

# EFFECT OF CURING TEMPERATURE ON THE THERMAL EXPANSION AND PHASE COMPOSITION OF HYDRATED LIMESTONE-SLAG CEMENT

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*The materials used in this investigation were ordinary Portland cement (OPC), granulated blast-furnace slag cement (GBFSC) and limestone (LS). The slag cement containing limestone shows small thermal expansion and shrinkage coefficient in comparison to neat OPC pastes. This is mainly due to the pozzolanic activity of the granulated slag as well as the filling effect of limestone. It was found that the partial substitution of slag by 5 wt.% LS improves the compressive strength. As the curing temperature increases, the C-S-H phases are deposited within the pore system, which can accommodate larger amounts of hydration products. This fact leads to relatively high compressive strength values of GBFSC when compared with OPC pastes. As the amount of limestone increases (15 wt.% LS), the compressive strength diminishes. The presence of 15 wt.% limestone changes the morphological shape of C-S-H crystals from fibers to crumbled foils with small fibers embedded of Ca(OH)<sub>2</sub> phase.*

## INTRODUCTION

Temperature is a key variable affecting the curing of cement-based materials because it influences both the early hydration kinetics and the properties of the hardened cement paste or concrete. Although concrete initially gains strength more rapidly when cured at elevated temperatures, the final strength is lower and the permeability is higher. The hydration temperature has a significant impact on the hydration of cement paste and concrete. The activation energy for the rate of early hydration is about 35 kJ/mol [1]; therefore, higher curing temperatures accelerate the rate of hydration and strength development during the first 12-24 hours after mixing with water. The exothermic reaction of cement pastes affects the internal structure to a higher extent than the surface, and higher ambient temperature leads to a greater internal temperature increase. Therefore, consideration of the effects of high curing temperatures and of heat treatment should not be limited to precast steam-cured materials, which are generally cured at anywhere from 40° to 100°C.

In general, solids expand on heating and contract on cooling. The strain associated with change in temperature will depend on the coefficient of thermal expansion of the material and the magnitude of temperature drops or rises. Except under extreme climatic

conditions, ordinary concrete structures suffer little or no distress from the changes in ambient temperature. Subsequently, cooling to the ambient temperature often causes the concrete to crack. Since the primary concern in the design and construction of massive concrete structures is that the completed structure remain a monolith, free of cracks, every effort to control the temperature rise is made through selection of proper materials, mix proportions, curing conditions, and construction practices.

Elevated temperatures also reduce the tendency for irreversible creep and shrinkage. Most of these effects can be related to the increased rate of silicate polymerization at elevated temperatures [2-4], which compact and stiffen the C-S-H phase as it forms. SEM studies [5] have shown that at elevated temperatures the outer-product of C-S-H gel is denser and does not fill the capillary pore space, as effectively, and thus the microstructure is more heterogeneous. Elevated curing temperatures increase the rate of hydration, particularly at early ages and decrease the setting time of blended cement containing silica fume and granulated blast furnace slag [6]. During the early hydration period when sulfate concentrations in the pore fluid are high, ettringite is more stable than monosulphate at ambient temperature. As the temperature increases, monosulphate eventually becomes the favored phase due to its smaller enthalpy of reaction.

The mineral additive content in blended cement varies with a required level of properties and with the type of the additive used. The use of granulated blast furnace slag in blended cement composition provides a very high resistance to chemical attack. Addition of limestone to OPC cement produces several effects on the mechanism and kinetics of cement hydration. The filler effect of limestone accelerates the hydration of OPC clinker phases at early ages especially C<sub>3</sub>A and C<sub>3</sub>S [7]. Limestone acts as nucleating sites for Ca(OH)<sub>2</sub> and produces the formation of hydrated calcium carboaluminates [8]. Limestone addition modifies the reaction between C<sub>3</sub>A and gypsum; initially, ettringite crystallizes and then if the sulphate is consumed, the ettringite converted to monosulpho-aluminate hydrate. First, the ettringite formation is accelerated by the presence of CaCO<sub>3</sub> [8]. Secondly, the ettringite conversion to monosulphoaluminate hydrate will be delayed or stopped when a large amount of carbonate is present in the hydrated paste. This phenomenon occurs because some sulphate ions can be interchanged by carbonate ions during the C<sub>3</sub>A hydration [9].

