SYNERGIC EFFECT OF NON-CLINKER CONSTITUENTS IN PORTLAND COMPOSITE CEMENTS

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Abstract
EN 197-1 Standard specifies eight non-clinker constituents for common cement production: granulated blast furnace slag (S), natural pozzolana (P), natural calcined pozzolana (Q), siliceous fly ash (V), calcareous fly ash (W), burnt shale (T), limestone (L, LL), silica fume (D). Mentioned non-clinker constituents should be used for composite cements production, which in opposite to Portland cements CEM I, contain one or more non-clinker constituents. Portland composite cements CEM II, composite cement CEM V and blast furnace slag cement CEM III amount to 60% European commercial scale of cement production. In respect of demands to reduce CO$_2$ emission in cement industry, further development of composite cements production can be anticipated. Respectively, composite cements containing lower content of energy-consuming Portland clinker are subject of comprehensive research works on their properties and building application conditions. In this paper, part of very extensive research works on Portland composite cements CEM II/B are presented. Cements CEM II/B containing only one non-clinker constituent and cements CEM II/B-M containing two or three non-clinker constituents have been analyzed. The normative properties of Portland composite cements containing one, two or three non-clinker constituents have been compared. Additionally, the performance quality data of concrete made of these cements, covering durability tests on carbonation corrosion, chloride penetration and sulfate resistance have been discussed.

Originality
It was stated that normative mechanical and physical properties of Portland composite cements CEM II/B-M containing two or three non-clinker constituents are generally better than cements containing only one non-clinker constituent. The same result was observed for performance properties, which stimulate durability of concrete. The synergic effect was especially clearly observed for CEM II/B-M (S-V) and CEM II/B-M (S-LL-Q). This phenomenon could be explained by microstructure SEM observation and phase composition determinations of mortar and concrete after curing in different exposure classes. The Portland composite cements containing two or three properly chosen and composed constituents give cement matrix and interface zone providing better concrete durability. The most important reason in creating better properties of analyzed Portland composite cements is probably very dense microstructure cement hydration product with specific forms of C-S-H phase.

Chief contributions
The production and usability of composite cements in concrete technology are subject of comprehensive research works. The development of blended cement production is a great driving force by possibility of energy saving and CO$_2$ emission decreasing in cement industry. Blended cements in European market amount of 60% of cement production. Depending on historical experience of the industry in any country, very different non-clinker constituents are used, most common are: siliceous fly ash, granulated blast furnace slag and limestone. In the presented paper, blended cements containing fly ash, slag, limestone and some kind of pozzolana (Q) were taken into consideration. Original compilations of mentioned constituents in composite cements were explored and analyzed. New interpretation of very good properties of these binders was given.

The research works realized for new kind of Portland composite cements very clearly confirmed synergic effect of non-clinker constituents in stimulation of normative and performance properties. The result in this matter gives possibility to produce high quality composite cements with minimization of energy consumption and CO$_2$ emission per unit of product.

Keywords: Portland composite cement, non-clinker constituent, synergic effect

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Introduction

Cements with non-clinker constituents become more popular in construction practice. Rapid production increase of composite cements containing one or more mineral constituents is especially observed in last decade. Manufacturing of such cements leads to reduction of cement cost production by supplementing some ordinary Portland cement clinker part with non-clinker constituents. On the other hand, great development’s dynamic of cements with mineral constituents production is connected with CO$_2$ tasks related with emission of carbon dioxide from production processes. Keeping CO$_2$ emission limits has to be taken into consideration in amount of cement production. Tendencies of development of composite cements production observed in Europe countries are presented in Figure 1a. In United Europe countries the production amount of this cements type reaches almost 70% of total cement manufacturing.

