

ALKALINITY CHANGE DURING HYDRATION OF THE BLAST FURNACE SLAG - FLY ASH COMPOSITES

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The alkalinity change of the alkaline activated blast furnace slag alone (a dose of 3 wt.% of Na₂O) and of the composites containing up to 20 wt.% of the fly ash component is nearly the same and ranges from the pH value 11.43 after 3 days of hydration to the value of approx. 11.2 after 42 days of hydration. An increase of the fly ash content (up to 60 wt.%) decreases the internal pH values approx. by 0.2 at each respective time of hydration.

INTRODUCTION

Alkaline cements including alkaline activated blast furnace slag (BFS) cements exhibit in generally higher mechanical strength, lower porosity and increased resistance to corrosion in comparison to the portland cements (PC) [1,2,3]. They can be blended with some highly disperse particulates (pozzolanic additives) without impairing their mechanical properties significantly, what may contribute to the economy of their exploitation [4].

The mineral particulates are less alkaline than clinker minerals of the PC, or an activator solution of the BFS cements. They tend to reduce OH⁻ content of the pore solution during hydration and consequently reduce the pH - a measure for the stability of siliceous components included into corresponding matrices.

Alkali content, as transmitted through pore solution, affects the nature of solids formed as well as the microstructure of the cement stone and affects the course of reaction between cement and other embedded solids [5]. The hydrous precipitated phases at hydration of alkali activated cements, are alkaline hydroaluminosilicate gels $\text{Me}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot (2-4) \text{SiO}_2 \cdot n \text{H}_2\text{O}$ ($\text{Me}_2\text{O} = \text{Na}_2\text{O}, \text{K}_2\text{O}$) which convert in time to zeolite type minerals being more stable and more durable than calcium hydrosilicates [6].

A pore solution chemistry at hydration of ordinary portland cements (OPC) is fairly well documented [5,7-11]. The information about the pore solution chemistry of alkaline activated cements is scanty. It is presumed that the pH at hydration of BFS cements is rather high, as high as favouring the formation of zeolites (pH = 13.5) [12].

High internal pH at hydration of OPC is more or less deleterious to the durability of glass fibers in corresponding cement matrices [13].

The purpose of the present investigation was to determine changes in pH at hydration of the alkali activated blends composed of the BFS and fly ash, at a relatively low dose of alkali, and to compare them with pH changes at hydration of the OPC.

The results will make possible an preliminary assessment of the durability of glass fibers in the composite BFS matrices.

EXPERIMENTAL PART

An alkaline activator was prepared from the commercial water glass solution ($S_M = \text{SiO}_2/\text{Na}_2\text{O} = 3.3$, $\rho = 1.346 \text{ g.cm}^{-3}$) and a 50% solution of NaOH ($\rho = 1.550 \text{ g.cm}^{-3}$) to $S_M = 1.9$. A content of the activator was set to introduce 3 wt.% of Na₂O to a hydrating system respective to the content of dry components. Water was added in preparing casts in order to keep the constant fluidity of the cement paste. The ratio of liquid to solid phases was kept in the range of 0.3 to 0.35 allowing for the increased water intake by the fly ash.

Cement casts (2 × 2 × 2 cm) were demoulded after 24 hours hydration in the moist air at room temperature and were left for further hydration in the moist air at 22 °C for the specified time.

The bulk densities of samples were measured from their weight and dimensions.

Fragments of samples after compressive tests were vibratory milled and used for preparation of cement suspensions for pH measurements. The suspensions contained 0.5 grams of the milled sample in 100 ml of distilled, freshly boiled and cooled water. The suspensions were kept in plastic vessels covered by thin PE foil at room temperature and frequently mixed. The pH of suspensions was measured in irregular intervals

during 125 days (Digital pH meter CPH 51 - Monokrystal Turnov, glass electrode HC 103). The initial values of suspensions were measured 10 seconds after mixing of the powder obtained from the hydrated sample with water.

RESULTS AND DISCUSSION

The chemical composition and further characteristics of basic raw materials are given in table 1. The composition of blends is given in table 2 and the average bulk densities of hydrating casts are given in table 3.

An increased content of the fly ash decreases the bulk densities of hydrating samples. On the other hand a slight expansion may be inferred until 14 days of hydration with an increase in bulk densities at further hydration. Reference samples of casts made from OPC and a pure water show an homogeneous increase in bulk densities since the origin of hydration.

