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Activation of blast furnace slag by a new method

F. Bellmann *, J. Stark

Institute for Building Materials Science, Department of Civil Engineering, Bauhaus-University Weimar Coudraystraße 11, 99423 Weimar, Germany

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ABSTRACT

Blast furnace slag is used as supplementary cementing material for the production of blended cement and slag cement. Its latently hydraulic properties can be activated by several methods. Most applications employ the use of high pH values in the pore solution (>13.0) to accelerate the corrosion of the glass network of the slag.

It is shown in this work that activation is also possible by lowering the pH to a range between 11.8 and 12.2 by the addition of calcium hydroxide and soluble calcium salts. Among the salts investigated in this study are calcium chloride, calcium bromide, calcium nitrate, calcium formate, and calcium acetate. Other salts can be used alternatively as long as they are able to increase the calcium ion concentration and thus reduce the pH in the pore solution via the calcium hydroxide equilibrium. Complex formation of organic anions with calcium ions in the pore solution is a serious handicap when using organic calcium salts.

This concept was tested on a particular slag improving its early compressive strength. It was possible to increase the strength of mortar bars produced from the pure slag from 3 MPa to 25 MPa after seven days by adding calcium hydroxide, calcium carbonate and calcium acetate. The early strength of slag cement containing 80% slag was increased from 6 to 16 MPa after two days by adding calcium chloride. The final strength was increased from 36 to 53 MPa after 28 days (water/cement-ratio = 0.40, 20 °C).

Analytical data is included to demonstrate that application of the aforementioned concept is able to increase heat liberation and degree of slag consumption.

1. Introduction

Blast furnace slag is a by-product of the manufacture of pig iron from iron ore, limestone and coke. The liquid slag is rapidly cooled by quenching to obtain an almost completely amorphous material. Its chemical composition mainly depends on that of the iron ore and potentially contains 27–40% SiO_2, 30–50% CaO, 5–15% Al_2O_3, and 1–10% MgO. Recent reviews of the properties of blast furnace slag and its utilisation for the production of blended cement were given by Taylor [1], Moranville-Regourd [2], Lang [3], and Glasser [4].

Blast furnace slag has been used as a secondary cementing material for more than 100 years and there is a broad knowledge regarding its application. Most commonly it is used for the production of blended cements and slag cements. Currently, there is high interest in the application of this alternative material because the production of Portland cement clinker contributes about 5% to the global man-made CO_2 emissions. Despite the fact that the amount of available slag is limited, there is an increasing demand for slag cement to reduce the CO_2 emissions due to the production of cement and concrete [5].

The hydration of blast furnace slag is slow when compared to Portland cement clinker, resulting in lower early strength and higher strength gain at later ages. The heat release during hydration at room temperature is significantly lower than during hydration of Ordinary Portland Cement (OPC). Due to its slow reaction, slag cement produces a very dense microstructure and is highly resistant to chemical attack. Blast furnace slag contains less lime than Portland cement clinker and calcium hydroxide is not formed during reaction of the slag particles. Instead of this, calcium silicate hydrate (C–S–H) with a low calcium/silicon-ratio, hydrotalcite, and ettringite or AFm phases are formed. Sulfur contained in blast furnace slag is mainly present in reduced form (S^{2-}) accounting for the dark colour of the concrete produced from cement with a high amount of slag before it is exposed to air. The hydration of slag proceeds via dissolution of slag particles followed by precipitation of hydrate phases from the supersaturated pore solution. In this process, the dissolution of the unhydrous material is the time determining step. The higher the dissolution, the faster the reaction of the material to hydrated phases. Since the corrosion of the glass-network of slag can be accelerated by high pH values in the pore solution (>13.0), there is a tendency to use Portland cement clinker with a high content of water soluble alkalis to produce blended cement containing slag.

There are two other forms known to activate the latent hydraulic properties of blast furnace slag, namely the addition of high amounts of calcium sulphate and alkali activation. Blends of 10–20% calcium sulphate, mainly in the form of anhydrite ($CaSO_4$) with very small amounts of OPC and 75–90% blast furnace slag are termed

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* Corresponding author. Tel.: +49 3643 584724; fax: +49 3643 584759.
E-mail address: frank.bellmann@uni-weimar.de (F. Bellmann).

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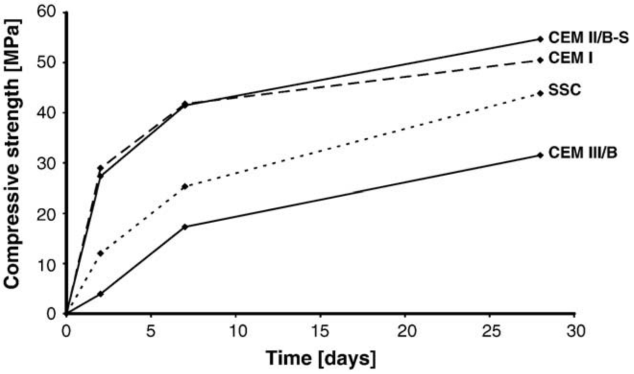

Fig. 1. Strength development of four cements with different slag content.

supersulphated cement [2]. Well made cements of this type are able to achieve final strengths in the same order as OPC. Their performance depends critically on the pH value in the pore solution [6]. A serious drawback is that concretes made from supersulphated cement require long curing periods, are sensitive to carbonation and frost attack. A special feature of these materials is that they are not compatible with other hydraulic materials. Calcium sulphate is not completely depleted during hydration and can lead to sulphate attack at the interface between concrete from supersulphated cement with other concretes.

Alkali-activated slag cements require the addition of up to 5% Na_2O or K_2O most commonly in the form alkali hydroxide, alkali carbonate or alkali silicate. The alkalis are added during mixing of the cement with water. They are partially bound in the hydration products during reaction. Concretes made from alkali-activated slag cements can have high strength, low permeability and high resistance to chemical attack. On the other hand, problems have been reported with excessive shrinkage and efflorescence. The most serious handicap is that the production of alkaline activator is very intensive with respect to energy consumption and CO_2 emissions.