Different non-clinker constituents for composite cement manufacturing are used in several countries, depending on local experience and tradition of cement industry. EN 197-1 Standard specifies eight non-clinker constituents for common cement production: granulated blast furnace slag (S), natural pozzolana (P), natural calcined pozzolana (Q), siliceous fly ash (V), calcareous fly ash (W), burnt shale (T), limestone (L, LL), silica fume (D). Limestone LL, siliceous fly ash V and slag S Portland cements are most frequent manufactured Portland composite cements in CEMBUREAU countries. Especially large amounts of limestone are used for composite cement production. These cements are main product in France, Italy and Denmark. Portland composite cements with more than one non-clinker constituent significantly participate in cements production in CEMBUREAU countries, Figure 1b.

Requirements in reducing clinker content in cements leads to extended researches on new types of cements containing large amounts up to 80% of two or more non-clinker constituents. Composite cements CEM X are considered as a new type of CEM V composite cements containing also, besides slag and pozzolanic constituents V, P, Q other constituents according to EN 197-1 Standard. Especially cements with LL are intensively examined. Work on this field, conducting by European Committee for Standardization CEN/TC 51 is presented in diagrams - Figure 2.

Performance properties of composite cements are next very main factor of their development progress. It was proved that some mechanical and physical properties of composite cements containing non-clinker constituents are better than these observed for Portland cement CEM I. Such cements give concrete and mortar with good mixture rheological properties, good mechanical properties and high corrosion resistance of aggressive medium. Particularly advantageous are obtained for composite cements with two or more non-clinker constituents. This synergic effecting, so beneficial creating the cement parameters due to each constituent interaction on properties is especially visible for slag-fly ash composite cements (Chladzynski, Garbacik, 2008).

Properties of chosen cements with non-clinker constituents, in particular CEM II/B-M cement types containing at least two mineral constituents were presented in this paper. There were cements with
granulated blast furnace slag (S), siliceous fly ash (V), natural calcined pozzolana (Q), and limestone (LL). Typical normative cements properties were compared. Original compilations of mentioned constituents in composite cements were explored and analyzed. Chosen results from wide performance properties examinations of concrete made of these cements were included in synergic effect analysis.

Materials

For investigation, the following Portland composite cements were used:

- Portland composite cements containing composition of non-clinker constituents: CEM II/B-M (S-LL), CEM II/B-M (S-Q), CEM II/B-M (S-V) and CEM II/B-M (S-LL-Q);
- Reference cements – Portland composite cements containing only one non-clinker constituent: CEM II/B-LL, CEM II/B-S, CEM II/B-V and ordinary Portland cement CEM I.

All mentioned cements were produced in the semi-industrial scale by means of ball mill with capacity of 100 kg. Blending system of initially ground ordinary Portland cement clinker with non-clinker constituents was applied for constant proportion 70% clinker and 30% non-clinker constituents and for constant mixing time 5 minutes. Proportions of CEM II/B-M cements constituents were kept for 1:1 or 1:1:1 ratio. Addition of gypsum as a setting time regulator provided constant 3% SO$_3$ content in cements. All materials for composite cements production are characterized in Table 1.

