

INVESTIGATIONS OF BLENDED LOW ENERGY CEMENTS

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Three kinds of Low Energy Cement (LEC) were prepared at lower temperatures than those necessary for the production of Ordinary Portland Cement - a high content Belite Cement (HBC) produced in a cement plant at 1260 °C and two kinds of Sulfoaluminate Belite Cement (SAB1 and SAB2) synthesised in laboratory at 1250 °C. HBC sets slowly (set point over 200 min), SAB1 and SAB2 are fast-setting cements (set point within 30 minutes). HBC blended with either SAB1 or SAB2 (70/30 on the weight basis) gives setting times inside of 60-80 minutes. The replacement of HBC by 30 wt.% of SAB2 improved mechanical strength, pore structure, absorption capacity and dynamic modulus of elasticity of the cured cement, while the combination with SAB1 showed decreased values of these parameters. The conduction calorimeter showed an expressive difference in the heat evolution curves of blended cements.

INTRODUCTION

Low Energy Cements (LEC) are receiving an increasing attention among cement researchers these days [1-7]. In spite of the favourable experimental results obtained throughout laboratories and the numerous manifested advantages their large scale production, with an exception of Chinese plants, has not received a favourable echo among producers and some doubts remain regarding their use as a masonry material in civil engineering.

The cement industry is an industry with a high demand for energy. A lot of investigations were carried out therefore in order to decrease this demand. One of the primary ideas in a development of LEC [1] was bound to reducing in the CaCO_3 content in the raw meal decreasing thus a part of the energy necessary for the decomposition of calcite. The decrease in CaCO_3 leads further to the deficit of the "high energy" mineral - C_3S - in the cement clinker and the simultaneous decrease in burning temperature ultimately to its complete absence.

This action results in an increase of the "low-lime" phase C_2S which synthesis is completed at significantly lower temperature (1200-1250 °C) than that necessary for the formation of C_3S , especially in the presence of SO_3 [8]. Its low reactivity could be compensated in sulfoaluminate belite cements by an introduction of $\text{C}_4\text{A}_3\text{S}$ and CS as clinker phases, whose formation takes place also at low temperatures. In an appreciation of energy savings at synthesis of LEC, it is also important to consider the energy for a grinding of the concerned raw materials and especially of clinkers themselves.

The attempts were undertaken to produce Active Belite Cements (ABC) [8-10] by stabilising the most active high temperature forms of C_2S ($\alpha\text{-C}_2\text{S}$ or $\alpha'\text{-C}_2\text{S}$), which are the common mineral phases also in OPC. Their stabilisation can be achieved by rapid quenching of clinkers [9, 10] or by an introduction of some minor stabilising oxides (alkalis, sulphates) [13, 14]. The rapid cooling of clinkers requires, however, an additional expenditure of the energy.

The main mineral phases of LEC of the SAB type are $\beta\text{-C}_2\text{S}$, $\text{C}_4\text{A}_3\text{S}$, C_4AF and optionally also CS . By varying the proportions of these phases, it is possible to obtain hydraulic binders with significantly different properties [1]. They include also compositions with a required rapid strength development and the high long term strength parameters. These binders, however, unfortunately exhibit very short setting times. The successful measures have been taken to prolong the setting time of SAB cements by means of admixtures [16]. In this work we try to achieve the equal effect by blending of cements, particularly those with short (SAB) and long (HBC) setting times respectively, each of them moreover belonging to the LEC type. The waste raw materials, next to the natural ones, have been used at SAB synthesis to fulfil the environmental requirements and effecting the further energy savings, particularly in clinkering reactions and milling operations.

In this paper usual chemistry cement notation is used in which: C = CaO , S = SiO_2 , A = Al_2O_3 , F = Fe_2O_3 , $\bar{\text{S}}$ = SO_3 , H = H_2O .

EXPERIMENTAL PART

High belite cement (HBC) has been burnt from natural raw materials (limestone, burnt clay, pyrite, sand) by the dry process in a rotary kiln equipped with 4 stage cyclones suspension heat exchangers and 2 grate plate coolers at Cimur s.a, Cimpulung (Romania) at 1260 °C. The reduction of clinkering temperature and the total amount of calcite have led to the energy saving of 400 kJ kg⁻¹ comparing with the production of OPC in the same plant. The clinker thus obtained was ground on an industrial close mill circuit with 3 wt.% of gypsum. Clinker characteristics are referred in table 1.