To the present time, supersulphated cement and alkali-activated slag cement are rather niche-products when compared to other cements such as OPC, blended cement or slag cement. This is due to the disadvantages mentioned above. At present, most applications try to activate blast furnace slag by maintaining a high pH in the pore solution to corrode the slag particles by adding OPC or Portland cement clinker. However, this approach is only feasible with limited proportions of slag in the cement. If very high fractions of slag are used for the production of cement, the early strength may be significantly reduced, which is of major concern for application in the construction industry. This is aggravated when a coarse slag is used. An example is displayed in Fig. 1. The compressive strength of mortar bars made according to DIN EN 196-1:1995-05 is shown for a CEM III/B containing 72% of slag. It is compared to the performance of supersulphated cement (SSC), OPC, and CEM II/B-S containing 27% of slag.

Although the data presented in Fig. 1 is far from being systematic, it illustrates the fact that the early strength of slag cement with a high amount of blast furnace slag can be very low when compared to other cements. This prevents the use of this material for most construction purposes. After two days storage under water, the CEM III/B in the aforementioned example achieves a strength of only 4 MPa whereas the CEM II/B-S gets as high as 27 MPa. However, the performance of supersulphated cement with 12 MPa indicates that there is a much higher potential of hydraulic capacity that can be activated. It is the scope of the investigations reported here to identify a new way for activation of blast furnace slag that can make use of the hydraulic potential of slag without applying such peculiar concepts as supersulphated cement or alkali-activation.

When supersulphated cement reacts with water, calcium sulphate serves as a reactant by precipitating aluminium dissolved from the slag in the form of ettringite ($C_3A\cdot 3CaSO_4\cdot 32H_2O$). Silicon released during dissolution is bound in the form of C–S–H. To prevent the formation of excessive amounts of ettringite and to avoid the presence of unreacted calcium sulphate after hydration, a different sink for aluminium was sought. Instead of calcium sulphate, a mixture of calcium hydroxide ($Ca(OH)_2$) and calcium carbonate ($CaCO_3$) was added. By this replacement, aluminium should be precipitated as monocarbonate ($C_3A\cdot CaCO_3\cdot 11H_2O$) rather than ettringite. The co-precipitation of C–S–H may proceed as in supersulphated cement. Binders made from blast furnace slag and calcium hydroxide are termed lime-slag cements [2]. A second concept has been used to accelerate the reaction of blast furnace slag even further. The addition of calcium hydroxide as reactant changes the composition of the pore solution. In the presence of calcium hydroxide, the pH in the pore solution is 12.5 at room temperature and even higher in the presence of alkali hydroxide. This is significantly higher than the pH in the pore solution of supersulphated cement (approximately 11.8–12.0). To reduce the pH in the presence of calcium hydroxide, soluble calcium salts were added. They maintain a very high calcium ion concentration in the pore solution. Such high calcium ion concentrations are able to reduce the hydroxide ion concentration (expressed as pH) via the calcium hydroxide equilibrium condition (Eq. (1)).

$$K_{SP} = \left\{Ca^{2+}\right\}\cdot\{OH^{-}\}^{2} \qquad (1)$$

The concepts sketched above have been tested by measuring the compressive strength development of mortar bars produced from laboratory-made binders with chemical admixtures. In connection with this, the composition of the pore solution during the hydration of hardened cement paste specimen has been studied with a special focus on the pH value. Additional details on the nature of the activation mechanism were obtained by XRD, heat conduction calorimetry and determination of degree of slag consumption of selected samples.

2. Materials and methods

Different binders were produced in this study based on ground granulated blast furnace slag and commercially available CEM II/A-LL 32.5 R. The properties of these two materials are provided in Table 1.

The materials specified in Table 1 were blended with mineral additions of reagent grade quality to produce new binder types. These additions comprised calcium hydroxide and calcium carbonate (2220 cm^2/g). During hydration of these binders, the composition of the pore solution was changed by adding admixtures such as calcium formate ($Ca(COOH)_2$), calcium acetate ($Ca(CH_2COOH)_2$), calcium chloride ($CaCl_2$), sodium chloride (NaCl), calcium nitrate ($Ca(NO_3)_2$), and calcium bromide ($CaBr_2$), all of reagent grade quality. The composition of all binders and the amounts of admixtures that were added during preparation of pastes and mortars are provided in

Table 1
Chemical and physical properties of slag and cements used in this study (w.s. — water soluble).

	Slag	CEM II/A-LL 32.5 R
SiO_2 [M.-%]	35.2	17.0
Al_2O_3 [M.-%]	11.9	5.0
Fe_2O_3 [M.-%]	0.6	2.6
CaO [M.-%]	41.9	61.3
MgO [M.-%]	6.2	1.0
MnO [M.-%]	0.21	0.07
TiO_2 [M.-%]	0.94	0.21
K_2O (w.s.) [M.-%]	0.44 (0.01)	0.47 (0.28)
Na_2O (w.s.) [M.-%]	0.42 (0.00)	0.11 (0.04)
SO_3 [M.-%]	0.6	2.8
L.O.I. at 1000 °C [M.-%]	0.6	8.6
Specific surface area (Blaine) [cm^2/g]	6050	4550

Table 2
Composition of binders, addition of admixtures, compressive strength and pH in the pore solution of samples investigated in this study.