Carbonate additions also influence the C<sub>3</sub>S hydration. Ramachandran and Zhang [10] reported that C<sub>3</sub>S hydration rate is accelerated when the amount and fineness of CaCO<sub>3</sub> increase. They found that C-S-H incorporates a significant amount of CaCO<sub>3</sub> into its structure. Additionally, the calcium silicocarbonate hydrates was formed during the hydration of C<sub>3</sub>S in the presence of large quantities of carbonate.

The addition of limestone fillers to ordinary Portland cement improves physically the denseness of cement composites; furthermore, they are reactive [11]. Evidently addition of limestone to neat cement pastes and mortars reduces the diffusion coefficient of chloride ions [12]. Limestone fills the pores between the cement particles due to the formation of carboaluminate phases [13]. It also constitutes nucleation sites of calcium hydroxide crystals at early hydration ages [14], accelerating the hydration of clinker particles especially the C<sub>3</sub>S [15]. Consequently, it improves the early strength, but it does not have pozzolanic properties and it does not produce C-S-H [16, 17].

This study aims to investigate the effect of different curing temperatures on the thermal expansion, the phase composition and microstructure of filled-slag cement pastes at 30, 40 and 50°C.

## EXPERIMENTAL

The starting materials used in this study were ordinary Portland cement (OPC) of Blaine surface area ≈ 300 m<sup>2</sup>/g, ground granulated blast-furnace slag

(GBFS) of Blaine surface area ≈ 360 m<sup>2</sup>/g, and limestone (LS) dust of Blaine surface area ≈ 310 m<sup>2</sup>/g. The chemical composition of starting materials is shown in table 1. The mix composition of the investigated mixes is seen in table 2. The ingredients were homogenized on a roller in a porcelain ball mill with four balls for 1 hour to assure complete homogeneity. The mixing of water with the blended cement pastes was carried out with the standard water of consistency [18]. The pastes were molded in 2 cm cubes for compressive strength determination and cylinder of 5 mm diameter-15 mm height for determination of thermal expansion. The thermal expansion was carried out by using a Shimadzu TMA-50 thermomechanical analyzer; the samples chamber was purged with nitrogen at a flow of 30 ml/min. The cubic pastes were cured in a relative humidity chamber at room temperature for 24 hours, then demolded and cured under tap water at 30, 40, and 50°C.

The change in height of each cylindrical specimen (5 mm in diameter, 15mm in height) was measured as the temperature increased from room temperature to 300°C at a heating rate of 10°C/min in the atmosphere of nitrogen under load of 5 g. Differential scanning calorimetry runs were conducted using a Shimadzu DSC-50 thermal analyzer at a heating rate of 10°C/min. The microstructure was carried out by the Scanning Electron Microscope of the type Jeol JSM-T20.

Table 1. Chemical composition of starting materials (wt.%).

oxide	OPC	GBFS	LS
SiO <sub>2</sub>	20.50	38.60	4.37
Al <sub>2</sub> O <sub>3</sub>	5.05	13.20	0.36
FeO <sub>3</sub>	2.99	3.53	0.29
CaO	62.00	33.76	52.99
MgO	2.07	5.36	0.90
SO <sub>3</sub>	2.40	0.55	0.10
L.O.I	3.10	1.14	41.2

Table 2. Mix composition of different blended cements (wt.%).