SAB1 and SAB2 were synthesised by a heating in an electric furnace at 1250 °C using mixture of limestone, gypsum, fly and pyrite ash. Basic characteristics of these clinkers are listed in table 1 as well.

Fabrication and curing of specimens: The mortars with cement to standard sand ratio of 1:3 by weight and $w/c = 0.5$ were prepared and fresh mixtures were castled in steel prism moulds of 160 × 40 × 40 mm. Mortar specimens were stored 24 hours at 20 °C in the wet air (100 % relative humidity R.H.) and then kept 27 days in water at ambient temperature. After this basic curing a half of the specimens was still maintained at 20 °C / 100 % R.H. for 62 days, and the second half was maintained at 20 °C / 60 % R.H.

Mortar specimens were tested on dynamic modulus of elasticity (DME) for 1 to 90 days, flexural and compressive strength for 28 and 90 days, and absorption capacity (AC) in both curing regimes. The test of AC is evaluated by the difference on weight of the specimen saturated by water and then dried at 105 °C. The decrease on weight is evaluated on wt.%.

The dimensional changes (expansion or shrinkage) of mortar specimens were measured by using dilatometer with dial gauge for length change observations at dif-

ferent curing time interval. The measuring distance between two metal points placed on the surface of mortar specimen was 100 mm. Specific gravity was determined by the pycnometric method as the weight of the volume unit of solid constituents of the mortar in a powdered state.

Total porosity was calculated on the basis of measured volume density and specific gravity of the mortar using the formula, $PS = (1 - \rho_{VD}/\rho_{SG}) \cdot 100$, where PS is total porosity (%), ρ_{VD} is volume density (kg m⁻³) and ρ_{SG} is specific gravity (kg m⁻³). Total porosity was then expressed as a content of pores and voids in mortars on vol.%. Pore structure of mortar specimens was investigated by means of the mercury porosimeter mod. 2000 (Erba Science).

The rate of hydration reactions has been monitored using conduction calorimeter described in [15].