Binder	Admixture	Compressive strength [MPa]			pH in pore solution		
		2 days	7 days	28 days	2 days	7 days	28 days
100% slag	–	0	2.6	17.0	11.8	12.2	12.4
85% slag + 10% $Ca(OH)_2$ + 5% $CaCO_3$	–	2.4	10.0	15.5	12.8	12.8	12.7
85% slag + 10% $Ca(OH)_2$ + 5% $CaCO_3$	5% $CaCl_2$	12.2	33.1	49.9	11.8	11.8	11.8
100% slag	5% $CaCl_2$	0.0	0.0	1.7	10.6	10.8	11.1
85% slag + 10% $Ca(OH)_2$ + 5% $CaCO_3$	5% NaCl	7.4	17.5	26.3	12.7	12.8	12.8
85% slag + 10% $Ca(OH)_2$ + 5% $CaCO_3$	5% $CaBr_2$	8.6	22.8	36.7	12.0	12.3	12.3
85% slag + 10% $Ca(OH)_2$ + 5% $CaCO_3$	0.5% $Ca(CH_2COOH)_2$	6.9	22.3	34.5	12.5	12.5	12.5
85% slag + 10% $Ca(OH)_2$ + 5% $CaCO_3$	1.0% $Ca(CH_2COOH)_2$	5.0	25.0	40.0	12.4	12.4	12.4
85% slag + 10% $Ca(OH)_2$ + 5% $CaCO_3$	1.5% $Ca(CH_2COOH)_2$	3.6	23.6	40.6	12.1	12.2	12.3
85% slag + 10% $Ca(OH)_2$ + 5% $CaCO_3$	2.0% $Ca(CH_2COOH)_2$	2.7	19.3	34.8	12.1	12.2	12.3
85% slag + 10% $Ca(OH)_2$ + 5% $CaCO_3$	4.0% $Ca(CH_2COOH)_2$	0.7	11.0	33.3	12.0	12.0	12.1
85% slag + 10% $Ca(OH)_2$ + 5% $CaCO_3$	1% $Ca(COOH)_2$	7.0	23.0	34.6	12.2	12.4	12.2
85% slag + 10% $Ca(OH)_2$ + 5% $CaCO_3$	2% $Ca(COOH)_2$	6.3	19.7	38.7	12.0	12.0	12.2
80% slag + 15% CEM II/A-LL + 5% $Ca(OH)_2$	–	5.6	24.6	36.5	12.8	12.9	13.0
80% slag + 15% CEM II/A-LL + 5% $Ca(OH)_2$	3% $CaCl_2$	15.6	36.8	52.9	12.0	12.2	12.3
80% slag + 15% CEM II/A-LL + 5% $Ca(OH)_2$	3% $CaBr_2$	15.2	37.8	48.8	12.2	12.5	12.6
80% slag + 15% CEM II/A-LL + 5% $Ca(OH)_2$	1% $Ca(COOH)_2$	6.1	31.9	47.4	12.4	12.6	12.8
80% slag + 15% CEM II/A-LL + 5% $Ca(OH)_2$	3% $Ca(NO_3)_2$	11.2	36.7	52.5	12.2	12.5	12.6

Table 2. The amount of chemical admixtures is given in this table relative to the amount of binder. Details about ionic concentrations expected after mixing the salts with water are available in Table 3.

Mortar bars were prepared, stored and tested according to DIN EN 196-1:1995-05 (sand 0/4:cement = 3.0, mortar bars 4 cm × 4 cm × 16 cm stored in water after demoulding) using binders and admixtures as detailed in Table 2. The only detail being different was the water/cement-ratio that was fixed to 0.40. Compressive strength was tested in the age of 2, 7 and 28 days. In addition to strength development, the composition of the pore solution of hardened cement paste specimen was investigated at the ages of 2, 7, and 28 days. For this purpose, cement paste was prepared at a water/cement-ratio of 0.50. All samples were stored in sealed plastic containers at 20 °C. The pore solution was obtained by the squeeze-out method at a maximum pressure of 270 MPa at the age appropriate for testing. The main focus of the investigations reported here was analysis of the pH value in the solution. It was carried out by employing a glass electrode, calibrated on standard buffer solutions.

XRD analysis was performed on selected samples after terminating hydration via removal of liquid water at 38 °C. Before qualitative analysis, the hardened cement pastes were ground to pass a sieve with a mesh width of 63 µm. The instrument used was a Siemens/Bruker AXS D5000 equipped with a copper tube operating at 40 kV and 40 mA. An angular range from 4 to 60° 2θ was examined using a counting time of 2.5 s and a step width of 0.05° 2θ.

The degree of slag hydration was measured by a selective dissolution technique described by Lumley et al. [8]. Loss of ignition was determined after heating the samples to 750 °C instead of 900 °C described in [8]. The degree of hydration was calculated correcting for dissolution of unhydrated material and for the water content using the loss of ignition results.

Isothermal heat conduction calorimetry has been used to measure the heat release in the first 100 h of hydration using a ToniCal Trio 7339 instrument.

3. Results

The results of the compressive strength tests are provided in Table 2. Graphical presentation of this data is given below.

The mortar was prepared at water/cement-ratio of 0.40. Due to this low water content, the samples showed low workability and were hard to compact. Thus different air contents in the hardened mortars bars may have affected the strength results to some extent. The air content of mortar was not recorded. Beside compressive strength, pH values measured in the pore solution are also available in Table 2.

The blast furnace slag used in this study is of typical chemical composition for slags used for the production of blended cements in Germany. Its specific surface area measured according to Blaine (6050 cm^2/g) is higher than in most blended cements (3000–5000 cm^2/g).

The hydration of the pure slag is comparatively slow. Compressive strength was very low after 2 and 7 days (Fig. 2), whereas 17 MPa was

Table 3
Amount of salt added during mortar preparation and expected concentrations in the mixing water ignoring effects of ion association and interaction with solid phases contained in the binder.

