

# ELECTRICAL PROPERTIES, PHYSICO-CHEMICAL AND MECHANICAL CHARACTERISTICS OF FLY ASH-LIMESTONE-FILLED POZZOLANIC CEMENT

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*In this paper fly ash was replaced partially up to fully by limestone dust. The change in the electrical conductivity was reported during setting and hardening after gauging with water. The phase composition was studied by XRD and DTA. Degree of hydration, gel/space ratio, reaction ratio, porosity and mechanical properties as well as free lime content was studied. The results show that the substitution of fly ash by 5-10 wt.% limestone in SRC pastes decreases the conductivity. Increase of limestone content (15 and 20 wt.%), the electrical conductivity increases than sample free from limestone (S.0). 5 wt.% limestone extended the final setting times. On the other side, the increase of limestone content, the final setting times are shortened, this is due to the filling effect of the limestone. The combined water, degree of hydration and the gel/space ratio increase with limestone content. It was shown that the free lime of S.0, S.5 as well as M.0, M.5 increase up to 7 days, and then decreases up to 90 days. On the other hand, the compressive strength and total porosity decrease with limestone content.*

## INTRODUCTION

Fly ash utilization is a research of considerable interest at the present time, where fly ash is employed as an active addition to Portland cement clinker and as partial substitution of cement respectively [1]. The suitability of fly ash use in the production of fly ash Portland cement is determined by its pozzolanic activity, which in turn is greatly influenced by its content of glassy phase, the higher content of glassy phase, the higher pozzolanic activity.

The incorporation of fly ashes to the Portland cement and concrete as active addition was investigated [2]. Due to their capacity for reacting with lime, principally originated during the hydration of the Portland cement, forms hydraulic compounds.

The replacement of a Portland cement by three different high-CaO fly ashes slightly decrease the non-evaporable water content in comparison with their low CaO-fly ashes [3].

Portland-pulverized fuel ash cements containing 20-40 wt.% PFA by intergrinding or blending the ashes with cement were studied [4,5]. The intergrinding leads to an improvement in the water-reducing properties of coarse PFAS and also their pozzolanic activity as indicated by compressive strength development at later ages. Setting time was the same for blended and inter-

ground cements, both being considerably longer than for ordinary Portland cements.

The effect of limestone on the properties of cement in relation to the source of limestone and type of cement was studied [6-9]. It was found that the advantage of limestone filler over silica depends on the quality of the clinker and its  $C_3A$  content. With a low  $C_3A$  content (9 %), the strength gain is negligible, and there is no monocarboaluminate formation. While, with a high  $C_3A$  content (14.5 %), the limestone addition increases the strength at both early and later ages. There is evidence that the influence of limestone depends on  $C_3A$  content because  $CaCO_3$  produces stable calcium carboaluminate hydrate during the reaction with  $C_3A$ .

The effect of limestone addition depends more on clinker type than on its fineness [10,11]. The addition of limestone to clinker with higher lime saturation factor (LSF) influenced predominantly early compressive strength, while the addition of limestone to clinker having low LSF influenced mostly the compressive strength after 28 days and recently. It was found that carbo-silicate hydrates might form in the reaction between  $CaCO_3$  and silicate phases.

The present work aimed to study the effect of substitute of limestone by fly ash on the electrical properties, physico-chemical and mechanical characteristics of SRC and OPC filled pozzolanic cement pastes.

## EXPERIMENTAL

The materials used in this investigation were limestone, ordinary Portland and sulphate resistant cements, provided from Helwan Portland Cement Company, Helwan, Egypt, as well as pulverized fly ash from Touthki, Aswan, Egypt. The chemical and phase composition of starting materials are shown in table 1.

Table 1. Chemical analysis and phase composition of the starting materials, (wt. %).

Oxides	FA	LS	SRC	OPC
SiO <sub>2</sub>	47.49	4.37	20.85	20.12
Al <sub>2</sub> O <sub>3</sub>	23.75	0.36	4.63	5.25
Fe <sub>2</sub> O <sub>3</sub>	7.96	0.29	5.38	3.58
CaO	4.81	52.99	63.15	62.13
MgO	2.44	0.90	2.34	1.53
SO <sub>3</sub>	0.54	0.10	2.05	2.54
L.O.I	1.98	41.20	1.61	2.64
K <sub>2</sub> O	4.02	--	--	--
Na <sub>2</sub> O	1.24	--	--	--
Cl <sup>-</sup>	0.40	--	--	--
C <sub>3</sub> S	--	--	50.33	51.79
β-C <sub>2</sub> S	--	--	21.80	18.61
C <sub>3</sub> A	--	--	3.12	7.81
C <sub>4</sub> AF	--	--	16.41	10.92

Different mixes were made from (80 wt.%) SRC or OPC with variable amounts of fly ash and limestone. Fly ash is substituted by limestone at 5, 10, 15 and 20 wt.%. The different mix compositions are shown in table 2. Each dry mix was homogenized in a porcelain ball mill with four balls for 1 h., to assure complete homogeneity. The water of consistency and setting times were measured [12,13]. The pastes were mixed with the water of consistency, molded into one inch cubes cured in a 100 % R.H. at 23 ± 2°C for 24 hours, then demolded and cured under tap water up to 90 days. After the predetermined curing time, the hydration of the pastes was stopped using the technique described

Table 2. Mix composition of the prepared pozzolanic-filled cement, (wt. %).

Mix. No.	SRC	OPC	FA	LS
S.0	80	-	20	0
S.5	80	-	15	5
S.10	80	-	10	10
S.15	80	-	5	15
S.20	80	-	0	20
M.0	-	80	20	-
M.5	-	80	15	5
M.10	-	80	10	10
M.15	-	80	5	15
M.20	-	80	-	20

elsewhere [14]. The kinetics of hydration was followed by the determination of combined water, free lime [15], insoluble residue [16], degree of hydration and gel/space ratio. The compressive strength, the bulk density and the total porosity  $\epsilon$  (17) of the cement pastes were measured up to 90 days. The electrical conductivity measurements were also carried out [18]. The test cell was of the co-axial type, which includes concentric inner and outer electrodes mounted on an insulated base plate as described in the previous work [19]. The electrodes were polished and the cement pastes were sandwiched in the space between the electrodes. The cell was then kept in a desiccator at 100 % relative humidity at 25 ± 2°C during the test period. The measurement began exactly 3 minutes after mixing (zero time). The electrodes were connected with Digital Conductometer "CONSORT-K120" with an accuracy of ± 0.01  $\mu$ S, for conductance measurements between the electrodes across the hydration stages of setting and hardening.

## RESULTS AND DISCUSSION

The electrical conductivity depends on the microstructure of cement pastes in several ways. In general, for an insulating material containing pores filled with a conductor, the bulk conductivity is usually related to the porosity and the conductivity of the material filling the pores [20]. Cement paste, is a more complicated composite conductor because its microstructure and conductivity of its fluid are interrelated and time-dependent.