RESULTS AND DISCUSSION

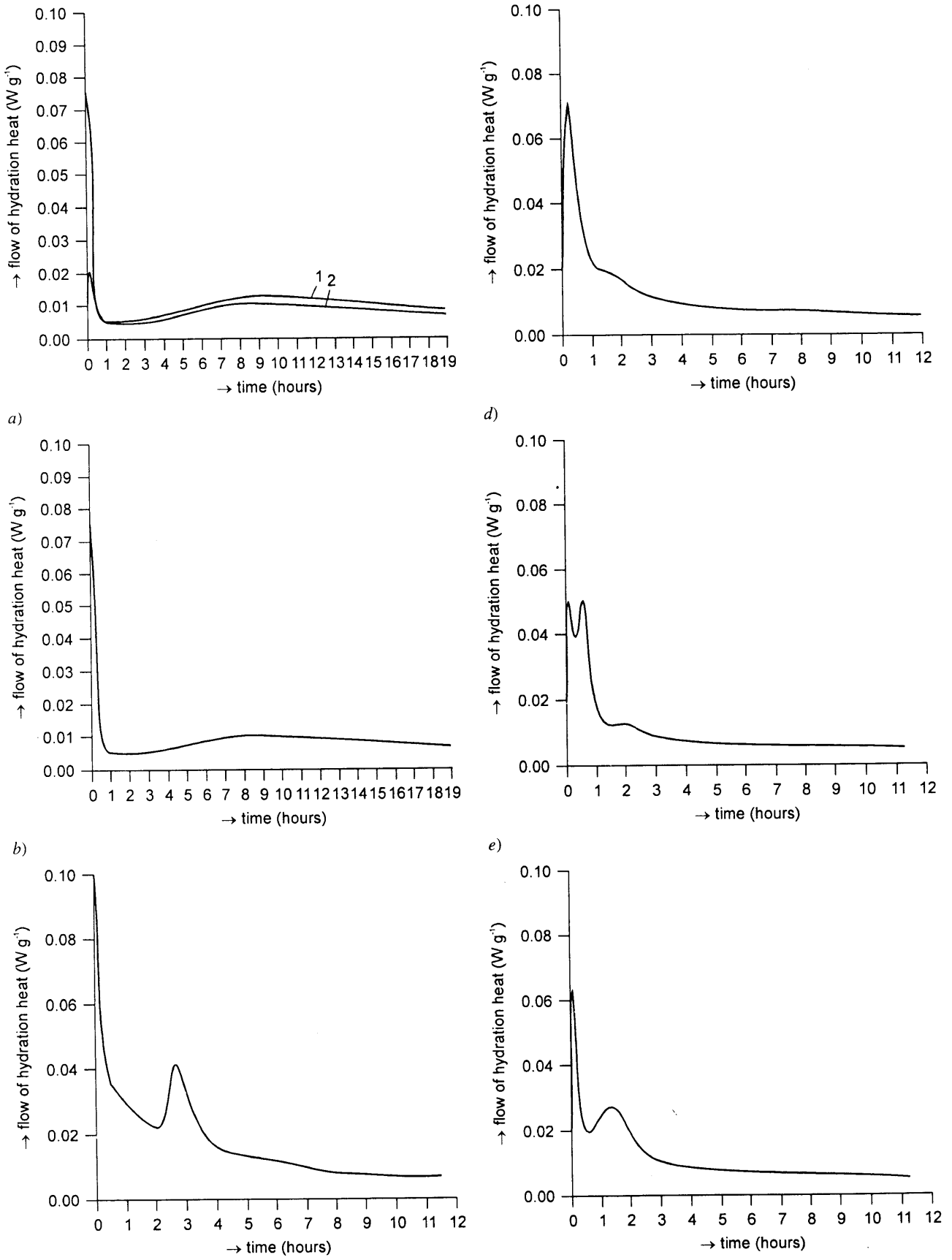
Blending ratio of HBC and SAB1 and of HBC and SAB2 has been optimised to the value 70 to 30 in wt. proportions beforehand in a series of many combinations with regard to the initial setting time as well as to maximum quantity of SAB1 and SAB2 respectively.

The hydration kinetics of LEC is summarised in figures 1a-f. As an illustration, heat evolution curves of HBC and OPC are shown in figure 1, apart from the quite initial period of hydration, a little difference is observed between both samples.

HBC after a small initial peak, observed when water first comes into contact with the cement, shows a slow rate of heat evolution. SAB1 does not show a second peak and is characterised by the absence of an induction period. SAB2 shows the higher initial and second peaks with a small induction period in between.

Table 1. Oxide and mineralogical composition of considered cements.

	HBC	SAB1	SAB2	HBC+ SAB1	HBC + SAB2
CaO	58.20	52.20	55.20	56.40	57.2
SiO ₂	20.20	20.50	19.30	20.30	19.90
Al ₂ O ₃	6.50	8.50	8.04	7.10	7.00
Fe ₂ O ₃	7.70	7.00	3.40	7.50	6.38
SO ₃	2.70	5.30	8.70	3.50	4.48
MgO	1.50	1.40	1.50	1.40	1.45
TiO ₂	-	0.30	0.50	0.09	0.15
C ₃ S	30.30	-	-	21.20	21.20
C ₂ S	37.80	62.80	58.50	45.30	44.00
C ₄ AF	24.70	9.00	10.80	20.00	20.50
C ₂ F	-	7.50	-	2.25	-
C ₄ A ₃ S̄	3.30	14.30	12.50	6.60	6.10
CS	3.90	7.00	12.30	4.60	6.40
C-free	0.27	0.95	5.70	0.50	1.70



a) 1-OPC + 2-HBC; b) HBC; c) SAB1; d) SAB2; e) HBC + SAB1; f) HBC + SAB2

All of the samples show an increasing strength development, but they have higher mechanical properties in wet curing condition than in the dry one. It can be noted that a 30 % replacement of HBC by SAB2 cement in mortar specimens leads to the increase in flexural and compressive strength as compared with the HBC and HBC + SAB1 ones. This strength increase gives a perspective to use LEC.

