

**STRUCTURAL STUDY OF COMPOSITE HIGH-STRENGTH SLAG
CONCRETE CONTAINING BLENDED CARBONATE ADDITIVE**

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Abstract

The X-ray diffraction (XRD) method is applied to analyze the hydration progress of composite slag cement concrete (SPC-BCP) prepared with blended carbonate powder (BCP). This analysis can be used to quantify the amount of basic and specific crystalline and amorphous phases. However, in SPC-BCP containing acid slag, two kinds of amorphous phases (C-S-H and unhydrated slag) are recorded. At a later stage, the positive effect of the applied preliminary mechanical-chemical activation of BCP on the proceeding of physico-chemical interactions is proved. The mechanism of the hydrate process is explained using this modern test method. The analysis results show that a combination of slag Portland concrete with carbonate powder accelerate the hydration of cement minerals and especially C_3S , C_3A and C_4AF . The strength increasing effect of BCP powder is more pronounced in the composite slag concrete (SPC-BCP) than in the composite Portland concrete (PC-BCP). The higher amounts of ettringite (AFt) and calcium monohydrocarboaluminate (Mc) in the SPC-BCP are formed compared to the concrete PC-BCP. These two phases fill pores and increase the compressive strength and the durability.

Key words: *blended carbonate powder, composite slag concrete, crystalline and amorphous phases, compressive strength*

1. INTRODUCTION

It is known that the cement industry releases about 7 % CO_2 of the total amount of harmful emissions on a global scale and strongly pollutes the environment with detrimental damages to human health, [1]. In this context, it is a well-considered scientific strategy to minimize the mentioned damages by utilization of natural and secondary industrial products either separately or in various combinations as active additives in the production of blended cements and composite high-strength concretes with improved properties.

The new European Standard EN 197-1 (2000) regulates development of blended cements. Natural pozzolana, fly ash, metallurgical granulated slag and natural carbonates are mineral raw materials, which are utilized like active additives, [2]. This Standard identifies four types of blended Portland cements containing limestone in amount from 6 wt. % to 20 wt. % (types II/A-L and II/A-LL) and from 21 wt. % to 35 wt. % (types II/B-L and II/B-LL).

According to U. S. and Canadian Standard requirements, however limestone can be used to reduce the quantity of cement up to 5 wt. %. The additional requirements for the mineral composition are: the calcite content is greater than 75 wt. %, the clay content is less than 1.2 g/100 g and the amount of total organic limestone is less than 0.5 wt. %.

The literature review shows that the behavior of pozzolana, fly ash, metallurgical granulated slag and natural carbonates have been thoroughly investigated in the traditional blended cements and composite

concretes. The important hydration phases are similar to these found in neat Portland cement, but the added of mineral additives may affect on the hydration rate and the stoichiometry of hydration products, [3, 4].

The fast advance of building industry during the last two decades is a basic precondition for the successful utilization of natural carbonates as topical mineral raw materials in the production of highly effective cement construction materials, [5]. Until now, the carbonates make used only as a fillers for concretes, but since 2001 year (application of EN 197-1), they may use like as mineral additives in composition of blended cements and concretes, [6]. These rival qualities are associated with the accelerating of cement hydration and the formation of specific crystalline phases. The latter modifies the mineral-phase composition of cement stone and improves the microstructure, compressive strength and durability.

Metallurgical slag is a by-product from non-ferrous or ferrous metallurgy. It is formed due to the reaction of limestone with materials rich in SO_2 and Al_2O_3 associated with the ore or present in ash from coke. It is a glassy material, which has different latent hydraulic properties. Many researchers devote considerable attention of the slag reactive ability. It is shown that the latter strongly depends of mineral-phase composition, glass amount, grain-size distribution, area and character of the grain surface and some technological factors (temperature, water-to-cement ratio, reducing amount of an additives), [7, 8]. By appropriate choice of the active additive and technology, the metallurgical slag can improve the technological properties and can raise the physico-mechanical properties and durability of concretes [9, 10].

It is known that the cement systems which containing granulated slag, two kinds of amorphous phases are recorded. One of them are the calcium hydrosilicates (C-S-H) formed by the hydration of calcium silicates and slag. The other is unhydrated slag. Both amorphous products show a diffraction halo too in an approximately position around $2\Theta = 31^\circ$ ($\text{CuK}\alpha$) by XRD method.