The electrical conductivity-time data of limestone-fly ash pozzolanic filled cement pastes are graphically plotted in figure 1. Such method has been used on cement pastes, in order to characterize the behavior of cement during setting and hardening [21-24]. The curves show an initial increase in electrical conductivity, when the cement comes in contact with water, followed by a gradual decrease during the initial stage of hydration leading to the first peak. After few hours the electrical conductivity increases, reaching a second maximum peak, following a sharp decrease.

The first conductivity maximum takes place after mixing with water (around 40-45 min., in S.0, S.5 and S.10) and (within 30-37 min., in M.0 and M.15) is due to the hydration, of cement yields Ca<sup>2+</sup>, OH<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. Also alkali sulphates present in the cement dissolve completely within seconds, contributing K<sup>+</sup>, Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> [25]. In case of limestone CO<sub>3</sub><sup>2-</sup> ions are present in the solution, these increase the conductivity. The decrease in electrical conductivity after the maximum is attributed to the formation of electrical insulating layers around the cement particles, which reduce ion mobility, therefore decrease the electrical conductivity.

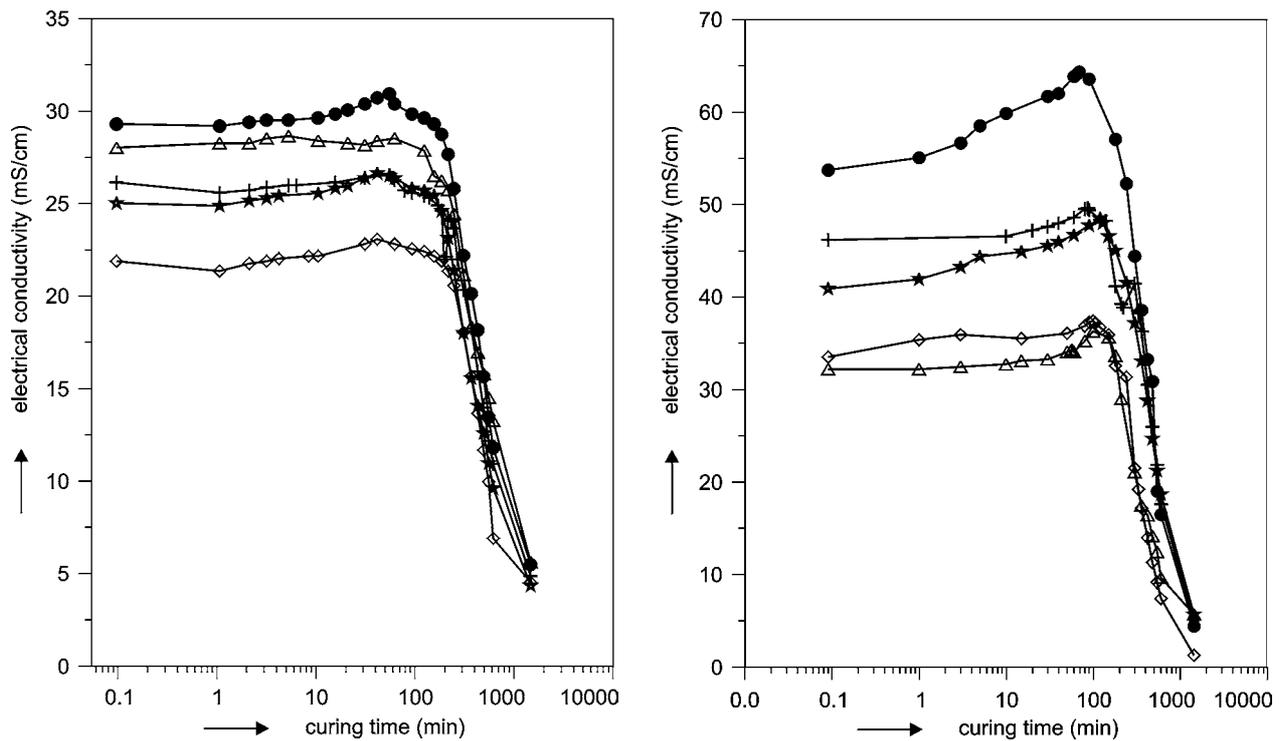


Figure 1. Electrical conductivity values of filled pozzolanic cement pastes containing different amounts of limestone up to 1440 min (SRC/OPC: + - S0/M0; ◇ - S5/M5; ☆ - S10/M10; △ - S15/M15; ● - S20/M20).

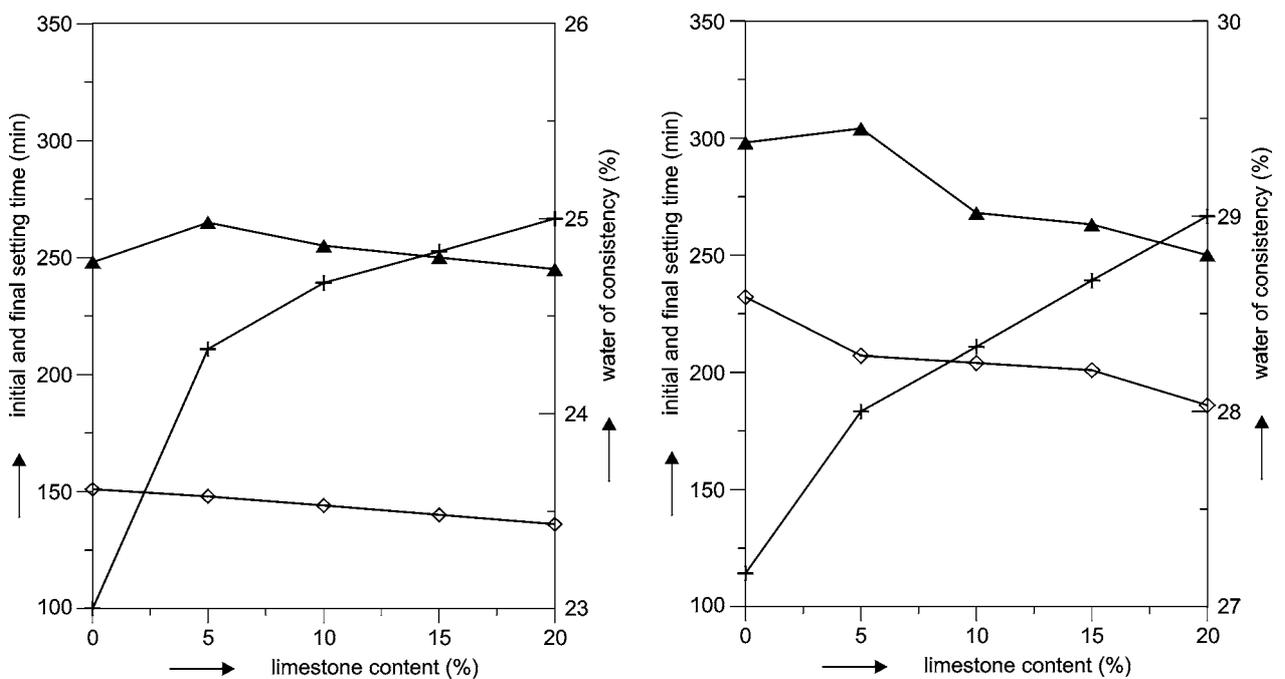


Figure 2. Water of consistency, initial and final setting time of filled pozzolanic cement pastes (SRC/OPC: + - consistency; ◇ - initial set; ▲ - final set).