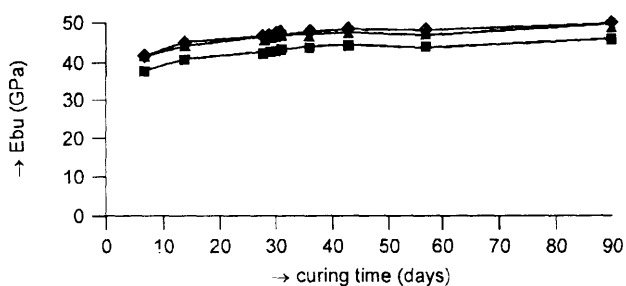


Figure 2. Dynamic modulus of elasticity of samples stored under wet air conditions.

◆ - HBC; ■ - HBC + SAB1; ▲ - HBC + SAB2

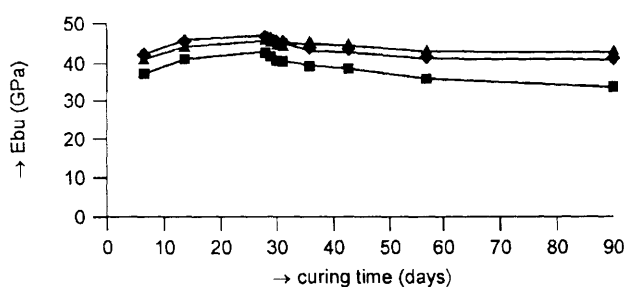


Figure 3. Dynamic modulus of elasticity of samples stored under dry air conditions.

◆ - HBC; ■ - HBC + SAB1; ▲ - HBC + SAB2

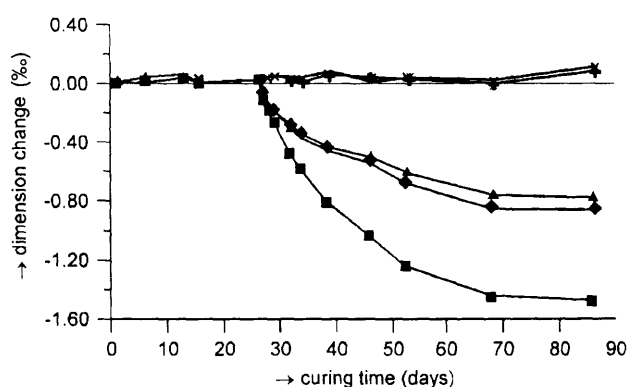


Figure 4. Dimensional change of samples stored under wet air conditions and under dry air conditions.

* - HBC; × - HBC + SAB1; + - HBC + SAB2

◆ - HBC; ■ - HBC + SAB1; ▲ - HBC + SAB2

The Absorption Capacity (AC) changes relatively with samples and with curing conditions.

Changes in Dynamic Modulus of Elasticity (DME) of mortar specimens cured either in wet air or dry air are illustrated in figures 2-3. A slight increase in DME is observed in mortar specimens submitted to wet air opposite to those exposed to dry air.

Dimensional changes under different curing regimes are illustrated by expansion/shrinkage curves in figure 4. It can be seen a negligible expansion in wet air, while under dry curing condition, cement mortar specimens show shrinkage of value 0.6 to 1.56 promile. These values are negligible compared with those of OPC [6]. Samples of HBC and HBC + SAB2 are the most dimensionally stable, while shrinkage tends to increase in the case of HBC + SAB1.