Amount of salt relative to weight of binder	Salt concentration [mmol salt/100 g cement]	Theoretical ionic concentration in solution after mixing [mmol/l]
3% $CaCl_2$	27.0	$[Ca^{2+}]$ = 676 mmol/l, $[Cl^-]$ = 1352 mmol/l
5% $CaCl_2$	45.0	$[Ca^{2+}]$ = 1226 mmol/l, $[Cl^-]$ = 2252 mmol/l
5% NaCl	85.6	$[Na^+]$ = 2139 mmol/l, $[Cl^-]$ = 2139 mmol/l
3% $CaBr_2$	15.0	$[Ca^{2+}]$ = 375 mmol/l, $[Br^-]$ = 750 mmol/l
5% $CaBr_2$	25.0	$[Ca^{2+}]$ = 625 mmol/l, $[Br^-]$ = 1250 mmol/l
3% $Ca(NO_3)_2$	18.3	$[Ca^{2+}]$ = 457 mmol/l, $[NO_3^-]$ = 914 mmol/l
0.5% $Ca(CH_2COOH)_2$	3.2	$[Ca^{2+}]$ = 79 mmol/l, $[CH_2COOH^-]$ = 158 mmol/l
1.0% $Ca(CH_2COOH)_2$	6.3	$[Ca^{2+}]$ = 158 mmol/l, $[CH_2COOH^-]$ = 316 mmol/l
1.5% $Ca(CH_2COOH)_2$	9.5	$[Ca^{2+}]$ = 237 mmol/l, $[CH_2COOH^-]$ = 474 mmol/l
2.0% $Ca(CH_2COOH)_2$	12.6	$[Ca^{2+}]$ = 316 mmol/l, $[CH_2COOH^-]$ = 632 mmol/l
4.0% $Ca(CH_2COOH)_2$	25.3	$[Ca^{2+}]$ = 632 mmol/l, $[CH_2COOH^-]$ = 1264 mmol/l
1% $Ca(COOH)_2$	7.7	$[Ca^{2+}]$ = 192 mmol/l, $[COOH^-]$ = 384 mmol/l
2% $Ca(COOH)_2$	15.4	$[Ca^{2+}]$ = 384 mmol/l, $[COOH^-]$ = 768 mmol/l

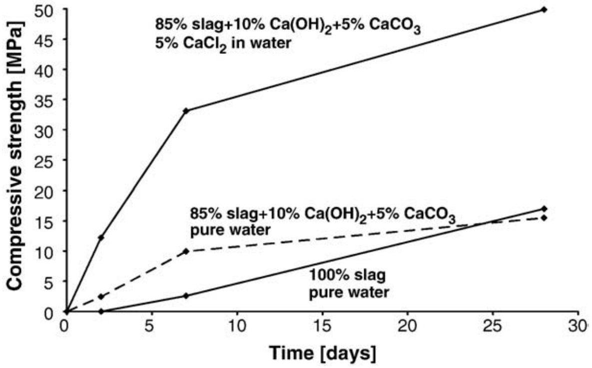

Fig. 2. Acceleration of blast furnace slag by the addition of calcium hydroxide, calcium carbonate, and calcium chloride.

reached after 28 days. Replacement of 15% of slag by a mixture of calcium hydroxide and calcium carbonate is able to accelerate the reaction of slag. Even further acceleration is achieved by the addition of calcium chloride to the mixing water (Fig. 2). The compressive strength after 2 days is significantly higher than obtained for pure slag without accelerator. Despite the fact that it is lower than that of Portland cement, it would warrant classification of this binder system in strength class 32.5 R or 42.5 N. However, the use of calcium chloride prohibits application in reinforced concrete, and therefore other means of acceleration need to be selected. To identify other salts that could be used to accelerate the reaction of slag, information on the mode of acceleration and the mode of action are required. The remaining part of this section is devoted to these investigations.

Results of XRD analysis obtained on hardened cement paste specimen stored under sealed conditions for 7 days are shown in Fig. 3. There are no crystalline hydration products detected in the sample consisting of pure slag and water. Also, in the presence of calcium chloride solution, no hydration product can be identified in the pure slag. After mixing the slag with calcium hydroxide and calcium carbonate, aluminium from the slag can react with these phases to monocarbonate or a similar AFm phase. This is observed by XRD after 7 days hydration. Apart from AFm, some calcium hydroxide and calcium carbonate are still present in the sample. The results of XRD analysis confirm that aluminium is precipitated as AFm phase thus accelerating the reaction of blast furnace slag. The reaction is further accelerated by addition of calcium chloride as evident from Fig. 2.

The accelerating effect of calcium chloride may be attributed to different aspects:

- Chloride ions may be consumed in an additional reaction forming a hydration product containing chloride thus directly stimulating the reaction of slag.
- A high calcium ion concentration in the pore solution is able to lower the pH which may have an accelerating effect (see below). Presence of calcium hydroxide is essential in this mechanism.
- The high calcium concentration is directly responsible for activation of the slag. In this case, calcium hydroxide is not required.

To test the first hypothesis, samples of binder containing slag, calcium hydroxide, and calcium carbonate were hydrated in the presence of calcium chloride and sodium chloride, respectively. If chloride ions have a positive effect on the reaction, the addition of sodium chloride should be able to accelerate the reaction in the same way calcium chloride does. The second and third hypotheses were investigated by replacing the aforementioned binder by pure slag. If there is no influence of the addition of calcium hydroxide on the performance, the calcium ion concentration is responsible for acceleration instead of pH in solution. The results of these investigations are presented in Fig. 4.

The data presented in Table 2 and Fig. 4 indicates that the addition of calcium chloride to pure blast furnace slag is not able to improve the strength development. The compressive strength after 2 and 7 days was not measurable because the samples were still soft. It can be inferred that calcium chloride does not act as a direct accelerator by reacting with the slag forming hydration products containing chloride. In contrast, a combined addition of calcium chloride, calcium hydroxide and calcium carbonate increases compressive strength and is thus able to activate blast furnace slag. This rules out the aforementioned hypothesis that high calcium ion concentrations are directly able to accelerate the hydration of slag.