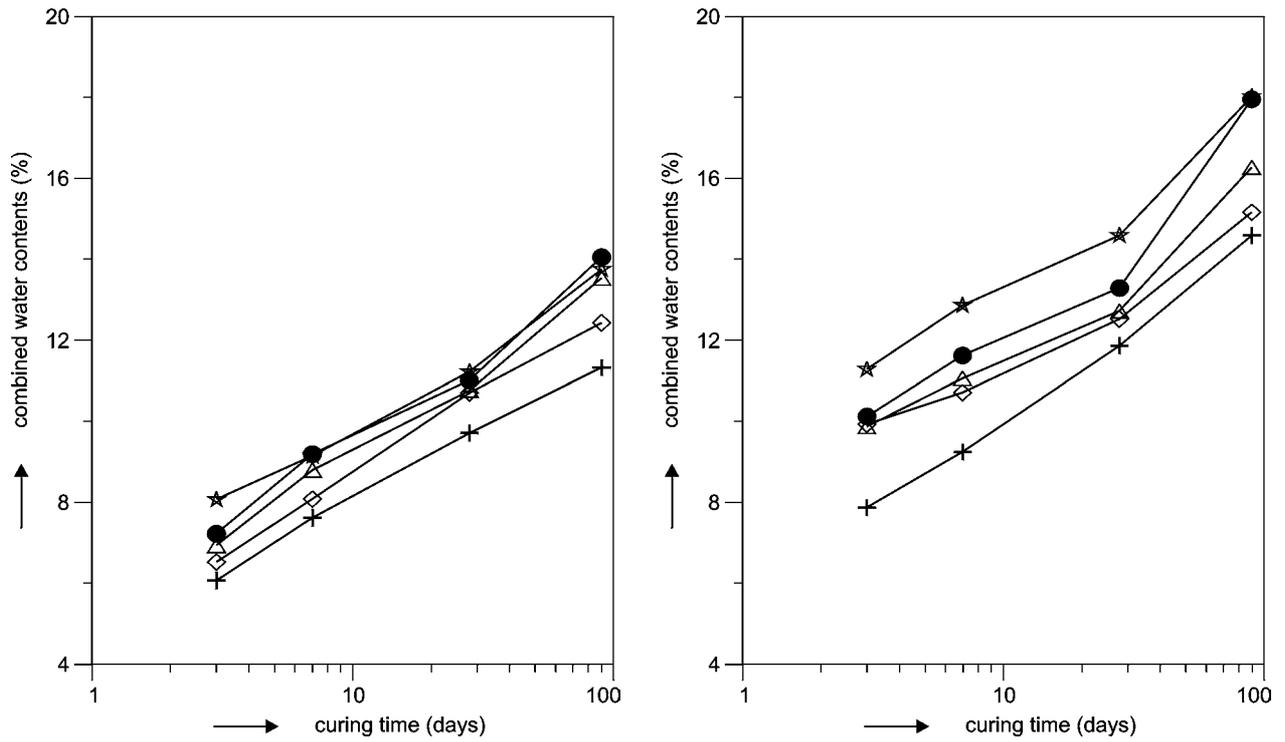


Figure 3. Variations of chemically combined water contents of filled pozzolanic cement pastes containing different amounts of limestone up to 90 days (SRC/OPC: + - S0/M0;  $\diamond$  - S5/M5;  $\triangle$  - S10/M10;  $\bullet$  - S15/M15;  $\star$  - S20/M20).

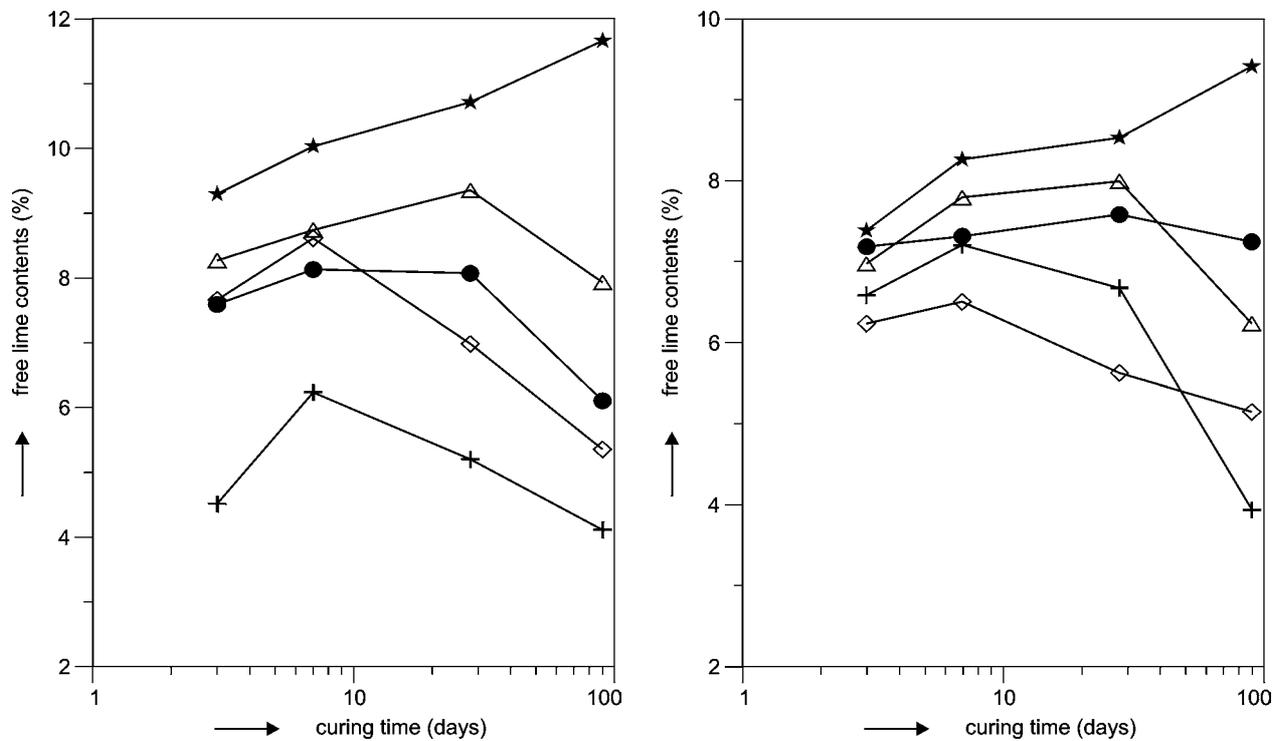


Figure 4. Free lime contents of filled pozzolanic cement pastes containing different amounts of limestone up to 90 days (SRC/OPC: + - S0/M0;  $\diamond$  - S5/M5;  $\triangle$  - S10/M10;  $\bullet$  - S15/M15;  $\star$  - S20/M20).

