



THE INFLUENCE OF TRIETANOLAMINE (TEA) ON CHARACTERISTICS OF FRESH AND HARDENED MORTARS CONTAINING LIMESTONE POWDER

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SYNOPSIS

Key words:

Triethanolamine,
surface activity,
accelerator,
limestone, setting
time, microstructure.

Based on the surface activity of Triethanolamine (TEA), some experiments are made in this study to check the behaviour of this substance used as an accelerator in the hydration and hardening process of Portland cement. In addition, the action of TEA is studied in combination with limestone powder presence, too. The results of experiments showed that this combination improves several properties of fresh and hardened mortars such as the setting time, strength development, total chemical shrinkage and volume stability, as well as the microstructure, permeability, etc.

INTRODUCTION

Limestone is currently being used as mineral admixture in cements produced throughout the world. The European Standard EN 197 – 1 allows three different dosage levels of limestone content in cements.

CEM I, or so called "Portland cement" may contain up to 5% minor additional constituents, of which limestone is one possible material.

CEM II/A-L and CEM II/B-L, both called "Portland limestone cement", contain 6% to 20%, and 21% to 35% ground limestone, respectively (Hawkins et al., 2003).

The use of limestone, as mineral admixture, in cements production is not only cost saving, but has an important ecological value. The main environmental problems associated with cement production are emissions to air and energy use. The cement industry is an intensive industry with energy typically accounting for 30-40% of production costs.

Clinker burning is the most important process of cement production in terms of emissions and energy consumption. A technique to reduce energy and emissions from cement industry is to reduce the clinker content of cements products. This can

be done by adding fillers such as sand, slag, limestone, fly ash, pozzolana, etc in the cement (European Commission, 2001)

The presence of finely ground limestone powder in cements upgrades several properties of mortar and concrete produced with them (Quy & Lam, 1999).

The practical positive effects of limestone are the physical improving of particle packing and the providing of the nucleation sites for clinker hydration products, which accelerate the hardening process as well as the formation of Ca(OH)_2 crystals. But, limestone behaves not only as an inert additive, because CaCO_3 reacts, to a small extent, with C_3A of cement to form the monocarboaluminate. The heat of hydration and the setting time of cements containing limestone are reduced compared to Portland cements.

Permeability is somewhat reduced by the use of limestone, probably due more to a reduction in the connectivity of the pores rather than to their volume. On the other hand, in the limestone Portland cements, the drying shrinkage is increased. The mechanical strength of mortars and concretes produced with Portland cement containing limestone are lower compared with those of mortars and concretes without limestone (Hawkins et al., 2003).

The negative effect of limestone addition in mechanical strength can be improved with the use of the chemical admixture Triethanolamine (TEA). When the limestone powder is used in cement in combination with TEA as an accelerator, the hydration and hardening process of Portland cement is changed. TEA is a surface active substance which is absorbed on the surface of cement particles and cement hydrated products. TEA enables the solution of some metallic ions like Fe^{3+} and Al^{3+} , thus increases the activity of C_4AF compound and inhibits the formation of Fe(OH)_3 and Al(OH)_3 on surface of cement particles. This action facilitates the hydration rate of silicate and aluminates phases in cement particles. Besides this, TEA also reduces, to some extent, the surface tension of the water that enables the cement powder wetting as well as dissolving highly reactive cement compounds.

So, the addition of TEA with the mixing water reduces the setting times, increases the drying shrinkage, but lowers the mechanical strengths of mortars and concretes.

In the literature, different authors give some possible reasons for the decrease of the mechanical strengths, such as:

- the rapid early hydration and the creation of a dense zone of hydration product around the cement grains retard the subsequent hydration;
- cement that has set in a few minutes has obviously not been thoroughly mixed, and consequently there will be a non-uniform distribution of hydration products within the structure that will prevent the development of full strength;
- rapid formation of ettringite may alter the initial matrix and disturb subsequent bonding characteristics;
- rapid setting may promote initial cracks (Ramachadran, 1976).

The use of both additives, the non-corroding accelerator TEA and ground limestone powder in a combination, gives hardened pastes with almost the same compression and flexure strengths compared with those without limestone and TEA, and much higher mechanical strengths compared with pastes where limestone and TEA are used separately (Quy & Lam, 1999).

Since the use of Triethanolamine together with limestone in the cement production does not deteriorate but rather improves the mechanical characteristics of hardened pastes, it has to be considered as an appropriate manner of safe disposal of the industrial waste containing TEA and its compounds that is released into the environment.

SUBJECT AND METHOD OF WORK

The aim of the experimental work presented in this paper, is the investigation of the influence of limestone, TEA and limestone – TEA combination on characteristics of fresh and hardened mortars.