Table 1. Chemical composition and physical characteristics of the raw materials.

| oxides | BFS (wt.%) | fly ash (wt.%) |
|--|-------------------------------------|--|
| LOI | 0.61 | 1.95 |
| CaO | 41.42 | 2.94 |
| SiO ₂ | 37.81 | 53.25 |
| Al ₂ O ₃ | 7.03 | 26.21 |
| Fe ₂ O ₃ | 0.61 | 6.93 |
| MgO | 8.89 | 2.39 |
| Na ₂ O | 0.10 | 0.13 |
| SO ₃ | 1.39 | 3.44 |
| granulometry | | |
| > 0.1 mm | 3.02 | 6.75 |
| 0.1-0.063 mm | 21.63 | 26.66 |
| < 0.063 mm | 75.05 | 66.18 |
| specific surface (m ² kg ⁻¹) | 290 | 500 |
| mineralogical composition | glass (akermanite- gehlenite) | glass mullite quartz (cristoballite) |

Table 2. Composition of blends (wt.%).

| sample | BFS | fly ash |
|--------|-----|---------|
| S-1 | 100 | 0 |
| S-2 | 95 | 5 |
| S-3 | 80 | 20 |
| S-4 | 60 | 40 |
| S-5 | 40 | 60 |

Table 3. Bulk densities of hydrating samples (g cm⁻³).

| | hydration (days) | | | | |
|-----|------------------|------|------|------|------|
| | 3 | 7 | 14 | 28 | 42 |
| OPC | 1.98 | 2.04 | 2.08 | 2.06 | 2.07 |
| S-1 | 2.07 | 2.06 | 2.06 | 2.07 | 2.08 |
| S-2 | 2.04 | 2.03 | 2.01 | 2.05 | 2.08 |
| S-3 | 2.01 | 2.00 | 1.99 | 2.03 | 2.05 |
| S-4 | 1.99 | 1.98 | 1.97 | 1.99 | 2.02 |
| S-5 | 1.92 | 1.91 | 1.91 | 1.92 | 1.93 |

Compressive strength of the BFS/Fly Ash composites

According to the figure 1 the compressive strength of the low filled BFS/fly ash composites exceeds significantly the compressive strength of samples made from OPC, containing no filler. The early strength (3 days) and the further strength development may be quite indicative for a differentiation among individual cements. Low and medium additions of the fly ash enhance the early strength of composites the strength increase in the next period hydration is relatively low. Higher additions decrease the early strength in comparison to the pure BFS, but the strength increase (up to 42 days) is continuous and quite appreciable. We may speculate that the addition of the fly ash in amount of ca 50 wt.% may lead to a fair compromise economizing the overall building material cost at acceptable early strength parameters a significant strength development at the next hydration. Only at 60% of fly ash in the mixture (S-5) a strength in the initial period of hydration is appreciably lower than a strength of the OPC samples. After 42 days of hydration, also in this case a strength of the composite is still higher than 45 MPa. A scatter of experimental strength data was found to be on the level of approx. 2-3 MPa.

A partial conclusion can be made from the strength data in a sense that already a content of 3 wt.% of Na₂O, introduced by the alkaline activator, brings about the appreciable compressive strength development of the BFS/fly ash composites and, secondly, as much as 40% of the BFS component can be substituted in created mixtures by the applied low cost waste material not impairing the strength of the composite significantly.

Changes in the alkalinity during hydration

An alkalinity of hydrating mixtures S-1 to S-5 is a result of reactions between BFS, fly ash and the alkaline solution. The initial measured *pH* characterize an amount of unbound alkalis of powdered composite cements after

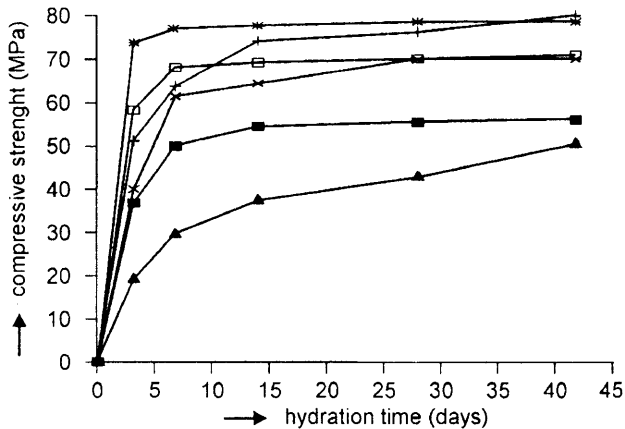


Figure 1. Compressive strength of BFS/fly ash composites and OPC in dependence on time of hydration.

+ - S-1; * - S-2; □ - S-3; × - S-4; ▲ - S-5; ■ - PC

certain periods of their hydration, liberated into solution. It is believed that such a pH value is directly proportional to the internal pH of the pore solution.