The second maximum (within 60-210 min., in S.15 and M.0 and around 200-337 min., in M.5 and M.0) may be due to the transformation of ettringite to monosulfate. During this process two moles of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions are formed per mole of ettringite, and also due to the osmotic pressure development around the cement particles, which leads to an increase in the ionic mobility (i.e. an increase of electrical conductivity is a result of an increase in the number or the mobility of ions) [21,26]. The time and height of this maximum can be changed with limestone content. The sharp decrease in electrical conductivity at later ages of hydration is due to the formation of hydrated products, resulting in a marked consumption of number of ions.

The substitution of fly ash by 5-10, wt.% limestone in SRC pastes decreases the conductivity. Limestone activates the pozzolanic reaction of fly ash by reacting with lime liberated during hydration of SRC. Increase the limestone content (10 wt.%) the electrical conductivity increases, but it is still less than the sample free of limestone (S.0), i.e. 5-10 wt.% limestone activates the pozzolanic reaction to consume more  $\text{Ca}^{2+}$  to form more hydration products, while the substitution of fly ash by 15 and 20, wt.%, limestone increases the electrical conductivity than S.0. This is due to the leaching of  $\text{Ca}^{2+}$  from limestone in addition to the liberated lime during the hydration of SRC. The conductivity decreases with the addition of 5, 10 and 15 wt.% limestone as a partial substitution of fly ash in OPC pastes. This is mainly due to the decrease of the alkali content of the fly ash by replacing with limestone. Therefore, the conductance decreases. The substitution of 20 wt.% fly ash with limestone increases the height of the conductivity peaks, this is due to the liberation of some  $\text{Ca}^{2+}$  ions, therefore, the conductivity increases [27]. The free lime content of the sample with 20, wt.% limestone is higher than all mixes at all ages of hydration.

The water of consistency and setting times are graphically represented as a function of limestone content in figure 2. The addition of limestone increases the plasticity of the mix, which needs more water for workability, i.e., the consistency increases with the amount of limestone. This may be attributed to the capacity of limestone to absorb water [28]. Also, the limestone can react with  $\text{C}_3\text{A}$  as well as  $\text{C}_4\text{AF}$  forming carboaluminate and carboaluminate ferrite hydrates which need high amount of water than calcium silicate hydrates.

The increase of limestone accelerates the initial as well as final setting time due to the filling effect of limestone. The final setting time is longer at 5 wt.% limestone. On the other side, the increase of limestone content, the final setting time is shortened due to its filling effect. The porosity decreases and then the setting is accelerated. Also, it may be due to the accelerating effect on the hydration of the calcium silicates of

cement [29-31] and/or formation of some carboaluminate hydrates, which have a high rate of hydration at early ages. Therefore, the setting times are shortened with limestone content in the pozzolanic-filled cement.

The combined water contents of filled-pozzolanic cement pastes cured up to 90 days are graphically represented in figure 3. The results show that the combined water content increases gradually with curing time for all cement pastes due to the progress of hydration. Generally, the combined water increases with limestone content, due to the fact that the limestone particles act as nucleation sites for the hydration products of CSH [32,33]. Limestone may react with  $\text{C}_3\text{A}$ ,  $\text{C}_4\text{AF}$  to form calcium carboaluminate or carboaluminate ferrite with higher water content than the calcium silicate hydrates.

The changes of the gel/space ratio of limestone-filled pozzolanic cement pastes are illustrated in table 3. The gel/space ratio of cement pastes was calculated based on the data of degree of cement hydration, i.e. from Wn contents. The results show that the degree of hydration and the gel/space ratio increase with curing time as well as limestone content for all hardened cement pastes. This suggests increase of the amount of hydration products, which fill the pores between the cement particles. Therefore, the porosity decreases and the gel/space ratio increases [34].

The variation of free lime contents of filled pozzolanic cement pastes cured up to 90 days are graphically illustrated in figure 4. The results show that the free lime of S.0, S.5 as well as M.0, M.5 increases up to 7 days due to fact that the lime liberation during the hydration of cement exceeds the rate of consumption by pozzolanic reaction. Further the free lime decreases up to 90 days, due to the pozzolanic reaction of fly ash (i.e., rate of consumption by fly ash increases at the expense of the rate of lime liberation). The mix M.5 shows lower free lime content than mix M.0. This may be due to the fact that 5 wt.% limestone activates fly ash to react with liberated lime. On the other side, the

Table 3. Gel/space ratio of filled pozzolanic cement pastes as a function of curing time.

Mix. No.	Gel/Space Ratio (%)			
	3 days	7 days	28 days	90 days
S.0	1.9850	1.9943	1.9994	2.0023
S.5	1.9898	1.9963	2.0014	2.0037
S.10	1.9918	1.9980	2.0027	2.0063
S.15	1.9918	1.9983	2.0022	2.0061
S.20	1.9961	1.9994	2.0039	2.0078
M.0	1.9897	1.9948	2.0006	2.0038
M.5	1.9949	1.9971	2.0004	2.0044
M.10	1.9950	1.9985	2.0018	2.0061
M.15	1.9955	1.9990	2.0022	2.0080
M.20	1.9980	2.0016	2.0043	2.0085

increase of the limestone to 10 and 15 wt.% increases the free lime content up to 28 days, and then decreases at 90 days. While the addition of 20 wt.% LS limestone increases the free lime up to 90 days. This is mainly attributed to the absence of fly ash, which consume the lime and also leaching of  $\text{Ca}^{2+}$  ions from limestone. Hence, the liberation of lime during the hydration of ( $\text{C}_3\text{S}$ ,  $\beta\text{-C}_2\text{S}$ ) in addition to the leaching some  $\text{Ca}^{2+}$  from the limestone leads to increase the free lime with limestone content [28,35].

Figure 5 illustrates the DTA thermograms of M.10 (80 % OPC +10% FA + 10 % LS) cured at 3, 7, 28 and 90 days. The DTA thermograms show the occurrence of six endothermic peaks at 90, 113, 165, 400°, 480, 720 and 760°C. The endotherms below 200°C are mainly due to the dehydration of interlayer of CSH (tobermorite-like phase) as well as ettringite or monosulphate and carboaluminate hydrates. The decomposition of ettringite and/or monosulphate is occurred at lower temperature and overlapped by the CSH. The endothermic peak at 400°C is attributed to the decomposition of hydrogarnet, whereas the endothermic peak at 480°C is due to decomposition of  $\text{Ca}(\text{OH})_2$ . The endotherms at 720°C and 760°C are due to the decomposition of amorphous and crystalline  $\text{CaCO}_3$ . The endotherm at 113°C may be attributed to the dehydration of CSH with various composition and crystalline state. The endotherm at 160°C may be attributed to sulphoaluminate and carboaluminate hydrates [36].