Some studies are reported about the hydration process of individual cement minerals from slag blended cement. Slag accelerates the hydration of C_3S , [11], but to delays the hydration of C_3A and C_4AF at an early age, [12]. However, studies on the hydration analysis of slag blended cements with natural carbonates have been very limited. One of the aims of this paper is the establishment of the recorded basic hydrate products, specific crystalline hydrates and amorphous phases – type, composition, quantitative participation and morphology in slag Portland cement concrete (SPC-BCP) blended with natural carbonate powder (BCP) at different ages - 2, 7, 14, 28 and 90 days.

Another aim is the investigation of the influence of the blended carbonates on the compressive strength of two composite cement systems – Portland cement concrete blended with BCP (PC - BCP) and slag Portland cement concrete blended with BCP (SPC - BCP). The effect of mineral additive (BCP) on the hydration of Portland cement has been reported by the same authors, as has the interactions between C_3A and BCP, [13]. They have been reported that the natural blended carbonates increase the strength of Portland cement. This effect is especially significant in the composite slag cement systems, too [14].

2. MATERIALS AND METHODS

2.1 Initial materials

The experiments were carried out with ordinary fine-grained Portland cement concrete (PC) and two composite fine-grained concretes (work composition of 1:3) – Portland cement with blended carbonate powder (PC-BCP) and slag Portland cement with blended carbonate powder (SPC-BCP). The initial materials are: neat Portland cement, natural fine-grained aggregate materials and blended carbonates

as a powder (BCP). The samples are prepared with a constant water-to-cement ratio - $W/C=0.40$ according to BDS 5771-85. The technology of preparation answers of requirements of the Bulgarian State Standard BDS EN 206-1. The mixing and homogenization of the components are topics of special attention, farther. The experimental samples are guarded by temperature 20°C for 2, 7 14, 28 and 90 days. At an each age, the hydration is stopped by immersion into alcohol. It is grinded before being used of the X-ray diffraction analysis.

Portland cement PC 42.5 is produced by the “Devnya” SA to BDS 196-1. The mineral composition is: $C_3S = 59.0\%$, $C_2S = 19.5\%$, $C_3A = 7.2\%$ and $C_4AF = 13.0\%$. The fineness of grinding determined according to the Bulgarian State Standard BDS EN 196-6 is 4.5% . The specific density is 3.16 g/cm^3 , respectively. The normal consistency is 21.0% , the beginning of setting – 2 hours and 5 minutes and the end of setting – 8 hours and 50 minutes.

The natural carbonates with blended composition are used as a natural mineral additive by the present experimental investigation. They are found as non-ore raw material or as a component of the host rocks surrounding ore beds, forming own mineral associations in the Kremikovtsi deposit, [15]. The bulk density is 2.88 g/cm^3 , the specific density is 3.44 g/cm^3 and the dispersity is $7.1\text{ }\mu\text{m}$. The following mineral phases have been identified: calcite, siderite, haematite and impurities. Calcite represents a polymorphic modification of CaCO_3 with bulk density of 2.87 g/cm^3 .

In the selection of mineral raw material type by production of slag Portland cement is preferred an ecological neat slag from non-ferrous metallurgy. This acid granulated slag has graphite-black color and porous structure. The chemical composition is: $\text{CaO} = 23.0\%$, $\text{SiO}_2 = 24.0\%$, $\text{Al}_2\text{O}_3 = 5.0\%$, $\text{MgO} = 1.5\%$, $\text{Fe}_2\text{O}_3 = 36.0\%$, $\text{CuO} = 0.5\%$, $\text{ZnO} = 2.0\%$, $\text{MnO} = 0.9\%$, $\text{Na}_2\text{O} = 1.0\%$, $\text{K}_2\text{O} = 1.0\%$ and $M_0=0.84$. The basic mineral phases have been recorded in it [16]. The presence of melilite (solid solution of gehlenite and okermanite), monticellite, CaO , wuestite and Fe_3O_4 has been proved. Melilite glass represents the basic component in composition of the slag. The specific density of the granulated slag is 3.73 g/cm^3 and the dispersity determines by the Blaine specific surface is $3800\text{ cm}^2/\text{g}$. The slag is produced according to a wet method of granulation. Its basic physico-mechanical parameters are measured using the standard test methods, its chemical activity – by measuring the swelling when treated in alkaline solutions and the released heat of hydration – by differential calorimetric method [17, 18].