Replacement of calcium chloride by sodium chloride yields strength results that are better than those obtained for the pure binder consisting of slag, calcium hydroxide and calcium carbonate, but significantly lower than those obtained for calcium chloride. Thus, sodium chloride is a much less effective activator than calcium chloride. The hypothesis that acceleration is due to the presence of chloride ions can therefore be abandoned.

The hydration of the aforementioned binders was investigated by isothermal heat conduction calorimetry (Fig. 5). There is only a negligible output of heat during the reaction of the pure slag, even in the presence of calcium chloride. Activation with calcium hydroxide and calcium carbonate yields a substantial increase of heat release

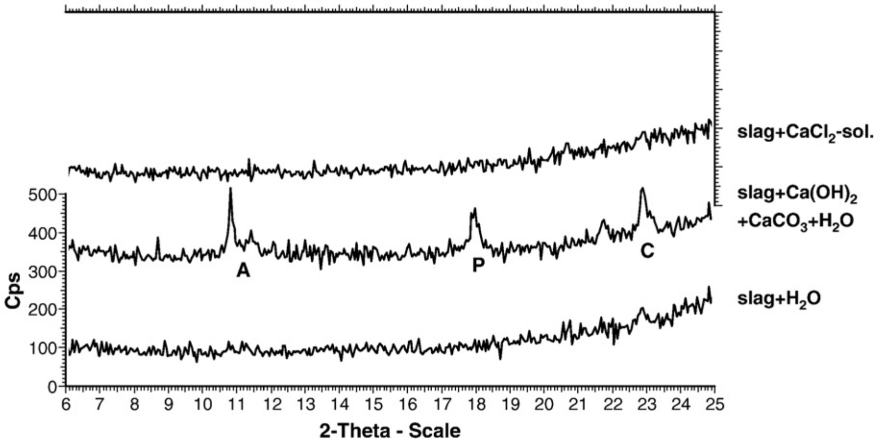

Fig. 3. Results of XRD analysis after 7 day hydration (A = AFm, P = Portlandite, C = calcite).

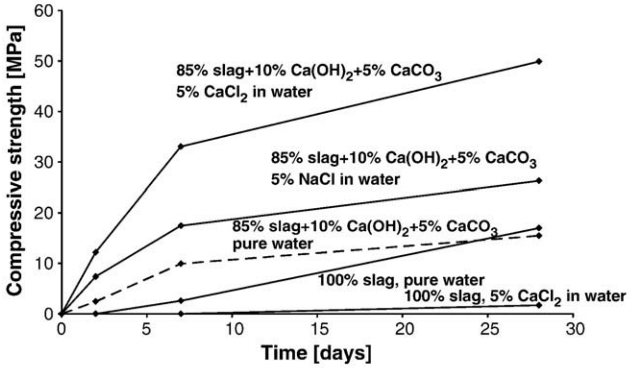

Fig. 4. Effect of calcium hydroxide, calcium carbonate, calcium chloride, and sodium chloride on the strength development of slag.

rates. Further acceleration and higher rates are obtained when adding inorganic salts that lower the pH in the pore solution such as sodium chloride and calcium chloride. The effect is most pronounced with calcium chloride. The amount of heat that is released during hydration of a binder consisting of slag, $Ca(OH)_2$ and $CaCO_3$ in the presence of $CaCl_2$ is in the range of low heat cements.

The degree of hydration of binder pastes at the age of 48 h is presented in Table 4. Data obtained by selective dissolution confirms that virtually no reaction is observed between the pure slag and water. The degree of slag consumption (2%) is within the tolerance of the analytical method. The addition of calcium chloride to the mixing water is not able to increase the degree of slag hydration (1%). Much higher degrees of hydration are observed when calcium hydroxide and calcium carbonate have been added to the slag. In agreement with results obtained by calorimetry, the extent of hydration depends on the addition of inorganic salts that manipulate the composition of the pore solution (see below). The degree of slag hydration observed for pure water (8%) can be increased by the addition of sodium chloride (15%) or calcium chloride (20%).

Table 4
Degree of slag hydration in the age of 48 h for selected binders.

Binder	Admixture	Degree of slag hydration [%]
100% slag	–	2
85% slag + 10% $Ca(OH)_2$ + 5% $CaCO_3$	–	8
85% slag + 10% $Ca(OH)_2$ + 5% $CaCO_3$	5% $CaCl_2$	20
100% slag	5% $CaCl_2$	1
85% slag + 10% $Ca(OH)_2$ + 5% $CaCO_3$	5% NaCl	15

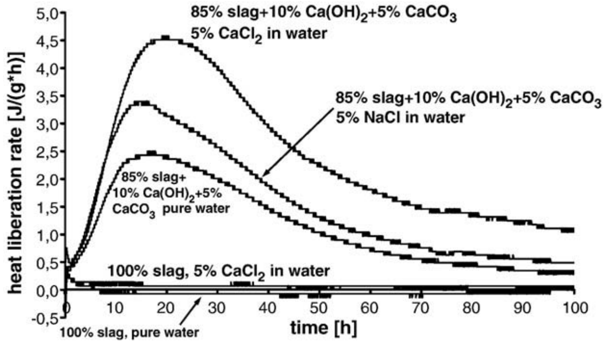

Fig. 5. Heat of hydration of selected binders.