Sample hydrated for 3 days shows the presence of CSH (tobermorite-like phase), sulphoaluminate, carboaluminate, gehlenite hydrate, portlandite and calcium carbonate with different crystalline state. Sample hydrated for 7 days illustrates the increase of CSH,

sulphoaluminate, carboaluminate as well as gehlenite hydrate and the portlandite as well as  $\text{CaCO}_3$  is still constant. As the hydration proceeds up to 90 days, the portlandite is slightly decreased, whereas the calcium silicate hydrate as well as sulphoaluminate hydrate and gehlenite hydrate increase. It is clear that the amount of hydrates as sulphoaluminate, CSH, carboaluminate or hydrogarnet series are increased with curing time due to the hydration of Portland cement phases and some of fly ash. The amount of portlandite is still constant from 3 up to 90 days. This indicates that the rate of liberation of free lime during the hydration of OPC phases ( $\text{C}_3\text{S}$ ,  $\beta\text{-C}_2\text{S}$ ) in addition to the leached  $\text{Ca}^{2+}$  from the limestone is nearly equal to the rate of consumption of free lime by fly ash. The endothermic peak at 720°C is mainly attributed to the secondary formation of  $\text{CaCO}_3$  from the carbonation of  $\text{Ca}(\text{OH})_2$ , whereas the endotherm at 760°C is attributed to the decomposition of  $\text{CaCO}_3$  from the natural limestone. It is evidence of figure 6, DTA thermograms of hydrated pozzolanic-filled cement pastes containing constant proportion of OPC with different amounts of fly ash as well as limestone cured at 90 days where the endothermic peak at 770°C increases with the amount of substituted limestone due to the decomposition of natural limestone.

Figure 7 illustrates the XRD patterns of M.10 (80% OPC + 10% FA + 10% LS) cured at 3, 7, 28 and 90 days. Paste hydrated at 3 days exerts the presence of portlandite, alite and belite as well as  $\text{CaCO}_3$ . Samples hydrated for 7 and 28 days show that the intensity of portlandite and  $\text{CaCO}_3$  peaks are still constant, whereas the peaks of the unhydrated OPC phases ( $\text{C}_3\text{S}$  and  $\beta\text{-C}_2\text{S}$ ) decrease with curing time due to the continuous hydration.

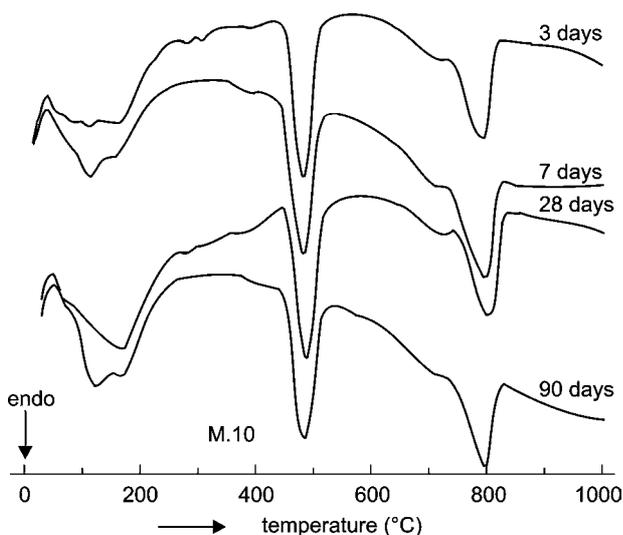


Figure 5. DTA curves of M.10 cured for 3, 7, 28 and 90 days.

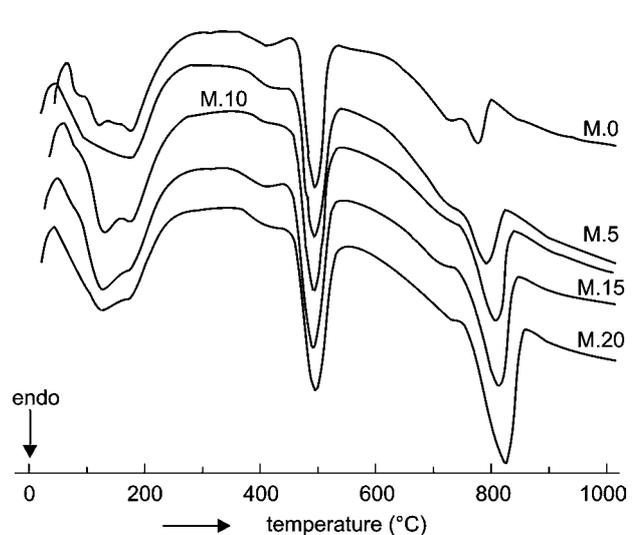


Figure 6. DTA thermograms of M.0, M.5, M.10, M.15 and M.20 hydrated at 90 days.

As the hydration proceeds up to 90 days, the peaks of portlandite and  $\text{CaCO}_3$  are slightly decreased due to the slight pozzolanic reaction. The results show also that although the pozzolanic reaction progresses, the total amount of portlandite available for pozzolanic reaction has not been consumed. This indicates that the rate of liberation of free lime during the hydration of OPC phases ( $\text{C}_3\text{S}$  and  $\beta\text{-C}_2\text{S}$ ) in addition to the leached  $\text{Ca}^{2+}$  from the substituted limestone is nearly equal to the rate of consumption of free lime by fly ash. This result is in a good agreement with that of DTA. The presence of belite ( $\beta\text{-C}_2\text{S}$ ) peaks of relatively higher intensity than alite ( $\text{C}_3\text{S}$ ) illustrates the fast hydration of alite than that of belite phase even at 90. However, the relatively low intensity of silicate peaks in pozzolanic filled cement pastes also support that the hydration of  $\text{C}_3\text{S}$  and  $\beta\text{-C}_2\text{S}$  in cement pastes is accelerated in the presence of limestone [29-31].

The XRD patterns for filled pozzolanic cement pastes with various amounts of fly ash and limestone cured at 90 days are illustrated in figure 8. The patterns illustrate that the intensity of portlandite peak increases with

limestone content due to the hydration of  $\text{C}_3\text{S}$  and  $\beta\text{-C}_2\text{S}$  as well as the leaching of  $\text{Ca}^{2+}$  from the limestone. Therefore, the peaks intensity of alite and belite are decreased. At 90 days of hydration, the XRD pattern of 20 wt.% limestone shows a comparatively small peak of belite, with very small peak of alite indicating the fast hydration of alite phase. From these results it can be concluded that the fly ash possesses a slight pozzolanic activity.

The insoluble residue contents of filled pozzolanic cement pastes cured up to 90 days are illustrated in table 4. It is clear that the insoluble residue content decreases with curing time as well as with limestone content for all hardened cement pastes, due to the decrease of the fly ash content. The decrease of insoluble residue at early ages depends on the amount of substituted fly ash by limestone. Generally, the insoluble residue decreases sharply up to 7 days and then slightly up to 90 days. This is due to the higher rate of reaction of amorphous calcium aluminosilicate phases present in FA at early ages. The rate of decrease of insoluble residue is slightly occurred after 7 days, due to the presence of crystalline phases.