2.2. Two-stage technology for the activating of natural blended carbonates

To increase of the reactive activity of the natural carbonates, a separate-stage technology has been applied. Preliminary technological stages are: grinding to a powder with high dispersity, optimizing of the quantity and its mechanical-chemical activation. The fine grinding contributes to significant increase of the specific surface, the surface energy activity of the minerals and their capability of transformation into other phases. In the course of activation, due to the high velocity of mixing the dispersity is an additionally increased and the crystalline-chemical surface features of the carbonate particles are further improved. New surfaces are formed for chemical interactions. At the same time, the chemical bonds in the crystal lattices of calcite and siderite are disturbed. Groups of free radicals and free ions, for example - Ca^{2+} cations and complex anions $(\text{CO}_3)^{2-}$ are formed. Adsorption centers are originated. Enhanced physico-chemical processes are tacked place of phase boundaries as surface wetting, adsorption and dissolution. Hence, the choice of this technological stage successfully ensures the preliminary intensification of hydration process. During the subsequent homogenization of blended carbonate powder with Portland cement or slag Portland cement chemically active products are additionally introduced. They improve the microstructure and physico-mechanical properties of the whole composite cement systems.

2.3. X-ray diffraction analysis

X-ray diffraction is one of the established methods used for identifying, estimating and elucidating the microstructure of cement compositions. It is applied for the quantification of basic hydrated crystalline products and amorphous phases. This method used to follow the kinetic of hydration and the quantitative analysis of hydrated cement products both in the presence and absence of various mineral additives. The XRD measurements are performed using a PHILIPS PW1050 computer-controlled powder diffractometer with filtered $\text{CuK}\alpha$ radiation, operated by 30 kV and 10 mA. Step scanning is applied with a scan speed of 2° /min. The angle interval is varied between 5° and 60° . The samples subjected to X-ray studies are tested after drying, grinding, sifting and pressing by a room temperature.

2.4. Mechanical testing

The compressive strength is determined by means of prismatic test specimens with dimensions $4 \times 4 \times 16$ cm. After removing the moulds at the 24th hour the specimens are cured under standard conditions – temperature $T = 20 \pm 3^\circ \text{C}$ and humidity of the air $W = 70\%$ till the corresponding age of testing – 2, 7, 28 and 90 days. The results are obtained as the mean arithmetic value from the single data of three prisms (6 half prisms).

3. RESULTS AND DISCUSSION

The results of X-ray diffraction analysis of three fine-grained concretes – PC, PC-BCP and SPC-BCP at age of 28 days are summarized in Fig. 1. In control sample PC peaks of hydrate crystalline phases as ettringite (AFt), calcium monosulfoaluminate (AFm), calcium hydroxide (CH), some of the remaining cement minerals (CM) and amorphous C-S-H are recognized. In composite concretes PC-BCP and SPC-BCP, the phases AFt, AFm, CH and calcium monohydrocarboaluminate (Mc) are recorded, too. For sample PC-BCP the phase AFm is observed only in the period from 14 to 28 days. Amorphous phases, which can be estimated as C-S-H and unhydrated slag for sample SPC-BCP are also fitting on the curves. These results indicate successful profil fitting by the XRD method to measuring of peaks of hydrated and amorphous phases and amorphous halo.

The evolution of peak intensity for basic hydrated products, specific crystalline hydrates and amorphous phases at different ages – 2, 7, 14, 28 and 90 days are presented from Fig. 2 to Fig. 8.

In sample PC, C_3S and C_2S react with water to produce CH and amorphous calcium hydro silicates C-S-H. At early ages their amounts grow rapidly, but later during the 14 – 90 day period selfsame are almost constant, Fig. 2 and Fig. 3.

The formation of ettringite (CH) in the composite Portland cement concrete PC-BCP is rather different from that in the control sample PC. The BCP stimulates the rapid formation of higher CH amount, which is an indication for the acceleration of hydration processes at the early stage. The CH increases up to the 14-th day, then decreases and again increases after 28 days, Fig. 2. The last growth is related with the accelerated dissolution and physico-chemical interactions of BCP with age. The carbonate particles ensure the physical effect of heterogeneous nuclei formation for the hydration of clinker minerals and dilute the solid solution, [19, 20]. The Ca^{2+} ions play the role of crystallization centers during the growth of CH, [21, 22].