In conclusion, the second hypothesis considering that a combined addition of calcium chloride and calcium hydroxide is responsible for acceleration is supported. However, it has to be tested by performing additional experiments. Calcium chloride can be replaced by another easily soluble calcium salt such as calcium bromide. In this case, the pH in the pore solution will also be lowered by a high calcium ion concentration and maintenance of the calcium hydroxide equilibrium (Eq. (1)). This equation indicates that calcium and hydroxide ion concentration (an expression for pH in the solution) are connected in the presence of calcium hydroxide. At high pH values, there is a very low calcium ion concentration in the pore solution. On the other hand, the pH can be shifted to values lower than the equilibrium value of portlandite in pure water (12.5) by maintaining a very high calcium ion concentration. This trend is confirmed by the data presented in Table 2. In the binder system comprising slag, calcium hydroxide and calcium carbonate, the pH value is approximately 12.8, due to the presence of calcium hydroxide and minor amounts of alkalis resulting from slag dissolution. The use of 5% calcium chloride reduces the pH value in the pore solution to 11.8 by establishing a high calcium ion concentration in the presence of calcium hydroxide.

It can be concluded from this data that the pH appears to play an important role for the activation of blast furnace slag in the presence of calcium hydroxide. To confirm this conclusion, tests have been carried out in which calcium chloride was exchanged by calcium bromide ($CaBr_2$). Such a replacement is also able to generate a high calcium ion concentration and a low pH in the pore solution. Data presented in Table 2 and Fig. 6 confirms that the addition of 5% $CaBr_2$ can accelerate the hydration of a binder consisting of slag, calcium hydroxide, and calcium carbonate. However, the addition of an equal weight of calcium bromide appears to be less effective than calcium chloride. This is due the higher molecular weight of calcium bromide compared to calcium chloride (Table 3).

From the data presented here, it can be deduced that the reaction of slag can be accelerated by maintaining a low pH value in the pore solution. Due to the addition of 5% calcium bromide, the pH is lowered from 12.8 to 12.0 after 2 days. It is even further reduced by the addition of calcium chloride (11.8), accounting for the better performance of this admixture at equal weight.

The use of calcium chloride or calcium bromide allows for the activation of blast furnace slag due to the maintenance of a high calcium ion concentration and reduction of pH in the pore solution. However, an application of such salts in the building industry is constrained by the fact that chloride and bromide ions promote pit-hole corrosion of steel. Consequently, the use of calcium chloride and calcium bromide as an accelerator is prohibited for the production of reinforced concrete. Other salts with similar properties need to be identified. Inorganic calcium salts may potentially be used to accelerate the reaction of slag with calcium hydroxide and water, but the anions present in most of these salts may also affect the resistance of steel against corrosion. To avoid this situation, organic calcium salts were tested, namely calcium acetate ($Ca(CH_2COOH)_2$) and calcium formate ($Ca(COOH)_2$). Also the amount of admixture was varied. The results are displayed for calcium acetate in Fig. 7.

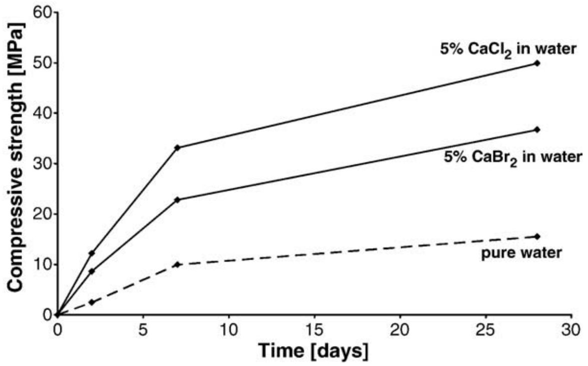

Fig. 6. Impact of additions of calcium chloride and calcium bromide on the strength development of mortar bars made from slag, calcium hydroxide, and calcium carbonate.

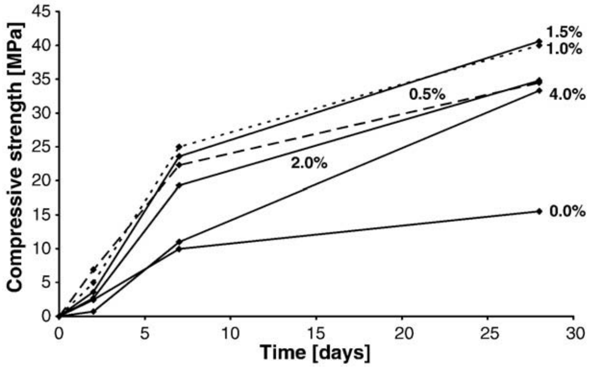

Fig. 7. Impact of the addition of calcium acetate ($Ca(CH_2COOH)_2$) on the strength development of a binder composed of 85% blast furnace slag, 10% calcium hydroxide, and 5% calcium carbonate.

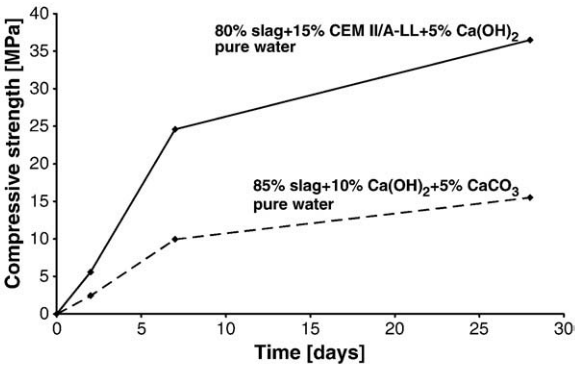

Fig. 9. Modification of compressive strength development by partial replacement of slag by Portland limestone cement.

The addition of calcium acetate is able to increase the final compressive strength of a binder consisting of slag, calcium hydroxide, and calcium carbonate. Compressive strengths up to 40 MPa were obtained at the age of 28 days by adding 1.0% and 1.5% of admixture. The final strength is not proportional to the amount of admixture added. Quantities exceeding the aforementioned optimum of 1.0 to 1.5% showed adverse effects on the final strength. The same trend was observed for early strength results. After two days, the highest compressive strength was measured for samples containing 0.5% calcium acetate, higher amounts yielding a reduction of the early strength. This behaviour could be attributed to complexation of calcium ions by acetate ions. If the concentration of acetate surpasses a critical level, the concentration of free, un-complexed calcium ions drops significantly. The lower the amount of acetate ions in solution, the less calcium ions are bound in the form of complexes. Further discussion requires knowledge of the complexation constant of calcium acetate [7].

