_2$ , the extended basicity according to EN 197-1, shows the best correlations. The role of Al<sub>2</sub>O<sub>3</sub> which can be both network former and network modifier is considered here indirectly as besides CaO, MgO, and SiO<sub>2</sub> generally mainly Al<sub>2</sub>O<sub>3</sub> is present in the slags. This can be expressed in a general way by modifying  $K_3$  to  $K'_3 = (\text{CaO} + \text{MgO} + x \cdot \text{Al}_2\text{O}_3)/(\text{SiO}_2 + (1 - x)\text{Al}_2\text{O}_3)$  with  $x$  being a

value between 0 and 1. In case of the investigated activated slags, a value of 0.5 can be assigned to  $x$ . The extended basicity reflects also the positive impact of MgO on compressive strength. A positive correlation was found between extended basicity and strength, chemical bound water, hydration degree, and a negative correlation to coarse capillary porosity for both activators. However, these correlations refer only to the investigated systems, and it might be different in case other slags or activators are used.

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