mix. no.	OPC	GBFS	LS
I	100	0	0
II	65	35	0
III	65	30	5
IV	65	25	10
V	65	20	15

## RESULTS AND DISCUSSION

## Thermal expansion

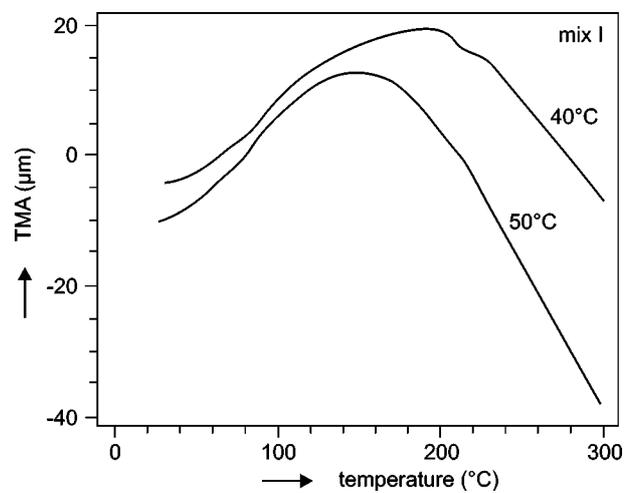
The thermal expansion coefficient being related to capillary forces will therefore pass through a maximum. Helmuth [19] attributed the variation in thermal expansion coefficient to the flow of water between gel and capillary pores of the cement phase. According to this mechanism, the internal flow of water causes volume changes in an opposite direction that simultaneously occurring due to thermal changes. The increase of the temperature from room to 120°C the water of gel flow to capillary pores is accompanied by swelling of the paste due to flow of water and the sample is expanded (strain start to increase) to reach the linear slope at temperature 120-145°C; on further increase of temperature there is no expansion (steady state) up to 185°C. Above this temperature, the strain start to decrease and contraction takes place and the sample tends to shrink.

The corresponding curves obtained for plain (OPC) and blended cement pastes have the same shape. Figure 1 and 2 illustrate the plots of strain vs temperature for plain (OPC) and slag (GBFSC) cement pastes hydrated for 28 days at 40°C and 50°C. Figure 1a shows that the OPC paste undergoes a thermal expansion at a rate of  $13.42 \times 10^{-6}/K$  at which the slope of curve is linear up to 130°C for the sample cured at 40°C, whereas the OPC cement paste hydrated at 50°C undergoes a thermal expansion at a rate of  $12.45 \times 10^{-6}/K$ ; the slope of curve is linear up to 135°C. The thermal expansion and shrinkage coefficients of OPC, slag cement (GBFSC) and blended cements are given in table 3.

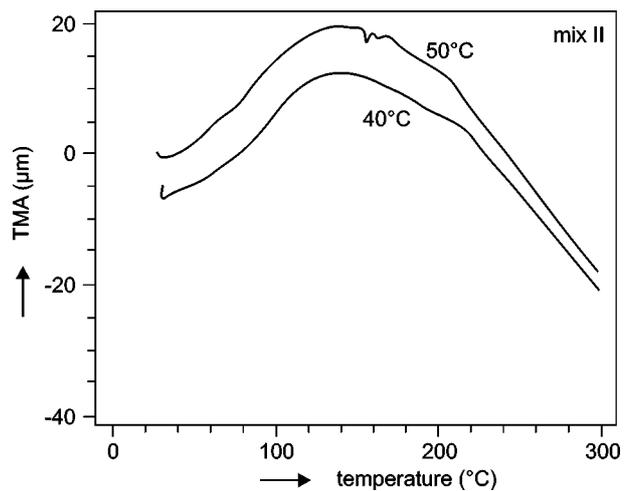
Table 3. Thermal expansion and shrinkage coefficients of OPC, slag and blended cement.

mix. no.	curing temperatures	thermal expansion coefficient $10^{-6} (K^{-1})$	shrinkage coefficient $10^{-6} (K^{-1})$
I	40° C	13.42	-16.61
	50° C	12.45	-24.91
II	40° C	12.25	-13.83
	50° C	12.38	-18.80
III	40° C	12.63	-14.51
	50° C	11.88	-18.12
IV	40° C	13.13	-15.99
	50° C	11.94	-17.85
V	40° C	12.25	-15.59
	50° C	11.54	-18.65

On addition of limestone, as a partial substitute of slag, the coefficient of thermal expansion decreases. This is due to the filling effect of limestone. Limestone fills the pores between cement particles due to the formation of carboaluminate hydrates [13], which may decrease the thermal expansion. Also, it activates the pozzolanic reaction of slag by reacting with the free lime liberated during hydration of OPC to form more hydration products.



a)



b)

Figure 1. Change of strain vs temperature for the pastes hydrated for 28 days at 40°C and 50°C; a) OPC and b) GBFSC.