The measured initial pH values are given in figure 2. Figure 3 shows changes of original pH values when keeping the respective cements in suspensions for a prolonged time.

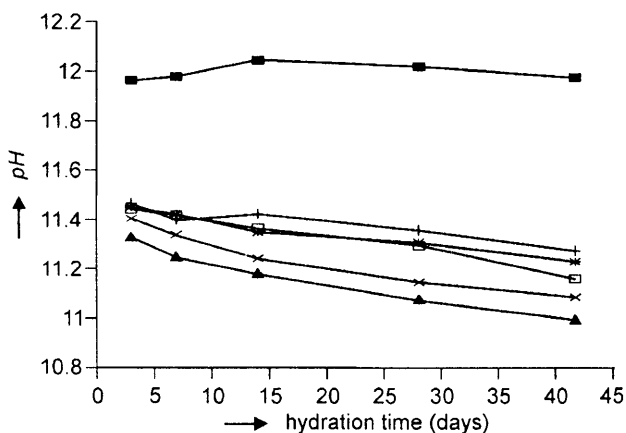


Figure 2. Initial pH values (10 seconds after mixing) of hydrated samples water suspensions.

+ - S-1; * - S-2; □ - S-3; × - S-4; ▲ - S-5; ■ - PC

From results summarized in figure 2 following conclusions can be made:

- the initial pH values of suspensions after 3 days of hydration are at a level of 11.35 - 11.45, what are values a half an order lesser than values for reference samples prepared from OPC.
- for all mixtures a decrease in initial pH values with

a time of hydration is observed what is a result of the expected depletion of free alkalis in the hydration process.

- the pH change in hydration is very similar for the pure BFS matrix and matrices with low additions of fly ash (up to 20%).
- higher fly ash additions lead to the well resolved pH decrease in the whole observed period of hydration.

A sample of the cement suspension prepared from OPC in an analogous way shows the initial pH after 3 days of hydration equal to 11.95 with a moderate increase after 7 and 14 days of hydration. This value is comparable to the pH of the pore solution expressed after 10 month of hydration of the OPC containing 20% of silica fume [7]. Other tested PC shown the higher (13.1-13.6) pH values [7,8]. The next expected pH increase due to portlandite formation was not observed because of the lack of the N_2 protection and a reaction of portlandite with CO_2 to calcium carbonate. The presence of calcium carbonate in suspension was seen by the presence of white flakes.

From measurements performed the significantly lower alkalinity of the simple slag cement as well as of the two component slag-fly ash composites can be seen in comparison to cement matrices of the OPC. After 42 days of hydration of the OPC pH of the hardened cement paste is approximately one order higher than pH of the composites with a higher content of fly ash (mixtures S-4 and S-5).

As mentioned figures 3a to 3e contain pH values of suspensions in dependence on the leach time in water. In all cases a certain, temporal increase of pH is observed. This indicates that in diluted suspension better conditions for a release of alkalis to the solution exist than to their incorporation into hydration products. pH in leach tests increased about 0.1 to 0.25. The peak value achieved was 11.60.

Next course is characterized by a decrease of suspensions pH values. The decrease is not always monotonous but is steady in time in all cases. At S-1 sample without fly ash pH decrease is slow (after 90 days to minimum of 10.30 and after 125 days up to 9.70). Samples S-2 and S-3 (5 and 20% of the fly ash) exhibit almost equal decrease of pH , higher that at a pure slag matrix S-1. After 125 days the shortly hydrated samples (e.i. introduced into suspension after 3, 7 or 14 days of hydration) coincide in their pH values at a level of 9.00 to 9.10. For mixtures with a higher content of the fly ash equal level of pH is reached sooner, e.i. after 90 days of leaching, or already after 80 days of leaching, whereas there is no change of the pH in the next period of leaching. To pH value of 9.0 would apparently follow also pH values of these mixtures hydrating for a longer time.