<table>
<thead>
<tr>
<th>Material/parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Ordinary Portland cement clinker</td>
<td>Industrial product; Finenesses Blaine - 3800 cm$^2$/g; Phase composition: C$_3$S - 60%, C$_2$S - 18%, C$_3$A - 9%, C$_4$AF - 9%; Na$_2$O - 0.81%; CaO - 1.5%</td>
</tr>
<tr>
<td>Granulated blast furnace slag (S)</td>
<td>Glassy phase - 98.5%; Initial (ground) finenesses Blaine - 4000 cm$^2$/g; CaO+MgO/SiO$_2$ ratio - 1.41; Al$_2$O$_3$ content - 7%</td>
</tr>
<tr>
<td>Siliceous fly ash (V)</td>
<td>Finenesses Blaine - 3800 cm$^2$/g; Finenesses, residue on 45 µm sieve - 36%; LOI - 3.5%; Unburnt carbon - 3.5%; Free calcium oxide - trace; Activity index - $K_a$ - 81%, $K_w$ - 90%</td>
</tr>
<tr>
<td>Natural calcined pozzolana (Q)</td>
<td>Calcined coal ash from FBC system; Finenesses Blaine - 4000 cm$^2$/g; LOI - 3.15%; Phase composition: Quartz, Metakaolinite, Anhydrite - 13%, Illite, Calcite - 3.6%, Free calcium oxide - 3%, Hematite</td>
</tr>
<tr>
<td>Limestone (LL)</td>
<td>Finenesses Blaine - 6000 cm$^2$/g; CaCO$_3$ content - 91%; TOC - 0.06%; Clay content - 0.15g/100g</td>
</tr>
<tr>
<td>Gypsum additive</td>
<td>Chemical gypsum; CaSO$_4$$\times$2H$_2$O - 95.5%; Finenesses Blaine - 4500 cm$^2$/g</td>
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</table>
Scope of determination and testing method

The following examinations for cements quality assessments were done:
- Normative mechanical and physical properties according to EN 196-1 and EN 196-3 Standards;
- Heat of hydration according to EN 196-9;
- Durability properties: sulfate resistance (P 18-837), carbonation resistance (EN 13295), chloride penetration (AASHTO T259-80);
- Microstructure of hardened cement matrix by SEM methods.

In the paper mechanical properties, durability performance criteria and microstructure observations are discussed.

Results and discussion

1. Mechanical properties of composite cements

Relation of compressive strength development of Portland composite cements containing one or more non-clinker constituents is shown in Figure 3.

![Figures showing compressive strength curves of different composite cements](image)

Figure 3: Compressive strength of composite cements

Compressive strength curve of Portland fly ash cement CEM II/B-V is typical for cement with pozzolanic constituent. Slow rate of strength increasing in first 28 days of hardening and high strength increasing after long hardening time is observed. This relation is created by pozzolanic reaction during hardening process. Similarly, slow strength increase in first days is also observed for Portland slag cement CEM II/B-S. High strength increase of this cement in longer period is mainly contributed to pozzolanic-hydraulic reaction. Portland limestone cement CEM II/B-LL has different strength increasing characteristic. CEM II/B-LL indicates good early strength and very poor strength increase in long term of hardening, Figure 3a. 28 days compressive strength of limestone cements decreases proportional to limestone addition in cement (Chladzynski, Garbacik, 2008).
Influence of slag S, fly ash V, limestone LL and pozzolana Q addition on compressive strength of composite cements is observed more intensive for cements containing two or more non-clinker constituents. That synergic effect is very clearly confirmed by data presented in Figures 3b,c,d. Synergic effect is particularly noticeable for fly ash-slag cements. Compressive strength of CEM II/B-M (V-S) is significantly higher than cements CEM II containing only one mineral constituent: slag or fly ash, Figure 3b.

It might be assumed that presented synergy effects of non-clinker constituents in composite cements are correlated with modification of hydration process and microstructure of cement hydration products and creating non-additive properties. Results of concrete examinations made of composite cements can prove this thesis.

2. Performance properties of concretes

Literature confirms good influence of composite cements on concrete properties (Al-Dulaijan et al., 2003, Giergiczny, Sokolowski, 2008, VDZ Congress, 2009, Wolter, 2010b). Portland composite cements CEM II/M, depending on non-clinker constituent type can achieve compressive strength similar to Portland cement CEM I, improve workability of concrete mix and create better durability properties of concrete, especially chemical resistance parameters (Muller, 2006).