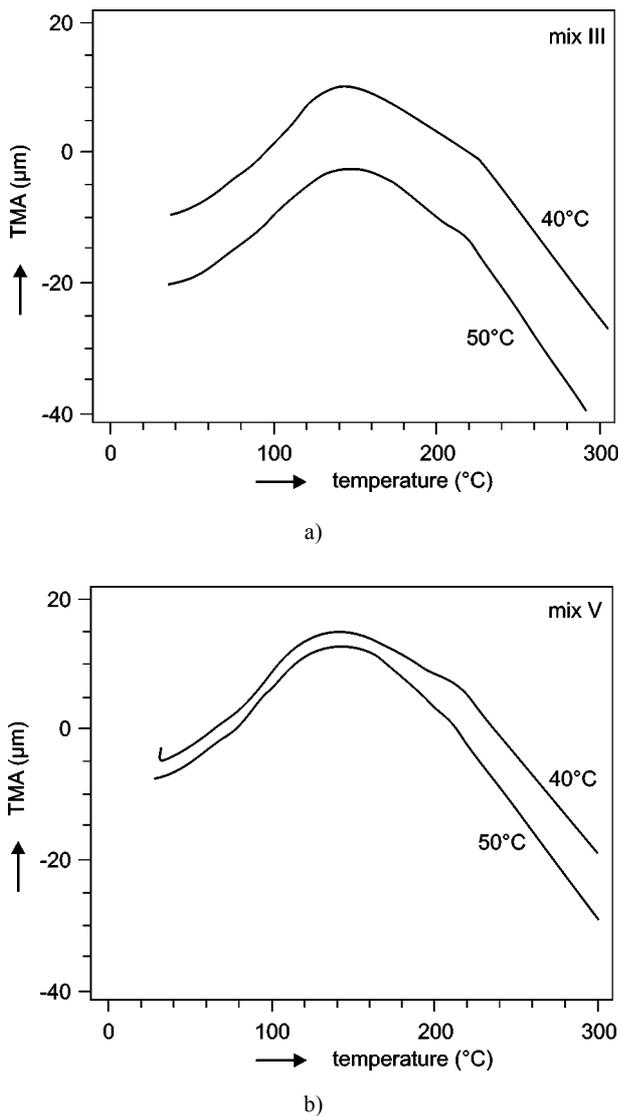


Figure 2. Change of strain vs temperature of hydrated slag-filled cement at 40°C and 50°C; a) 5 % LS and b) 15% LS.

#### Compressive strength of slag-filled cement

Figure 3 illustrates the typical development of compressive strength for plain and slag-filled cement pastes cured under water for 28 days at 30, 40, and 50°C. The compressive strength at 28 days increases irregularly with curing temperature; whereas, the highest compressive strength values were found at 40°C at later ages (28 days). A most significant increase of the compressive strength can be observed; with curing temperature for 30 and 40°C, whereas, this increase is irregular when the curing temperature is raised to 50°C. The compressive strength values of plain (OPC) cement pastes are nearly equal with differences not significant at all hydration temperature, but at 50°C the strength is lower

than the other two curing temperatures (30°C and 40°C). The strength reduction at higher curing temperatures is believed to be the rapid formation of dense inner product hydrate layers on the surface of the cement grain, resulting in a reduced hydration rate and an increased porosity [20]. Micro-cracks caused by thermal stresses and similar phenomenon may weaken the matrix further.

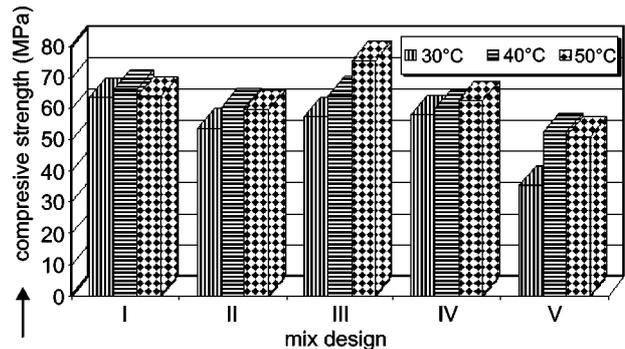


Figure 3. Compressive strength of plain (OPC) and blended cement pastes cured at different temperatures at 28 days.