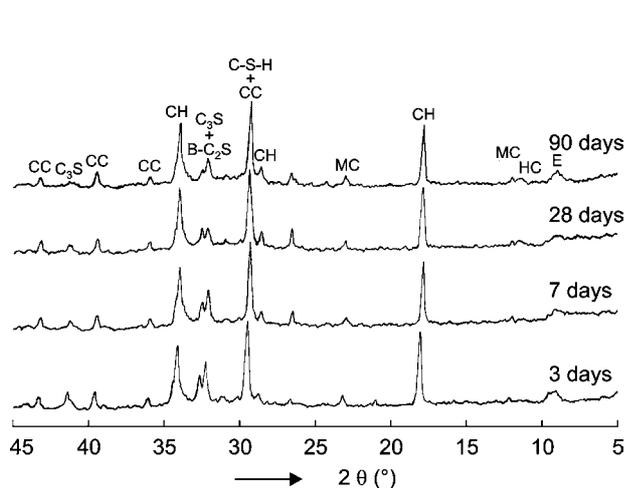


Figure 7. XRD patterns of M.10 cured for 3, 7, 28 and 90 days (C-S-H: calcium silicate hydrate, CH: calcium hydroxide, CC: calcium carbonate,  $\text{C}_3\text{S}$ : alite,  $\beta\text{-C}_2\text{S}$ : belite, E: ettringite, MC: monocarbonate, HC: hemicarbonate).

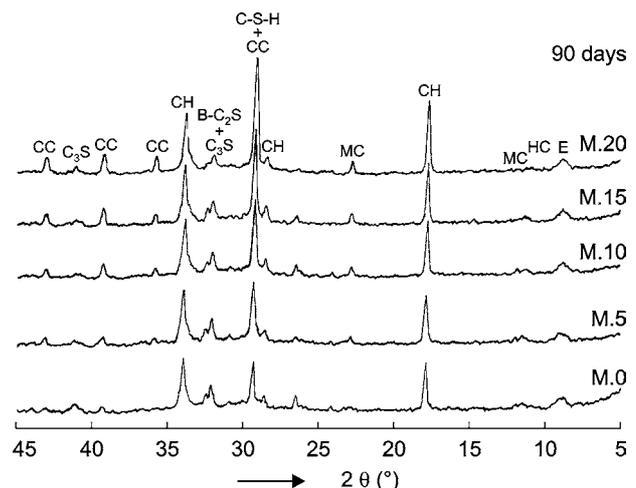


Figure 8. XRD patterns of M.0, M.5, M.10, M.15 and M.20 hydrated at 90 days (C-S-H: calcium silicate hydrate, CH: calcium hydroxide, CC: calcium carbonate,  $\text{C}_3\text{S}$ : alite,  $\beta\text{-C}_2\text{S}$ : belite, E: ettringite, MC: monocarbonate, HC: hemicarbonate).

Table 4. Insoluble residue and reaction ratio of filled pozzolanic cement pastes as a function of curing time.

	Insoluble residue cements (%)				Reaction ratio (%)			
	3 days	7 days	28 days	90 days	3 days	7 days	28 days	90 days
S.0	15.33	14.52	13.86	13.21	9.18	15.50	21.24	31.03
S.5	11.69	10.68	10.32	9.58	13.87	18.68	26.55	34.64
S.10	8.34	7.66	7.00	6.81	12.40	22.37	26.70	36.96
S.15	5.05	4.47	4.29	4.22	10.32	17.16	23.40	32.88
M.0	15.01	14.24	13.64	13.52	13.51	18.77	21.88	34.09
M.5	12.11	10.57	10.55	9.78	24.97	26.01	33.44	48.87
M.10	8.38	7.53	7.25	6.65	22.59	27.32	35.70	55.46
M.15	4.71	4.37	4.18	3.98	15.24	21.32	27.69	51.49

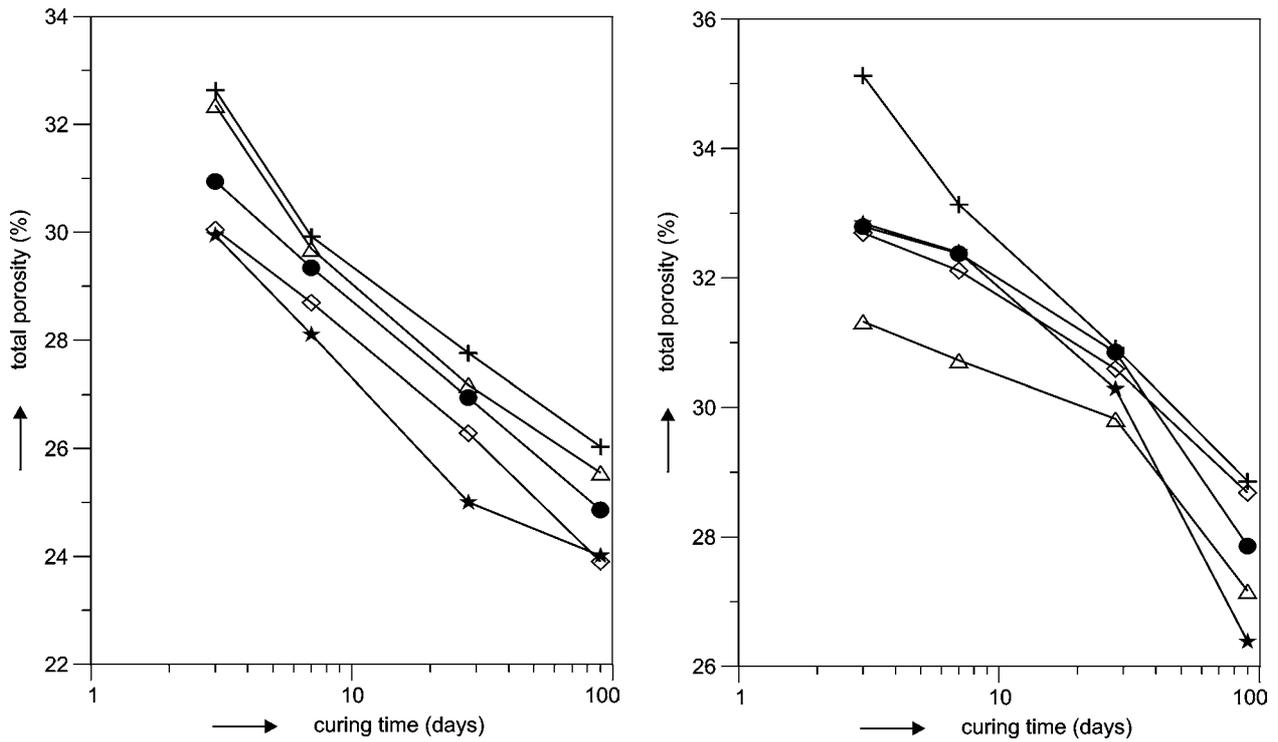


Figure 9. Total porosity of filled pozzolanic cement pastes as a function of curing time (SRC/OPC: + - S0/M0;  $\diamond$  - S5/M5;  $\triangle$  - S10/M10;  $\bullet$  - S15/M15;  $\star$  - S20/M20).