The pH in the solution did not reflect the optimum additions of calcium acetate. It was found that the pH in solution decreases continuously with rising amounts of admixture (Table 2). The pH in the pore solution falls from 12.5 (0.5% calcium acetate) to 12.0 (4.0% calcium acetate). This data does not support the discussion of the role of pH and the influence of complexation of calcium ions by acetate.

The accelerating effect of calcium formate was compared to the performance of samples containing calcium acetate (Fig. 8). Also, calcium formate is able to improve compressive strength development in the same way calcium acetate does. The final strength was about 40 MPa for optimum additions of calcium formate. The early strength is very low for both organic salts (<10 MPa after 2 days).

Nevertheless, the aforementioned discussion demonstrates that blast furnace slag can be activated by the addition of calcium hydroxide and soluble calcium salts. The early strength was increased but is still far from being able to compete with the performance of Portland cement or blended cement. In addition to this, a high amount of calcium hydroxide was added. The amount of this material has to be reduced in order to produce cements with a very low specific emission of carbon dioxide. To improve the early strength and to reduce the amount of calcium hydroxide added during binder preparation, a part of the slag was replaced by cement. A serious disadvantage is the high specific emission of carbon dioxide during Portland cement clinker production. However, the benefits of this replacement are:

- an improved early strength due to the reaction of the clinker,
- a lower requirement of the amount of calcium hydroxide due to the liberation of calcium hydroxide during reaction of the clinker, and finally
- easier use of the product under existing standards.

The latter is due to the fact that the European standard for the production of concrete allows application of specific cement types only in a defined range of environments. Such environment classes are not specified for a binder containing blast furnace slag and some inorganic materials such as calcium hydroxide and calcium carbonate. They are, however, available for cement containing a very high amount of slag. According to European regulation, such cements are CEM III/B containing 66–80% blast furnace slag, 20–34% Portland cement clinker and CEM III/C containing 81–95% blast furnace slag, and 5–19% Portland cement clinker. Up to 5% of minor constituents such as calcium carbonate are allowed in both cements. For the investigations reported below, a binder containing 80% blast furnace slag, 15% cement and 5% calcium hydroxide was used.

The cement was a CEM II/A-LL 32.5 R with a very low content of alkalis (Table 1). A high alkali content would require a high amount of

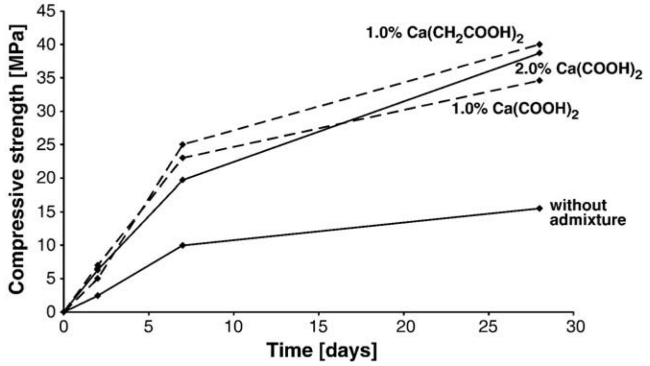

Fig. 8. Comparison of compressive strength development when using calcium acetate and calcium formate for accelerating a binder consisting of 85% slag, 10% calcium hydroxide, and 5% calcium carbonate.

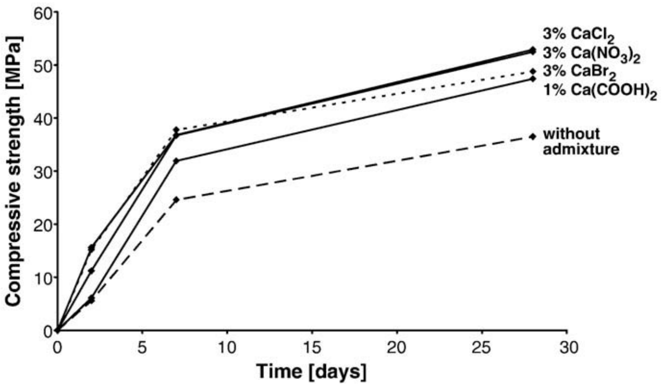

Fig. 10. Influence of chemical admixtures on mortar strength of a binder consisting of 80% blast furnace slag, 15% CEM II/A-LL, and 5% calcium hydroxide.

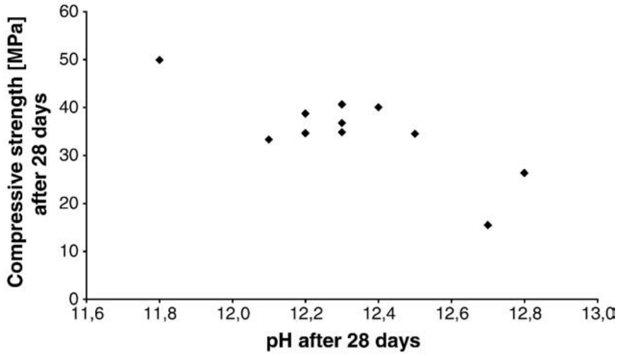

Fig. 11. Compressive strength of mortar bars and pH in pore solution after 28 day hydration of a blend of slag, calcium hydroxide and calcium carbonate with different admixtures.

calcium salts to lower the pH value. Preference was given to CEM II/A-LL instead of pure Portland cement CEM I. Limestone present in CEM II/A-LL can replace calcium carbonate that was used for the production of the binder described in the first part of this study. Beside this, an increased amount of calcium carbonate may be beneficial for reducing the induction period before the precipitation of C–S–H starts and may thus be able to improve the strength development. Calcium hydroxide was also included in the mix (5%).