In sample SPC-BCP the amount of CH is decreased. It is owed of the higher total content of substitute components in slag cement system (10 wt. % BCP and 15 wt. % acid slag).

In sample PC-BCP the introducing of blended carbonates in the form of a finely dispersed powder intensifies the hydration of C_3S at early age and shortens its latent period. The result is expressed in the formation of a greater amount of amorphous calcium hydrosilicates C-S-H compared to sample PC regardless of the reduced with 10 % PC content in series PC-BCP, Fig. 3

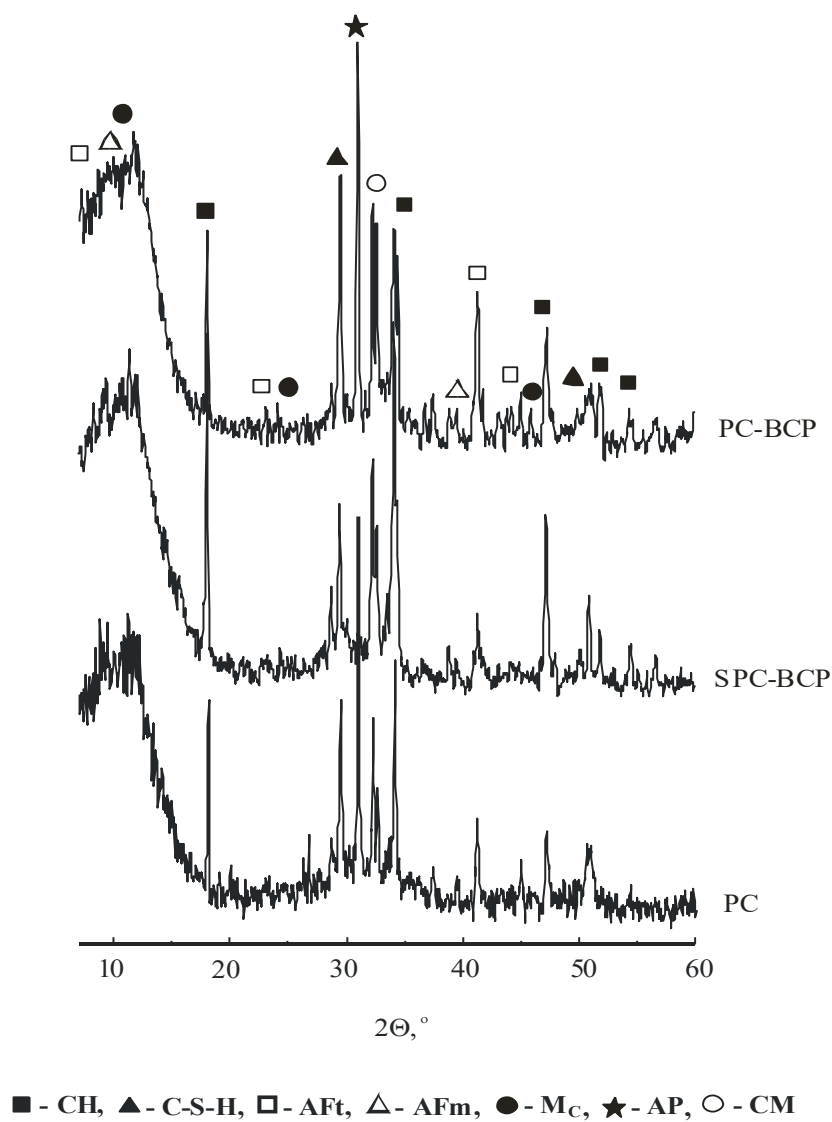


Fig. 1 - X-ray diffraction analyses of samples PC, PC-BCP and SPC-BCP

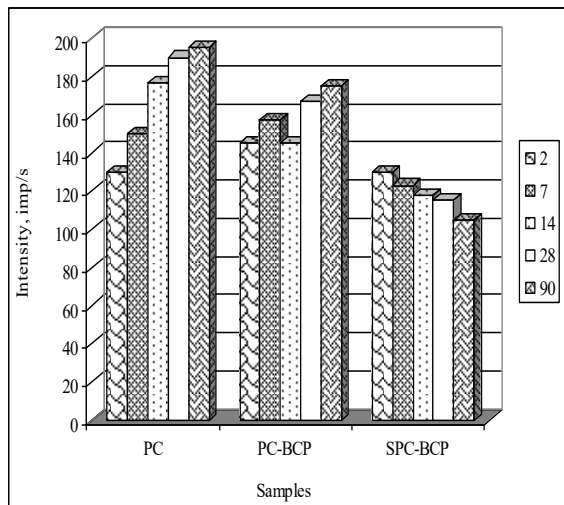


Fig. 2 Amount of CH in samples PC, PC-BCP and SPC-BCP