Concrete made of cement with limestone, pozzolana, fly ash and/or granulated blast furnace slag give more compacted matrix structure with lower permeability created on the physical (filler effect) and chemical (hydration products) way. Pozzolanic reaction products, which seal cement matrix have dominating role in limiting chloride ion diffusion stream. Diffusion coefficient for concretes made of pozzolana-slag cements is significantly lower than for limestone cements (Muller, 2006). Test results presented in Figure 4 confirm these relations. Stream of chloride diffusion in concrete made of pozzolana-slag cements is almost stopped after long time of hardening process. Similar relations are observed for CEM II/B-M (S-Q) versus CEM II/B-LL composite cements for carbonation depth data listed in Table 2.

![Figure 4: Chloride penetration in concretes made of limestone and pozzolana-slag composite cements after 8 months of curing in 3% NaCl](image)

Table 2: Depth of concrete carbonation

<table>
<thead>
<tr>
<th>Cement</th>
<th>3 months</th>
<th>8 months</th>
<th>3 months</th>
<th>8 months</th>
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<tbody>
<tr>
<td>CEM I</td>
<td>&lt;0,1</td>
<td>1,18</td>
<td>0,14</td>
<td>1,61</td>
</tr>
<tr>
<td>CEM II/B-LL</td>
<td>0,45</td>
<td>4,64</td>
<td>2,10</td>
<td>19,88</td>
</tr>
<tr>
<td>CEM II/B-M (S-LL)</td>
<td>1,47</td>
<td>4,40</td>
<td>1,78</td>
<td>16,95</td>
</tr>
<tr>
<td>CEM II/B-M (S-Q)</td>
<td>0,49</td>
<td>4,61</td>
<td>1,25</td>
<td>11,67</td>
</tr>
<tr>
<td>CEM II/B-M (S-LL-Q)</td>
<td>0,50</td>
<td>4,58</td>
<td>1,42</td>
<td>13,48</td>
</tr>
</tbody>
</table>
Especially high sulfate corrosion resistance of pozzolana-slag composite cements can be also explained by very dense matrix structure. As it is presented in Figure 5 Portland composite cement containing 15% S and 15% Q shows extremely low expansion in sodium sulfate solution. In comparison Portland composite cement containing limestone LL has significantly worse sulfate resistance. Analysis of microstructure after one year sulfate exposure confirms pozzolanic reaction function in creating very densified, better resistant matrix for chemical attack. SEM observations given in Figures 6-7 show almost absence of sulfate corrosion products in samples made of CEM II/B-M (S-Q) cement. Contrary, cements containing limestone LL loose sulfate resistance properties. In this case large amounts of expansive ettringite and gypsum can be identified, Figures 8-9.

![Figure 5: Expansion of composite cements mortars stored in Na₂SO₄ solution](image)

![Figure 6](image)  
**Figure 6**: Microstructure of CEM II/B-M (S-Q) mortar after sulfate corrosion. No signs of sulfate destruction like breakings or matrix nonpermanence

**Figure 6 Point 1**: Primary flaked ettringite.

![Figure 7](image)  
**Figure 7**: Very adherent structure of interface zone on coarse quartz grain, honeycomb C-S-H phase with low C/S ratio
Figure 8,9: Microstructure of CEM II/B-LL mortar after sulfate corrosion

Figure 8 Point 1: Needle-like ettringite in destroyed area. Figure 9 Point 1: Interface zone of damaged cement matrix on coarse quartz grain with gypsum as a product of corrosion

Conclusions

Presented in this paper results of mechanical properties of composite cements containing two or more of non-clinker constituents confirmed synergic effect of non-clinker constituents on performance properties of cement. Especially synergic effect has been documented for Portland composite cement containing composition of pozzolanic constituents V, Q and slag S. Such relations are proved by examinations of mortar and concrete performance properties.

Synergy effect of mineral constituents in composite cements can be mainly explained by cement matrix microstructure. Important condition in this subject seems to be modeling tight matrix microstructure, which is a result of advantageous physical interaction of particular non-clinker constituents on hydration processes and products, especially in amount and morphology of C-S-H phase with low C/S ratio.

References

- 6th International VDZ Congress. 2009.