The compressive strength of the aforementioned blend was measured (Table 2) and compared to the performance of the binder composed of slag, calcium hydroxide and calcium carbonate (Fig. 9).

The data displayed in Fig. 9 shows that the compressive strength of the binder is significantly enhanced by the addition of 15% cement. The final strength is increased from 16 MPa to 36 MPa after 28 days. Even without addition of admixture, the blend of 80% slag, 15 CEM II/A-LL and 5% calcium hydroxide passes the requirements for strength class 32.5. A further increase of compressive strength can be obtained by adding admixtures. Again, easily soluble calcium salts were used, namely calcium chloride, calcium bromide, calcium formate and calcium nitrate. The results obtained by these tests are provided in Table 2 and Fig. 10.

It can be inferred from Fig. 10, that all soluble calcium salts used in this investigation were able to accelerate the reaction of a binder consisting of slag, Portland limestone cement, and calcium hydroxide. Besides the slag activation, also the hydration of the clinker fraction is stimulated by calcium salts. Final strengths between 47 and 53 MPa are obtained after 28 days. In the early stage, the strength depends much on the anion of the calcium salt. Strengths below 10 MPa are obtained for organic anions. The addition of salts with inorganic ions such as calcium chloride, calcium bromide and calcium nitrate enables the production of mortar with compressive strength higher than 10 MPa after 2 days.

4. Discussion

The aforementioned results have shown that it is possible to activate blast furnace slag by low pH values in the pore solution in the presence of calcium hydroxide. Pure slag blended with calcium hydroxide and calcium carbonate showed mortar strengths up to 50 MPa after 28 days. The pH values in the pore solution after 28 days are plotted against the compressive strength after 28 days in Fig. 11. The data shows that pH has a major impact on compressive strength under the conditions used in this study. The highest strength is obtained at the lowest pH in the pore solution. However, some other effects are at play and there is no straight line observed for the interrelation of compressive strength-pH in solution.

The performance obtained here allows for the production of cement with a high final strength containing a very high content of blast furnace slag. Corrosion of steel reinforcement has to be avoided by proper selection of chemical admixtures. Therefore, the use of calcium chloride or calcium bromide has to be neglected. Instead, organic calcium salts such as calcium acetate and calcium formate should be employed. In all samples investigated in this study, the pH in pore solution was higher than the threshold level for reinforcement corrosion. According to Taylor [1] and Metha and Monteiro [9] corrosion will not take place at pH values higher than 11.5. However, the pH values obtained in this study are much lower than observed when blast furnace slag is activated by the maintenance of a very high pH (13.0–14.0). This indicates a reduced resistance to chloride induced pit hole corrosion.

Using a selective dissolution technique it was shown that a high degree of slag consumption correlates with a high compressive strength.

The early strength development can be increased by adding more clinker to the blend. Testing has to be repeated at a water/cement-ratio of 0.50 but requirements of strength class 42.5 can be met at higher amounts of clinker.

5. Conclusions

Blast furnace slag is usually activated by mixing with Portland cement clinker. At very high pH values (>13.0) corrosion of the slag particles is enhanced and the reaction of blast furnace slag is accelerated. Alternatively, the use of low pH values (11.8–12.4) was investigated in this study. It has been shown that activation is possible by the addition of calcium hydroxide and soluble calcium salts. The addition of calcium hydroxide has two benefits. First, it acts as reactant precipitating aluminium in an AFm phase. Second, in the presence of calcium hydroxide, soluble calcium salts can decrease pH in the pore solution as long as the equilibrium condition of calcium hydroxide is maintained.

It is demonstrated for selected binders that higher compressive strength is linked to a higher degree of slag consumption and a higher heat release during hydration.

Inorganic salts such as calcium chloride and calcium bromide have the disadvantage that their anions stimulate corrosion of steel reinforcement. Organic substances such calcium acetate and calcium formate are helpful to enhance late strengths but less effective than the inorganic calcium salts.

The aforementioned concept can be used to improve the performance of slag cements containing very high amounts of slag.

References

[1] H.F.W. Taylor, Cement Chemistry, Thomas-Telford, London, 1997.
[2] M. Moranville-Regourd, Cements made from blast furnace slag, in: P.C. Hewlett (Ed.), Lea's Chemistry of Cement and Concrete, Arnold, London, 1998, pp. 633–674.
[3] E. Lang, Blast furnace cements, in: J. Bensted, P. Barnes (Eds.), Structure and Performance of Cements, Spon Press, London, 2002, pp. 310–325.
[4] F.P. Glasser, Chemical, mineralogical, and microstructural changes occurring in hydrated slag-cement blends, in: J. Skalny, S. Mindess (Eds.), Materials Science of Concrete II, American Ceramic Society, Westerville (Ohio), 1991, pp. 41–81.
[5] J. Lukasik, J.S. Damtoft, D. Herfort, D. Sorrentino, E.M. Gartner, Sustainable development and climate change initiatives, in: Proceedings of the 12th International Congress on the Chemistry of Cement, 8.-13.7.2007, Montreal, MPL-1.
[6] T. Matschei, F. Bellmann, J. Stark, Hydration behaviour of sulphate-activated slag cements, Adv Cem Res 17 (4) (2005) 167–178.
[7] J.F. Young, A review of the mechanisms of set-retardation in Portland cement pastes containing organic admixtures, Cem Concr Res 2 (4) (1972) 415–433.
[8] J.S. Lumley, R.S. Gollop, G.K. Moir, H.F.W. Taylor, Degrees of reaction of the slag in some blends with Portland cement, Cem Concr Res 26 (1) (1996) 139–151.
[9] P.K. Mehta, P.J.M. Monteiro, Concrete, (2nd ed.), McGraw-Hill, New York, 1993.