The values of compressive strength of slag cement show a significant increase with the increase of curing temperature. The increase of curing temperature is associated with an important increase in compressive strength for the slag cement paste; this indicates the higher reactivity of slag from the pozzolanic activity point of view. By addition of 5 wt.% LS (mix III; 65 % OPC 30 % GBFS, 5 % LS) instead of blast-furnace slag (GBFS), the strength increases markedly with increasing temperature from 30°C to 50°C. This behaviour can be attributed to the higher curing temperature; accelerate the degree of hydration [21]. The increase of curing temperature leads to densification or crystallization of more hydrates. Addition of 5 wt.% LS improves the pore filling and enhances the strength. As the amount of limestone increases, the compressive strength diminishes; this is attributed to the high hydraulic properties of granulated slag than limestone, which is characterized, by less hydraulic or non-hydraulic properties. Increase the addition of LS up to 10 - 15 wt.% increases the dilution effect produced by filler addition (LS), and high replacement levels of limestone filler produce a decrease of strength. Limestone acts as an active participant at later ages, some of it is taken into the system and reacts with  $C_3A$  or ferrite phase to form hemihydrate and monohydrate or a mixture of both [22]. The decrease of compressive strength due to the addition of limestone may be due to the idea that the C-S-H phase is morphologically different than in ordinary Portland cement. In addition, when the limestone content increases, calcium hydroxide crystallizes in the

form of large crystals and concentrates in some areas to form bridges between the calcareous grains. The increase of the curing temperature leads to an increase in the binding capacity of carboaluminate to other  $C_3A$  hydrates which is probably affected by its compact structure [23].

#### Differential scanning calorimetry

Figure 4 shows the DSC thermograms of hardened OPC and slag-filled cement pastes hydrated for 28 days at 30, 40, and 50°C. The thermogram of OPC shows two endothermic peaks at 135°C and 470°C. The first endothermic peak, which located at 135°C, is due to the dehydration of water from C-S-H phase and the second endothermic peak is due to the dehydration of  $Ca(OH)_2$ . For slag-filled cement pastes (mix II, mix III, mix IV and Mix V) there is a stepwise loss of water of the C-S-H phases, which giving two subpeaks. It was found