The pore structure of HBC + SAB2 mortar specimens is characterised by the lowest median of micropore radius in dry curing regimes as compared with those of HBC and HBC + SAB1 mortar specimens. The porosity of mortars is similar at the same time and curing conditions. Under the same conditions differences in porosity of mortars vary in the range of +/- 1-2 %. As it can be seen in table 4, porosity of HBC cured on dry air for 90 days is 12.5 %, those of HBC + SAB1 ones 13.5 % and HBC + SAB2 mortar specimens is about 13 %. It is clear from these results (see figures 5, 6, 7) that blended HBC + SAB2 mortar specimens contain the largest portion of micropores with radii between

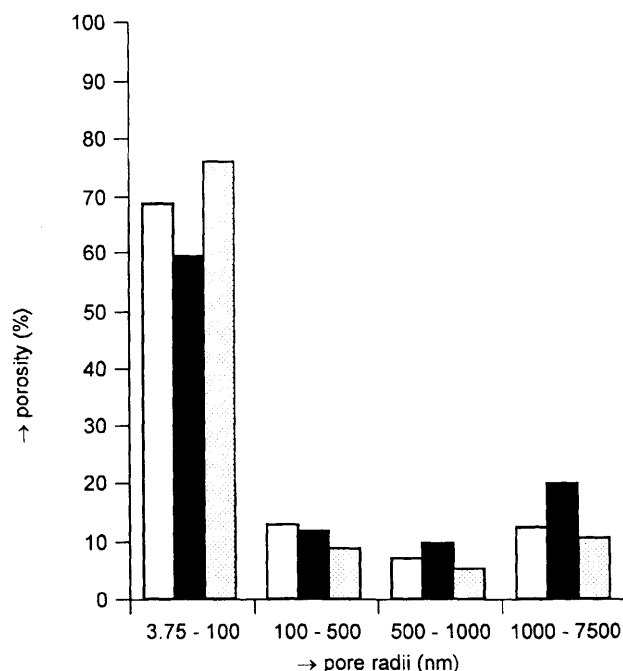


Figure 5. Pore size distribution of sample specimens after 28 days of exposure under wet conditions (20 °C / 60 % R.H.).

□ - HBC; ■ - HBC + SAB1; ▒ - HBC + SAB2

3.75-100 nm on the one hand and the lowest representation of macropores with radii between 1000-7500 nm on the other hand when submitted to the same conditions. It is evident that the blend consisting of 30 % of SAB2 cement and 70 % of HBC by weight is characterised by improved pore structure as compared with those of HBC and HBC + SAB1 mortar specimens and consequently also by increased strengths. This effect is contrary when SAB1 is mixed with HBC in the mortar. The more compact pore structure of HBC + SAB2 mortar specimens is evidently the main cause of the lowest shrinkage of mortars cured at 20 °C / 60 % R.H. because the rate of drying up of HBC + SAB2 mortar

specimens is more steadily than those of HBC and HBC + SAB1 ones with more permeable structure.

When HBC is mixed with SAB2, a high part of micropore is observed after 28 days, 90 days cured in wet or dry regimes. The dense structure of HBC + SAB2 can be explained by the reaction leading to the formation of ettringite from a suitable mineralogical composition. Indeed, it is well known that C_4AF and C_2F very little contributes to the strength development. The presence of C_2F , though in little quantity, can be expected as the main cause of the lowest properties of SAB1 respectively of HBC + SAB1.

Table 4. The pore structure of mortar specimens.

	curing time (days)	relative humidity (%)	volume of micropore radius (mm ³ g ⁻¹)	median of micropore (nm)	porosity (%)
HBC	28	100	64.2	49.1	17
	90	100	43.9	41.7	9.5
	90	60	58.6	62.7	12.5
HBC+SAB1	28	100	67.6	54.5	16.5
	90	100	52.4	54.7	11.1
	90	60	63.7	92.0	13.5
HBC + SAB2	28	100	72.0	49.7	16.7
	90	100	47.6	45.2	10.2
	90	60	61.1	53.1	13.0