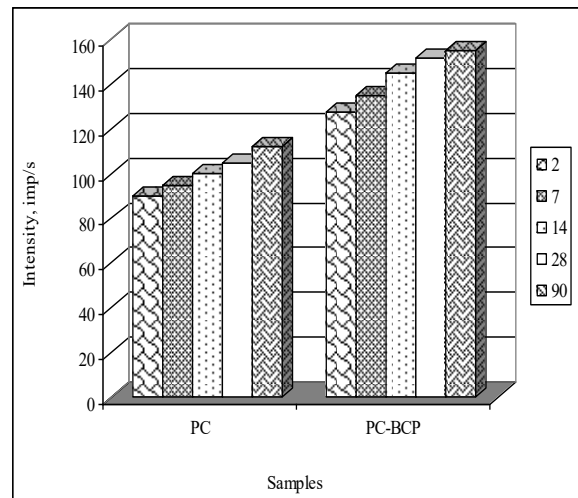


Fig. 3 Amount of amorphous hydrosilicates C-S-H in samples PC and PC-BCP

In slag composite concrete SPC-BCP the produced amount of amorphous hydrosilicates C-S-H is less in comparison with this amount by PC-BCP, Fig. 3 and Fig. 4. In sample PC-BCP, natural blended carbonates are showed greater effect of the produced amount of C-S-H at every age. This phenomenon can be explained by the fact, that amount of C-S-H from slag is less consequence to the slower reaction of slag compared to calcium silicates (sum of C_3S and C_2S). But total amount of the amorphous phases in the cases of SPC-BCP are greater than the samples of PC and PC-BCP. It is owed of the unhydrated slag participation in composition of the amorphous phase, Fig. 3 and Fig. 4.