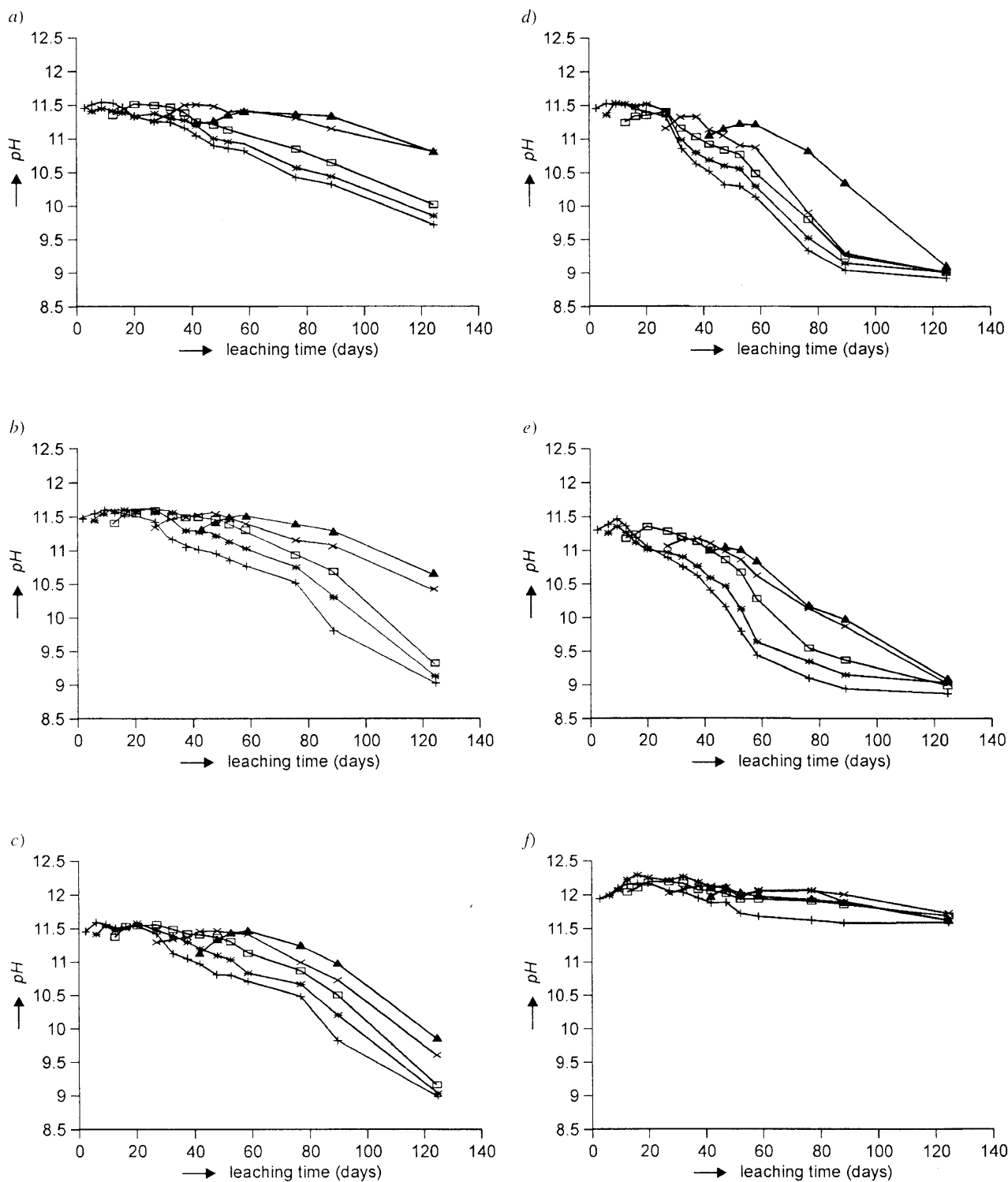


Figure 3. Changes in *pH* values of BFS/Fly Ash composites and OPC suspensions on time of leaching.

a) S-1, b) S-2, c) S-3, d) S-4, e) S-5, f) PC

(time of hydration: + – 3 days; * – 7 days; □ – 14 days; × – 28 days; ▲ – 42 days)

Lowering of *pH* in leach tests indicates the ability of solids "to consume" alkalis. It is possible either by a reaction of alkalis to form low soluble sodium hydro-

aluminates and hydrosilicates or by a sorption to pozzolanic fly ash particles with a high specific surface. In each instance the fly ash, because of its low calcium

content, is able to accommodate a higher portion of alkalis than the slag itself what is ascertained by the pH value of the respective mixtures after the longer periods of hydration.

At reference samples of hydrated cement pastes pH values in leach tests (figure 3f) are in a range from 12.25 to 11.60 and the decrease of pH after certain time of hydration depends again on a formation of CaCO_3 issuing from $\text{Ca}(\text{OH})_2$.

CONCLUSIONS

Composites from industrial wastes which include milled granulated blast furnace slag and as received fly ash show good strength characteristics already at a low dosage of the alkaline solution (3 wt.% of Na_2O) at preparation of cement casts.