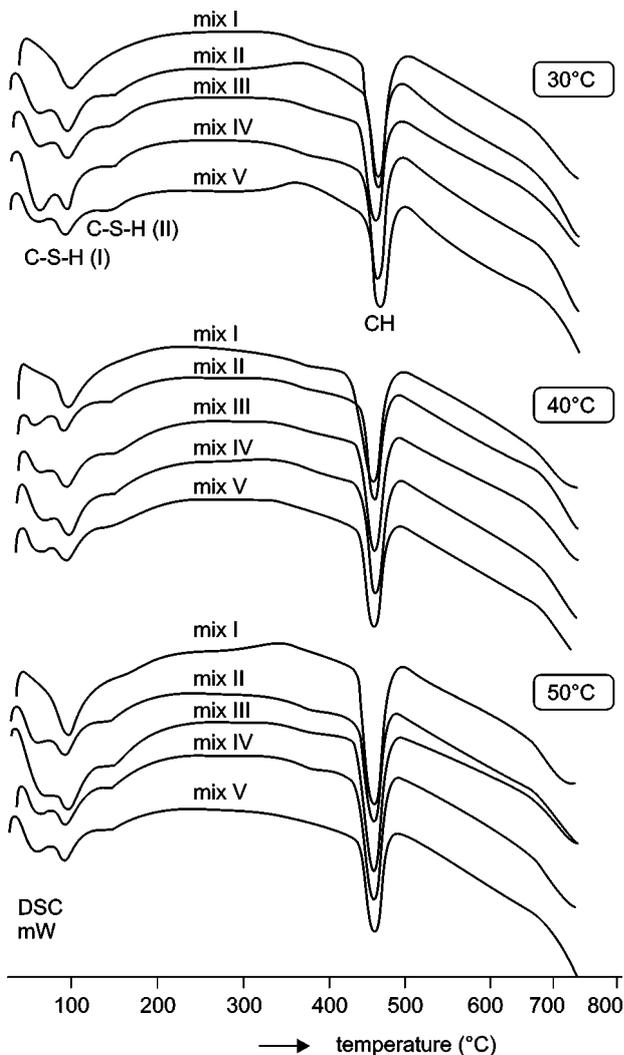


Figure 4. DSC thermogram of plane (OPC) and blended cements hydrated at 30°C, 40°C and 50°C.

that the relative sizes of the two subpeaks are similar in general but can have variations in their exact proportions from sample to sample.

The thermograms obtained for slag-filled cement pastes show the occurrence of four endothermic peaks at 60, 110, 160 and 470°C. The endotherms below 200°C are mainly due to the dehydration of interlayer of C-S-H (tobermorite-like phase) as well as ettringite or monosulphate and carboaluminate hydrates. The endotherms located at 60°C and 110°C are mainly attributed to the dehydration of ettringite and C-S-H with various composition and crystalline state. The endothermic peak at 160°C may be attributed to the more crystallized C-S-H and carboaluminate hydrates. In addition, the formation of carboaluminate hydrate increases with increasing LS content; and therefore, this peak overlapped by the peak of calcium aluminate and C-S-H hydrates. The formation of carboaluminate hydrate increases on the expense of calcium sulphoaluminate hydrate. This is due to the leaching of  $Ca^{2+}$  from limestone in addition to the liberated lime during the hydration of OPC. Also, the limestone can react with  $C_3A$  as well as  $C_4AF$  forming carboaluminate and carboaluminate ferrite hydrates which need high amount of water than calcium silicate hydrates.

#### Scanning electron microscopy of pozzolanic-filled cement

Figures 5 and 6 show the SEM micrograph of samples I (100 % OPC), III (65 % OPC, 30 % slag and 5 % limestone) and V (65 % OPC, 20 % slag and 15 % limestone) hydrated at 40 and 50°C, respectively. Figure 5a shows hexagonal crystals of  $Ca(OH)_2$  as stacked parallel layers embedded in an accumulation of fibrous layer of C-S-H.

Figure 5b shows the SEM micrographs of the slag-filled cement paste made with 5 wt.% LS. Evidently, the pore spaces are available for the deposition of hydration products. The micrograph shows the formation of C-S-H phases, which deposited within the pore system, which can accommodate larger amounts of hydration products leading to relatively high compressive strength values as compared with those of OPC and GBFSC pastes. The carbonate acts as a carrier for the fibers of C-S-H as shown in the micrograph. The presence of LS made the structure more denser due to the deposition of carboaluminate hydrate particles. The increase of the amount of limestone in the mix V seemed to enhance the filling of the pores rather (micrograph 5c) rather than the catalytic effect found in the micrograph 5b. The presence of limestone causes morphological changes in the shape of C-S-H crystals from fibers to crumbled foils with small fibers and embedded crystals of  $Ca(OH)_2$ . The substitution of 5-10 wt.% LS is considered as the optimum mix, which influences the microstructure to a certain extent.

The hydration is accelerated by an increase of curing temperature (50°C) as shown in SEM micrograph (figure 6). Figure 6a shows the concentration of crystallized hydration products with large pores between the grains. Micrograph 6b shows more compact structure with the formation of hydration products within the pore system. LS fill the microvoids in the grains packing and thereby improve the compactness of the space matrix. Carboaluminate hydrated products are formed as tubular mass formed occasional of hexagonal plates.

The slight decrease of compressive strength value of OPC paste at 50°C is due to the formation of inner hydration products, which was attributed to a greater

degree of finer porosity in the paste and C-S-H that formed during the treatment has less water content, which is beneficial for reducing the compressive strength.