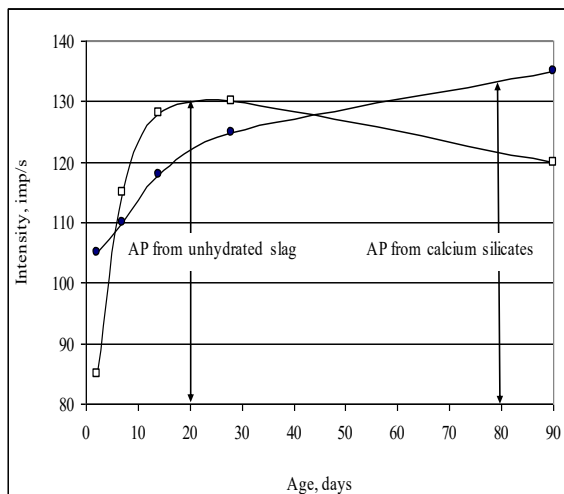


Fig. 4 Amount of amorphous phases in sample SPC-BCP

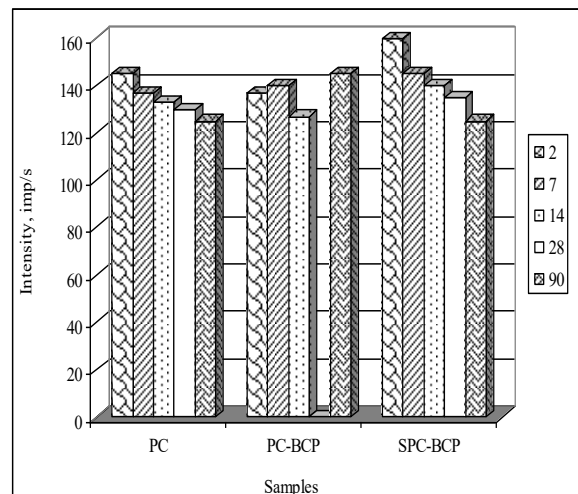


Fig. 5 Amount of Aft in samples PC, PC-BCP and SPC-BCP

C₃A also reacts with gypsum to produce AFt and AFm at an early age, Fig. 5. In the XRD pattern the conversion of ettringite to calcium monosulfoaluminate is detected too. In sample PC this change provokes a progressive increase of the monosulfoaluminate peaks for the whole investigated period. It has been proved that the addition of BCP to PC enhances the formation of AFt and retards or creates the AFm formation at an early age, [21, 23, 24]. A large amount of AFt is formed in the PC-BCP sample at the first 7 days, afterwards in the 14-28 day period it is converted into AFm due to the lack of gypsum, Fig. 5 and Fig. 6.

In series PC-BCP during the hydration of C₃A in the presence of BCP and gypsum, calcium monohydrocarboaluminate is formed at early ages, Fig. 7. The amount increases after 28 days of hydration age. This growth is related with the concentration of calcium ions and the later formation of calcium monosulphoaluminate AFm. However, the phase is rapidly consumed by BCA to form additional amounts of calcium monohydrocarboaluminate and sulphate ions, which activate the reconversion of AFt. At the age of 90 days, AFm is already missing, Fig. 6. Several authors explain that the reconversion of AFm to calcium monocarboaluminate releases more heat in the cement system, [25, 26].

The whole amount of AFt in sample SPC-BCP compared to the series of PC-BCP is generated at early age and did not transform into AFm, Fig. 5 and Fig. 6. It is greater than this amount by samples PC and PC-BCP. Later hydration became different. Phase AFt is consumed by BCA to form additional amount of calcium monohydrocarboaluminate which indirectly stabilizes AFt, Fig. 7. This stabilization leads to increase of the total amount of the solid phases, respectively to increase the compressive strength and to decrease of porosity in slag Portland cement stone, Fig. 8, Fig. 9.

The compressive strength of samples PC, PC-BCP and SPC-BCP is presented in Fig. 9. It shows that BPC has a decisive influence in increasing of the compressive strength at the 2 day period compared of sample PC-BCP. It is respectively about 5 MPa and 4 MPa higher than that of PC and SPC-BCP. When SPC is mixed whit blended carbonate powder at the same age, the 2-day compressive strength of series SPC-BCP is lower. However, after 7 days of hardening, the strength is higher then that of remaining samples. After 28 days, the compressive strength of SPC-BCP has greatly surpassed that of the other two others concretes.