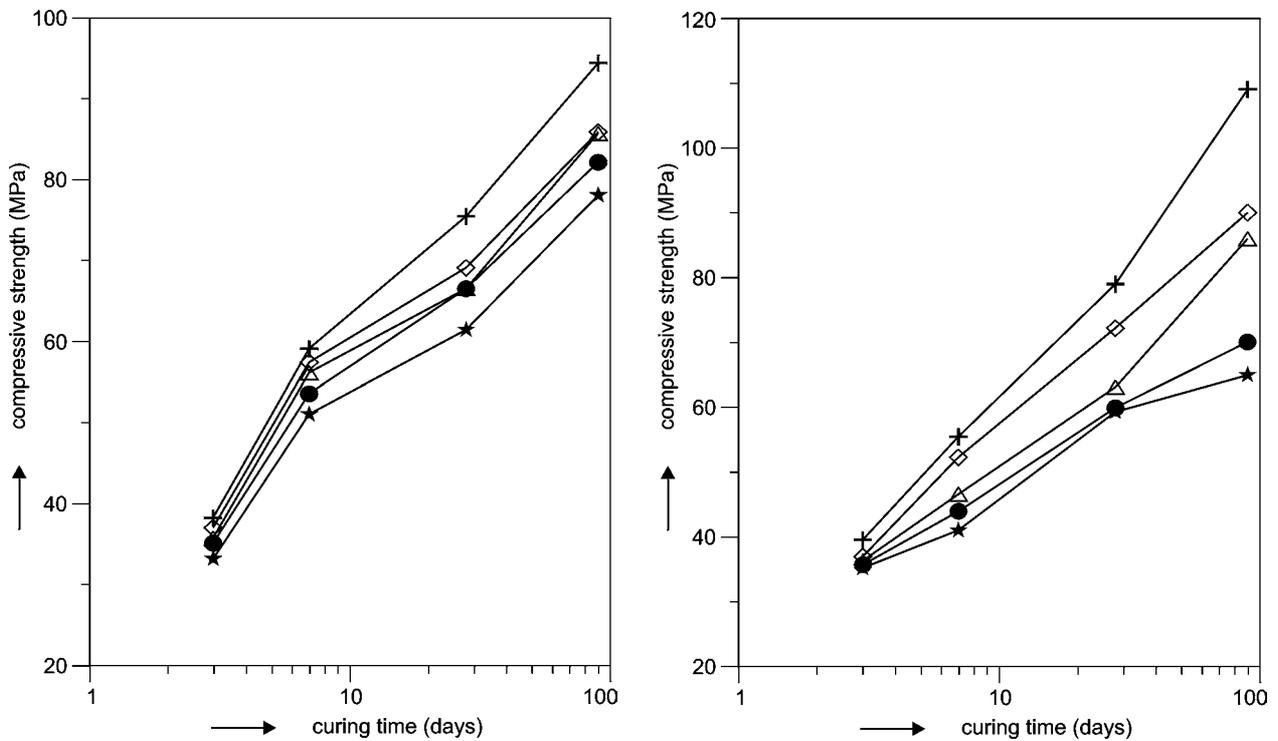


Figure 10. Compressive strength of filled pozzolanic cement pastes with curing time (SRC/OPC: + - S0/M0;  $\diamond$  - S5/M5;  $\triangle$  - S10/M10;  $\bullet$  - S15/M15;  $\star$  - S20/M20).

The reaction ratio of filled pozzolanic cement pastes cured up to 90 days are illustrated as a function of curing time in table 4. The reaction ratio increases for all hardened cement pastes up to 90 days. Obviously, the substitution of fly ash by 5 wt.% limestone leads to a sharp increase in reaction ratio, whereas 10 and 15 wt.% limestone decrease the reaction ratio especially at early ages. This is attributed to fact that 5 wt.% limestone activates the pozzolanic action. This is consistent with the results of electrical conductivity at early ages, where 5 wt.% LS has the lowest electrical conductivity values and free lime. At 90 days the results show that the reaction ratio increases with limestone up to 15 wt.%. This is mainly attributed to the fact that the limestone represents as nucleation sites for the hydration products as well as enhances the hydration of calcium silicate phases [29-31].

Replacement of 5 % FA with limestone leads to a sharp increase in silica-alumina reaction ratio. Limestone activates FA via leaching of  $\text{Ca}^{2+}$  ions. Further replacement of FA with limestone, silica-alumina reaction ratio decreases, this is due to the decrease of the amount of active silica-alumina to react with the liberated lime during hydration.

The total porosity of filled cement pastes cured up to 90 days are graphically illustrated as a function of curing time in figure 9. The total porosity decreases with limestone content for all cement pastes. This is due to the continuous filling up of a part of the available pores with the formed hydrated products [28]. Obviously, the substituted limestone decreases the porosity, due to the filling effect and the acceleration of hydration, i.e. more hydration products are formed.

The compressive strength of the hardened cement pastes cured up to 90 days are graphically plotted as a function of curing time in figure 10. The compressive strength increases with curing time for all cement pastes, due to the formation and later accumulation of hydration products within the available pore spaces. This leads to the increase of strength. On the other side, the compressive strength decreases with the limestone content. The limestone dilutes the pozzolanic reaction. The compressive strength development depends primarily on the formation of the hydrated calcium silicates and its crystallization states, having strong binding forces and/or their transformation into other hydration products having weaker binding forces [27]. It is also due to the decrease of the amount of CSH by the increase of limestone content. Therefore, this is certainly attributed to the replacement of a hydraulic material ( $\beta\text{-C}_2\text{S}$  &  $\text{C}_3\text{S}$ ) with a non-hydraulic limestone. Accordingly, the magnitude of the strength loss is increased with limestone content. Figure 10 shows also that addition of limestone, the compressive strength decreases by 10-20% and 20-50% in the case of SRC and OPC at 90 days respectively.

## CONCLUSIONS

The main conclusions derived from this study can be summarized as following:

1. The substitution of fly ash with 5-10 wt.% limestone decreases the conductivity. Increase of limestone substitution (15 and 20 wt.%), the electrical conductivity increases.
2. Limestone accelerates the initial and final setting times, while the final setting time is extended with the substitution of 5 wt.% limestone.
3. Increase of limestone contents, the degree of hydration, the gel/space ratio and combined water contents increase.
4. Free lime contents of samples containing 0 and 5 wt.% limestone increase up to 7 days, and then decreases up to 90 days. On the other hand, the increase of the limestone up to 15 wt.%, the free lime contents increase up to 28 days, and then decreases at 90 days.
5. Substitution of 5 wt.% limestone leads to a sharp increase in reaction ratio, whereas 10 and 15 wt.% limestone decrease the reaction ratio especially at early ages, whereas at 90 days the reaction ratio increases with limestone up to 15 wt.%.
6. Increase of limestone content, the compressive strength decrease, this is attributed to the decrease of the hydraulic material in the preference of non-hydraulic limestone.