The increase of compressive strength values in specimens containing GBFS and LS at 50°C is due to two factors (physical and chemical factors). The physical factor is due to the ultrafine habit of LS; it acts as a filler at the spaces between the cement grains. Limestone reduces the pore volumes with development of highly refined pore structure. The reduction in pore volume leads to improve the paste performance, i.e. decreases the thermal expansion.

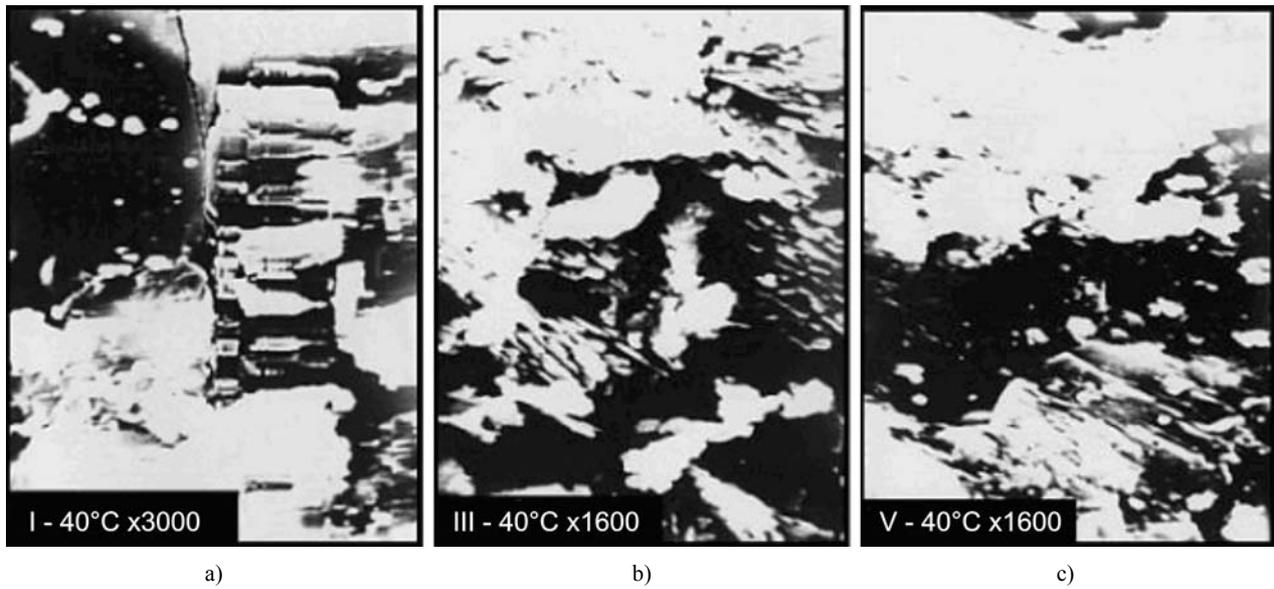


Figure 5. SEM micrographs of mixes I, III and V at 40°C.