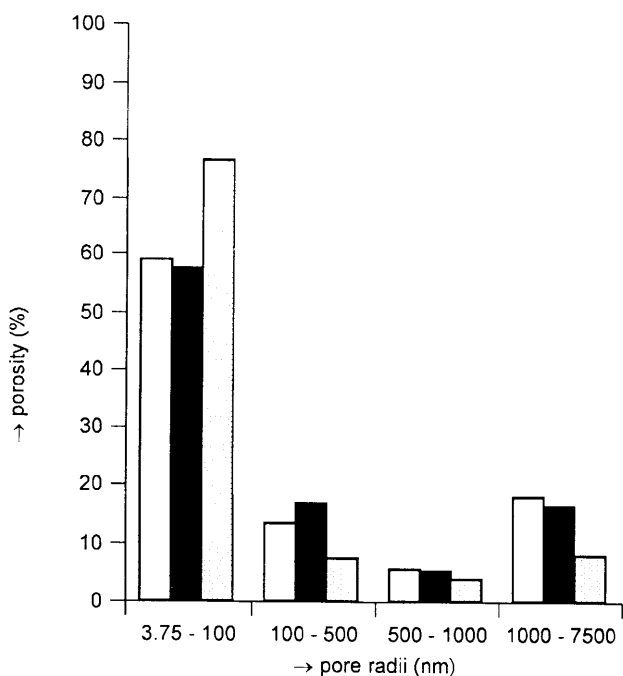


Figure 6. Pore size distribution of sample specimens after 90 days of exposure under wet conditions (20 °C / 100 % R.H.).

□ - HBC; ■ - HBC + SAB1; ▒ - HBC + SAB2

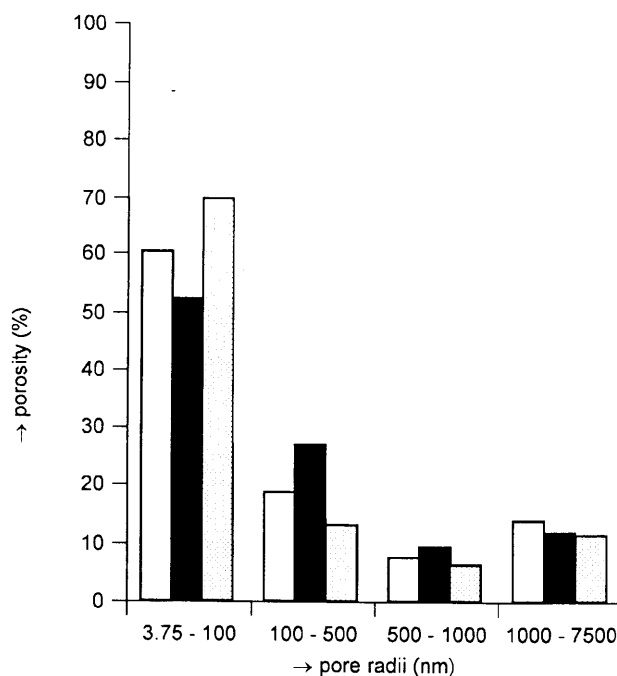


Figure 7. Pore size distribution of sample specimens after 90 days of exposure with 28 days under wet conditions (20 °C / 100 % R.H.) + 62 days under dry conditions (20 °C / 100 % R.H.).

□ - HBC; ■ - HBC + SAB1; ▒ - HBC + SAB2

CONCLUSION

An attempt has been undertaken to investigate the possibilities of use of LEC. It is possible to activate cements with high content of dicalcium silicate by blending them with high reactive suphoaluminante belite cements, and thus, some energy can be saved. Mechanical and physical properties depend on the type of SAB added to HBC. The results thus obtained show that such type of cement or its blended forms can be used successfully in the replacement of OPC.

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ŠTÚDIUM

ZMESNÝCH NÍZKOENERGETICKÝCH CEMENTOV

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V práci sa prešetrovali vlastnosti nízkoenergetických zmesných cementov, ktoré sa získali miešaním poloprevádzkovo pripraveného belitového cementu a laboratórne pripraveného sufoaluminátového belitového cementu. Prvý z nich sám o sebe vykazuje pomalý nárast pevností, sulfoaluminátové cementy (SAB1 a SAB2) vykazujú rýchly rast pevností, rovnako ako aj veľmi včasný počiatok tuhnutia. Zmesné cementy sa charakterizovali prostredníctvom vývoja tlakovej pevnosti, zmien porozity, absorpčnej kapacity, dynamického modulu pružnosti a chovania pri hydratácii meranej prostredníctvom vodivostnej kalorimetrie. Výhodným kompromisom, v prvom rade s ohľadom na počiatok tuhnutia, je zmesný cement obsahujúci 70 hmot.% belitového a 30 hmot. % sulfoaluminátového cementu (typ SAB2).