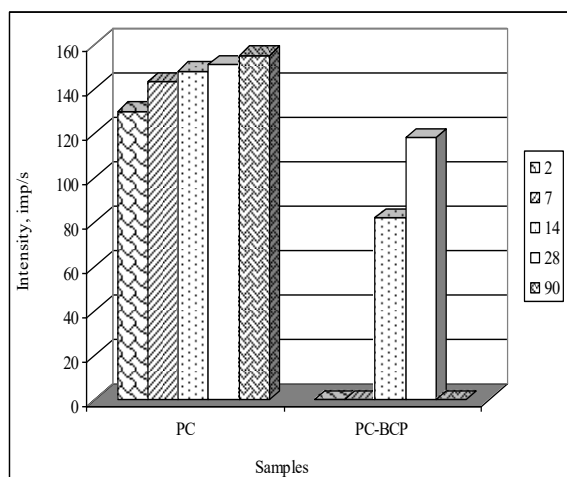


Fig. 6 Amount of AFm in samples PC and PC-BCP

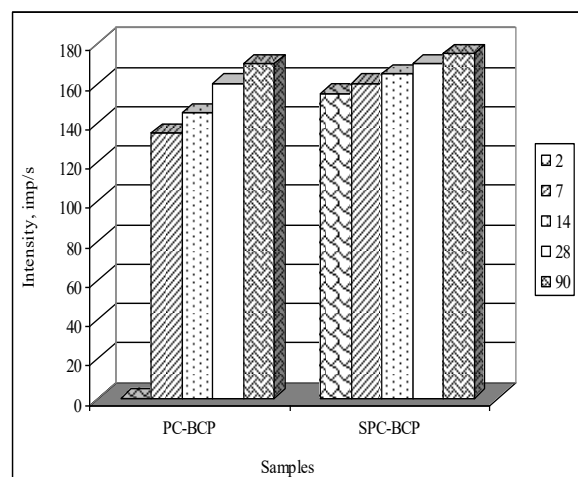


Fig. 7 Amount of Mc in samples PC-BCP and SPC-BCP

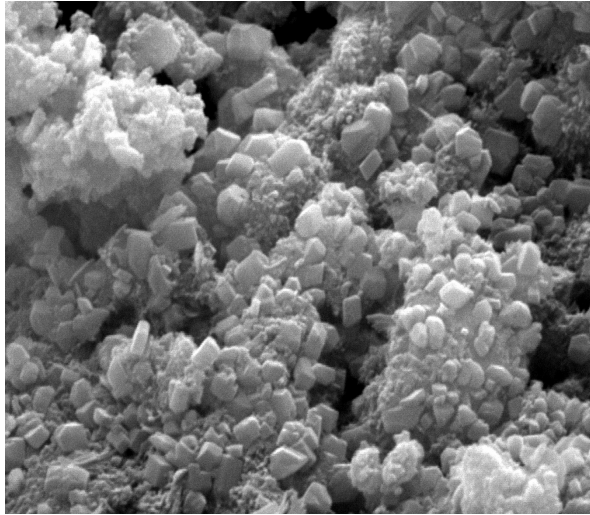


Fig. 8 Microstructure of slag blended composite concrete SPC-BCP, 8000 μm x

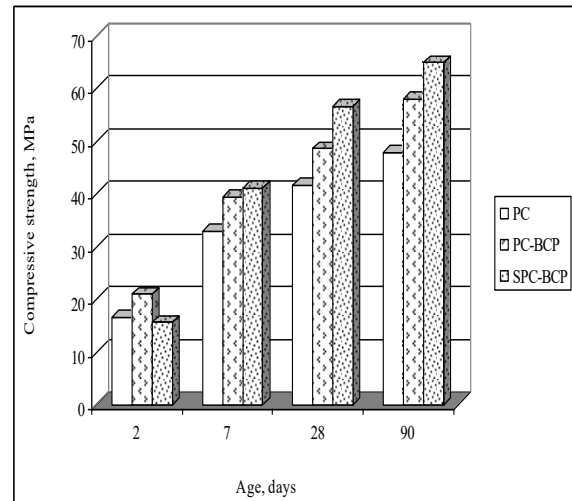


Fig. 9 Compressive strength of samples PC, PC-BCP and SPC-BCP

4. CONCLUSIONS

The formed microstructure in fine-grained composite concretes PC-BCP and SPC-BCP have been investigated by X-ray diffraction analysis and scanning electron microscopy. Information is indicated about the type, composition, amount and morphology of the recorded basic and specific crystalline hydrates and amorphous phases and their changes with time.

It is shown that the blended carbonates react with clinker minerals. The mechanism of its activity is displayed in two aspects: 1) physical effect of heterogeneous nuclei formation of the fine carbonate particles; 2) chemical effect with a specific phase formation – calcium monohydrocarboaluminate, which modifies the formation of AFt and AFm. The Mc improves the microstructure and increases the compressive strength and mechanical properties in two cement systems - PC-BCP and SPC-BCP.

The positive role from the introducing of a new BCP additive to composite concretes PC-BCP and SPC-BCP is confirmed by specific density calculated as a function of the amount of BCP. It has been shown that the fill up ability is optimum only for slag composite system SPC-BCP, because it is successfully is regulated to maximum amount of AFt and Mc phases.

In conclusion, the results proved the effectiveness of the XRD method as an analysis for slag cement hydration relating to various properties of composite high-strength concretes. The introducing of the natural mineral additive like blended carbonates (BCP) to composite Portland concrete and to composite slag Portland concrete exerts not only technical, economic and ecological effects, but leads also to improvement in concrete performance with respect to microstructure formation, compressive strength, durability and workability.

REFERENCES

1. Mehta P. Concrete technology for sustainable development. Concr Intern, 1999; 21(11): 47-53.
2. European Committee for Standardization, Cement: Composition, Specifications and Conformity

Journal of International Scientific Publication:
Materials, Methods & Technologies, Volume 4, Part 2

Criteria, Part 1: Common Cements, EN 197-1, EN/TC51/WG 6 rev, 2000.