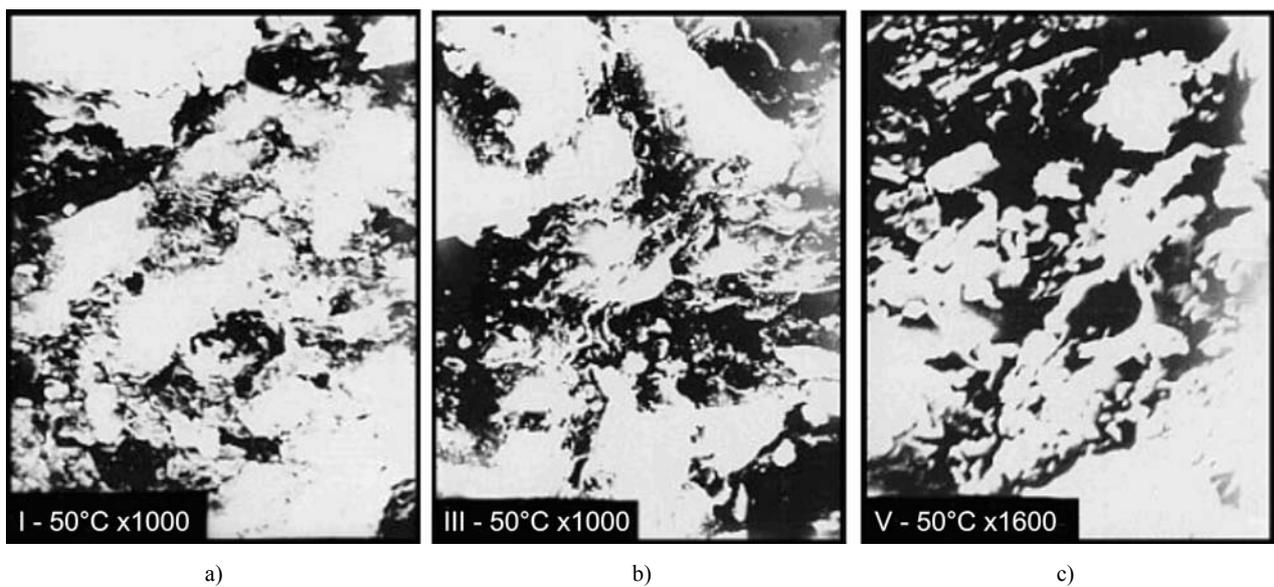


Figure 6. SEM micrographs of mixes I, III and V at 50°C.

The chemical effect is due to pozzolanic reaction of slag to form additional amounts of C-S-H as well as the effect of LS resulting in the formation of carboaluminate hydrates in the preference of sulphoaluminate hydrated products.

### CONCLUSIONS

The main conclusions derived from this study may be summarized as follows:

- 1) By addition of limestone decrease the coefficient of thermal expansion. Limestone fills the pores between cement particles due to formation of carboaluminate hydrate, which may decrease the thermal expansion.
2. The curing temperature increase yielded an important increase in compressive strength for slag cement indicating the higher reactivity of slag arises from the pozzolanic activity point of view. As a result, the values of compressive strength of slag cement show an increase with curing temperature.
3. The increase the curing temperature leads to an increase in the binding capacity of carboaluminate hydrate to other C<sub>3</sub>A hydrates which is probably affected by its compact structure.
4. Addition of 5 wt.% LS improves the pore filling and enhances the strength. As the amount of limestone increases (15 wt.% LS), the compressive strength diminishes; this is attributed to the less hydraulic or non-hydraulic properties of LS in comparison with the hydraulic activity of slag.
5. The presence of LS made the structure more denser due to the deposition of carboaluminate hydrate particles. The carbonate acts as a carrier for the fibrous of C-S-H. The C-S-H phases are deposited within the pore system, which can accommodate larger amounts of hydration products leading to relatively high compressive strength values as compared with those of OPC and GBFSC pastes.
6. The presence of 15 wt.% LS causes morphological changes in the shape of C-S-H crystals from fibers to crumble foils with small fibers and embedded Ca(OH)<sub>2</sub>.

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### VLIV TEPLoty ZRÁNÍ NA TEPLoTNÍ ROZTAŽNOST A FÁZOVÉ SLOŽENÍ HYDRATOVANÝCH VÁPENCOVO-STRUSKOVÝCH CEMENTŮ

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Zkoumanými materiály byl obyčejný portlandský cement (OPC), granulované vysokopecní strusky (GBFSC) a vápenc. Struskový cement s vápencem má malou tepelnou roztažnost a koeficient smrštění ve srovnání s čistými OPC pastami. Je to způsobeno hlavně aktivitou pozolánu v granulované strusce a dále plnivovým vlivem vápence. Bylo zjištěno, že částečné nahrazení strusky pěti procenty vápence zlepšuje pevnost v tlaku. S poklesem teploty zrání C-S-H fáze vypadává v pórech, které mohou přijmout větší množství hydratačních produktů. To vede k vyšší relativní pevnosti v tlaku GBFSC past ve srovnání s OPC pastami. Když stoupne obsah vápence na 15%, pevnost v tlaku klesá. V přítomnosti 15% vápence se mění tvar C-S-H krystalů z jehlicovitých na rozpadlé lístečky s malými jehličkami Ca(OH)<sub>2</sub>.