## References

1. Valenti G.L., Cioffi R.: *Cem.Concr.Res.* 18, 91 (1988).
2. Luxán M.P., Madruga F., Savedra J.: *Cem.Concr.Res.* 19, 63 (1989).
3. Diamond S., Lopez-Flores F. in: *Proc.Mater.Res.Soc.*, p. 112-123, Annual Meeting, Symposium N, Boston 1981.
4. Osborne G.J., Nixon P.J.: *Sil.Ind.* 1, 23 (1982).
5. Monk M.: *Mag.Concr.Res.* 35, 131 (1983).
6. Negro A.: *Bachiorrini Cussinol, Interazione Carbonato di Calcio-Alluminati*, p. 219-230, Ed. Murat M., Soustelle M., *Alluminati di Calcio, Seminario Internazionale*, Torino, 1982.
7. Bedard C., Bergeron M. in: *The effect of steam curing upon high-early strength Portland cement containing carbonate addition*, p. 51-59, Ed Klieger P., Hooten R.D., *Carbonate Addition to Cement*, STP-1064, ASTM, Philadelphia 1990.
8. Cochet G., Sorrentino F.: *Limestone filled cements, properties and uses*, p. 266-295 Ed. Sarkar S.L., Ghosh S.N., *Mineral admixtures in cement and concrete*, Vol. 4, ABI Books, New Delhi 1993.

9. Tsivilis S., Chaniotakis E., Badogiannis E., Pahoulas G., Ilias A.: *Cem.Concr.Compos.* 21, 107 (1999).
10. Vuk T., Tinta V., Gabrovšek R., Kaučič V.: *Cem.Concr.Res.* 31, 135 (2001).
11. Pera J., Husson S., Guilhot B.: *Cem.Concr.Compos.* 21, 99 (1999).
12. ASTM Designation: C187-92, Standard test methods for normal consistency of hydraulic cement, ASTM Standards 1992.
13. ASTM Designation: C191-82, Standard test methods for time of setting of hydraulic cement by Vicat Needle, ASTM Standards 1992.
14. El-Didamony H., Haggag M.Y. and Abo-El-Enein S.A.: *Cem.Concr.Res.* 8, 351 (1996).
15. Hewlett P.C.: *Lea's chemistry of cement and concrete*, 4<sup>th</sup> ed., John Wiley & Sons Inc., New York 1998.
16. ASTM Designation: C114-88, Standard test methods for chemical analysis of hydraulic cement, ASTM Standards, p. 710-736, (1990).
17. Copeland L.E., Hayes T.C.: *J.Amer.Concr.Inst.* 27, 633 (1956).
18. Tareev B.: *Physics of dielectric materials*, Mir Publishers, Moscow 1975.
19. Heikal M., Aiad I., Helmy I.M.: *Cem.Concr.Res.* 32, 1805 (2002).
20. Tamás F.D.: *Cem.Concr.Res.* 12, 115 (1982).
21. Abo-El-Enein S.A., Kotkata M.F., Hanna G.B., Saad M., Abd-El-Razek M.M.: *Cem.Concr.Res.* 25, 1615 (1995).
22. Heikal M., El-Didamony H., Morsy M.S.: *Cem.Concr. Res.* 30, 1827 (2000).
23. Garboczi E.J.: *Cem.Concr.Res.* 20, 591 (1990).
24. Heikal M., Morsy M.S., El-Didamony H.: *l'Industria Italiana del Cemento* 76, 422 (2001).
25. El-Didamony H., Salem T., Gabr N., Mohamed T.: *Ceramics-Silikáty* 39, 15 (1995).
26. Tamas F.D., Bakonyi I., Farkas E.: *Ceram. Trans.Adv. Cem.Mat.* 16, 123 (1991).
27. Tamas F.D., Farkas E., Roy D.M.: *Brit.Ceram.Proc.* 35, 237 (1984).
28. Tamas F.D., Farkas E., Vörös M., Roy D.M.: *Cem.Concr.Res.* 17, 340 (1987).
29. Bensted J.: *World Cem.* 11, 395 (1980).
30. Bensted J.: *World Cem.* 14, 383 (1983).
31. Ramachandran V.S., Zhang C.-M.: *il Cemento* 83, 139 (1986).
32. Barker A., Cory H. in *Proc. Of the Inter. Confer. on Blended Cements in Construction*, Sheffield, Elsevier Science Ltd, London, Sep. 9-12, 1991.
33. Jiang S.P., Mutin J.C., Nonat A. in: *Proc. 3<sup>rd</sup> Inter. Symp. on Cement and Concrete*, p. 126-131, Beijing 1993.
34. Bonavetti, V.L.: M.Sc. Thesis, Universidad del Centro 1998.
35. Kuzel H.J., Pöllmann H.: *Cem.Concr.Res.* 21, 885 (1991).
36. Cabrera J., Rojas M.F.: *Cem.Concr.Res.* 31, 177 (2001).

ELEKTRICKÉ, FYZIKÁLNĚ-CHEMICKÉ A MECHANICKÉ VLASTNOSTI PUCOLÁNOVÉHO CEMENTU PLNĚNÉHO POPÍLKEM A VÁPENCEM

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V této práci byla část nebo všechny popílek při přípravě pucolánového cementu nahrazen vápencovým prachem. U takto připraveného cementu byla pozorována změna elektrické vodivosti po jeho smíchání s vodou a během jeho tvrdnutí. Fázové složení cementu se sledovalo rtg difrakcí a DTA. Byl sledován stupeň hydratace, poměr gelu a volného prostoru, reakční poměr, porozita, mechanické vlastnosti a dále obsah volného vápna. Ukázalo se, že nahrazení popílku pěti až deseti procenty vápence v SRC pastě snížilo její vodivost. Zvýšením obsahu vápence na 15 a 20 hmot.% se elektrické vodivosti pasty zvýšila ve srovnání s cementem bez volného vápna (S.0). Přídavek 5 hmot.% vápence zvýšil čas tuhnutí. Na druhé straně zvýšením obsahu vápence se celkové časy tuhnutí zkrátily, protože vápno působilo jako plnivo. Kombinovaný vliv vody, stupně hydratace a poměru gel/volný prostor se zvyšoval s rostoucím obsahem vápence. Ukázalo se, že obsah volného vápna v cementu S.0, S.5 a rovněž M.0, M.5 roste do sedmi dnů a pak až do devadesáti dnů klesá. Naopak pevnost v tlaku a celková porozita s rostoucím obsahem vápence klesá.