The alkalinity of composite matrices after 3 days of hydration is approximately half an order lower and in 42 days hydration as much as one order lower in comparison to reference samples from OPC. The bonding of alkalis into newly formed phases is stable what results in a levelling of pH values at $pH = 9.5-9.7$ for samples with a low content of fly ash and at values equal 9.0 for samples with a high content of fly ash.

The results indicate the essential difference for an alkalinity change in hydration of the OPC cement and of the presently studied composites. The alkaline component of the composites is exhausted in hydration leaving the low pH of matrices what might be especially suitable in a case of glass fibre reinforced composites.

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ZMĚNA ALKALITY BĚHEM HYDRATACE KOMPOZITU Z VYSOKOPECNÍ STRUSKY A ELEKTRÁRENSKÉHO POPÍLKU

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Alternativním pojivem, nahrazujícím běžné cementy, může být jemně mletá vysokopecní struska (granulovaná, skelná), jejíž hydraulické vlastnosti se nabudí prostřednictvím roztoků některých sloučenin alkalických kovů, především Na. Tyto tzv. struskoalkalické cementy se po zatuhnutí vyznačují vysokými počátečními i dlouhodobými pevnostmi, nízkou pórovitostí a zvýšenou odolností vůči korozi. Přídavek elektrárenského popílku do směsi zvyšuje ohybové pevnosti hmot. Během hydratace do přidáné alkalické roztoky podléhají na tvorbě stabilních hydratačních produktů - CSH fází a hydroalumosilikátů sodných - přičemž nevznikají ani $\text{Ca}(\text{OH})_2$ ani AF_1 fáze jako při hydrataci portlandských cementů. Vysoké pH matrice hydratujícího PC výrazně snižuje pevnost a tím i použitelnost skleněných vláken, aplikovaných jako výztuž.

Záměrem práce bylo porovnat pH těchto hmot s hodnotami pH maticí vytvořených z alkalicky aktivovaných směsí vysokopecní strusky a elektrárenského popílku. Připravily se vzorky ze strusky a jejich směsí s popínkem až do obsahu 60 % popílku, prostřednictvím roztoků vodního skla s modulem $S/N = 1.9$, při dávkě 3 hmot. % Na_2O vzhledem k tuhým složkám. V termínech 3, 7, 14, 28 a 42 dní hydratace se stanovily objemové hmotnosti a pevnosti v tlaku. Úlomky po pevnostních zkouškách se mlyly ve vibračním mlýně a pro sledování pH se připravily suspenze 0,5 g vzorku ve 100 ml destilované vody. pH suspenzí se měřilo kombinovanou skleněnou elektrodou během 125 dní.

Pevnostní zkoušky prokázaly velmi dobré mechanické vlastnosti všech kompozitů, s hodnotami pevností v tlaku od 40 do 80 MPa po 28 dnech. Okamžité hodnoty pH v 10. sekundě po přípravě suspenzí byly od 11,35 do 11,45 (po 3 dnech předchozí hydratace) a poklesly na 11,30 až 11,00 po 42-denní hydrataci kompozitu. Tyto údaje pH odpovídají množství volných, nevázaných alkálií v matici, jejichž podíl tedy klesá s dobou hydratace. Oproti porovnávacím vzorkům z PC jsou tyto hodnoty pH nižší o 0,5 až 1 řád. Během vyluhování vzorků v suspenzích (konstantního objemu a teploty, často promíchávaných) se zjistil malý krátkodobý nárůst pH o 0,1 až 0,25 v důsledku uvolnění dalších alkálií. Následná etapa loužení vzorků je spojená se soustavným klesáním pH . U kompozitů s nízkým podílem popílku klesne pH po 125 dnech na 9,0 až 9,2 pro krátkodobě hydratované vzorky (3, 7 nebo 14 dní), o něco vyšší ještě zůstane pH pro později připravené suspenze (déle hydratující vzorky). Směsi S-4 a S-5 s velkým podílem popílku vykazují rychlejší pokles pH : na úroveň 9,0 už po 90, resp. 85 dnech, po 125 dnech už u všech vzorků. Snižování pH při vyluhovacích testech svědčí o schopnosti systému "konzumovat" alkálie, t.j. vázat je do málo rozpustných hydratačních produktů nebo sorbovat na povrchu přítomných fází, a to ve větší míře při vyšším zastoupení popílku v kompozitech. V suspenzích porovnávacích vzorků z PC bylo pH stále okolo 12, s mírným poklesem asi na 11,60 při zreagování vyloučeného $\text{Ca}(\text{OH})_2$ na CaCO_3 .

Velmi dobré mechanické pevnosti a nižší úroveň pH maticí dovoluje uvažovat o využití těchto kompozitů pro přípravu stavebních prvků armovaných skleněnými vlákny.