3. Taylor H W. Cement Chemistry. Thomas Telford Publishing, London, 1997.

4. Tsivilis S, Chaniotakis E, Badogiannis G, Pahoulas A, Ilias A. A study on the parameters affecting the properties of Portland limestone cements. *Cem and Concr Comp*, 1999; 21(2): 107-116.

5. Li Y, Du X L, Huo D. Utilization of limestone as mineral admixture in cement and concrete. *Cem Engineering*, 2003; 3(3): 11-14.

6. Baron J, Dourve C. Technical and economical aspects of the use of limestone filler additions in cement. *World Cem*, 1987; 18: 100-104.

7. Douglas E, Zerbino R. Characterization of granulated and palletized blast furnace slag. *Cem and Concr Res*, 1996; 16: 662-670.

8. Lumley J S, Gollop R S, Moir G K, Taylor H W. Degrees of reaction of the slag in some blends with Portland cement. *Cem and Concr Res*, 1996; 26(1): 139-151.

9. Escalante J, Gomez L, Johal K, Mendoza G, Mancha H, Mendez J. Reactivity of blast furnace slag in Portland cements blends hydrated under different conditions. *Cem and Concr Res*, 2001; 31: 1403-1409.

10. Wang S D, Scriviner K L. Hydration products of activated slag cement. *Cem Concr Res*, 1995; (3): 561-571.

11. Ogawa K, Uchikawa H, Takemoto K. The mechanism of the hydration in the system C_3S -pozzolana. *Cem and Concr Res*, 1980; 10: 683-696.

12. Asaga K, Kuga H. Effect of inorganic material powder on the hydration speed of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. *Cem and Concr Res*, 1996; 50: 68-73.

13. Petkova-Rousseva V, Simeonova- Ivanova E, Avdeev G. Structural study of Portland cement with blended carbonate additive, Editor: N. Barovsky, XII-th International conference of MTCM, 2009: 104-109.

14. Shimobayashi S, Iwabuchi T. Effect of limestone powder on cement strength. *Cemento-Gijutu-Nenpo*, 1969; 33: 84-87.

15. Mincheva-Stefanova I. Polymetallic deposits affiliated to sedimentary rocks in West Balkan Mountains. *Technics*, Sofia, 1988; 175-192.

16. Petkova V Y, Simeonova E M. Investigation of the contact zone of high strength fine-grained slag concrete. Editors: Ribalsky N, Nenov V, XIII Int. Symposium „Ecology”, 2004: 517-524.

17. Petkova V. Composite mortars prepared with combined by-products. *Building*, 1992; (3-4): 16-18.

18. Petkova V. Calorimetric assessment of a silicate composite. *Ecology and Industry*, 1998; (1-3): 82-84.

19. Soroka I, Setter N. The effect of blended materials on strength of cement mortars. *Cem and Concr Res*, 1997; 7: 449-456.

20. Kadri E, Duval R. Effect of ultrafine particles on heat of hydration of cement mortars. *ACI Mater J*, 2002; 99 (2): 138-142.

Journal of International Scientific Publication:
Materials, Methods & Technologies, Volume 4, Part 2

21. Barker A, Cory H. The early hydration of limestone filled cements. N. Swamy (Ed.), Blended Cements in Construction, Elsevier, London, 1991, p. 107-124.
22. Ye G, Liu X, Schutter De, Poppe G, Taerwe L. Hydration and microstructure studies on self-compacting cement paste containing limestone powder as blended material. submitted to Cem and Concr Res.
23. Pera J, Husson S, Guilhot B. Influence of finely ground limestone on cement hydration. Cem and Concr Comp, 1999; 21: 99-105.
24. Kakali G, Tsivilis S, Aggeli E, Bati M. Hydration products of Portland cement in the presence of CaCO_3 . Cem and Concr Res, 2000; 30: 1073-1077.
25. Van Breugel K. Simulation of hydration and formation of structure in hardening cement based materials. PhD thesis, Delft University of Technology, Delft, 1997.
26. Lothenbach B, Le Saout G, Gallucci E, Scrivener K. Influence of limestone on the hydration of Portland cements. Cem and Concr Res, 2008; 38: 848-860.