Main raw materials used for the tests:

- Portland cement, CEM I (95 % clinker + 5 % of gypsum), type 42.5 N, produced in Fushë-Kruja Cement Factory, Albania.
- Ground limestone, a raw material used in cement production in Fushë-Kruja Cement Factory, Albania, is rated as partial substitute of Portland cement. The oxide composition of Portland cement and limestone is shown in Table 1.
- Chemical reagent TEA of density 1.12 g/ml is added together with the mixing water during the preparation of mortar pastes.
- Washed river sand with bulk volume 1.58 kg/m³, is used as aggregate. Its particle gradation is shown in Table 2.

Table 1: Oxide composition of cement and ground limestone.

Oxide (in %)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	N ₂ O	Loss on ignition
Portland Cement	20.46	5.96	2.99	60.88	2.25	2.89	0.68	0.25	-
Ground limestone powder	0.25	0.31	0.24	54.10	0.78	0.21	-	-	44.04

Table 2: Particle gradation of aggregate.

2–4 mm	1–2 mm	0.5–1 mm	0.25–0.5 mm	0.125-0.25 mm	< 0.125 mm
31.8 %	26.3 %	17.3 %	12.1 %	7 %	5.5 %

Three sets of experiments have been carried out.

- In the first one, three mortar mixes are prepared with limestone powder used as partial substituent of Portland cement in the content of 5, 7 and 9%. The samples are tagged with L letter.

- In the second set, three other mortar mixes are prepared with Triethanolamine added with the mixing water in the content 0.6, 1 and 1.4 ml TEA/l water. The samples are tagged with T letter.

- In the third set, three mortar mixes are prepared, too, with limestone powder used as partial substituent of Portland cement, as well as Triethanolamine added with the mixing water. These samples are tagged with P letter.

The ten mix proportions of mortar pastes tested are represented in Table 3.

Table 3: Mortar mix proportions.

Type of specimens	w/c ratio	Dosage of TEA (ml/l)	Rate of limestone powder addition (%)	Portland Cement (%)
H (Control)	0.35/0.47	-	-	100
L ₅	0.35/0.47	-	5	95
L ₇	0.35/0.47	-	7	93
L ₉	0.35/0.47	-	9	91
T _{0.6}	0.36/0.47	0.6	-	100
T ₁	0.35/0.47	1	-	100
T _{1.4}	0.35/0.47	1.4	-	100
P ₁	0.35/0.47	1	7	93
P ₂	0.35/0.47	0.6	9	91
P ₃	0.35/0.47	1.4	5	95

The setting time and drying shrinkage are measured for the fresh mortar pastes. The water-to-cement ratio for these pastes was 0.35. Mortar bars 4 x 4 x 16 cm are prepared with each paste with water-to-cement ratio 0.47. The compressive and flexure strengths at 7th and 28th day are determined and the tests of resistance to frost are carried out for all cement pastes with and without limestone powder and TEA. In addition, the microstructure of hardened cement pastes is examined by XRD, SEM and thermal analyses.

RESULTS WITH DISCUSSION

The results of the tests carried out for each mortar paste are shown in the figure 1 and figures 3-14.

SETTING TIME

The setting times of the fresh mortars are determined with Vicat apparatus. The values of the fresh mortar setting time of all mortar mixes tested, including the control sample (without admixtures), are shown in the Figure 1.

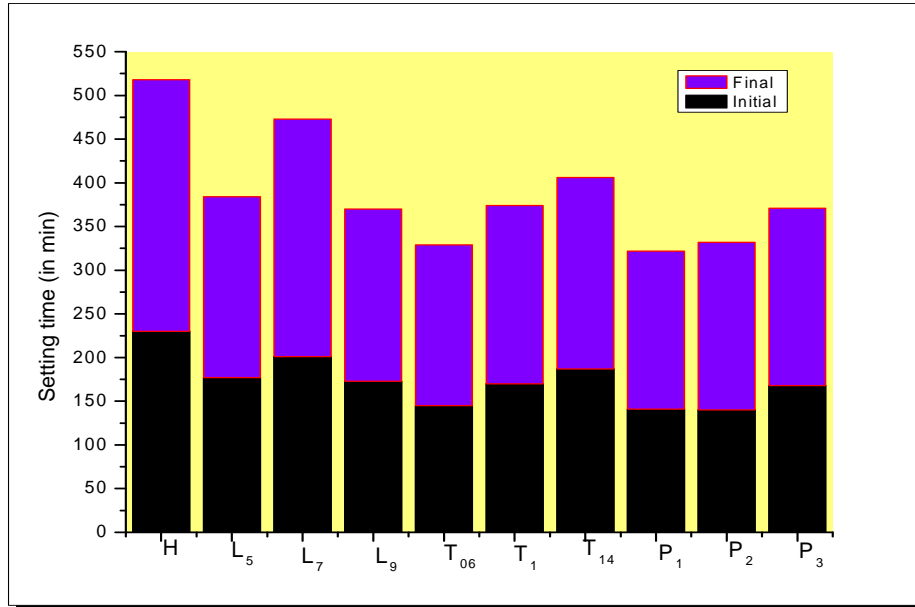


Figure 1: The initial and final setting times for pastes with and without limestone powder and TEA.

Tests results show that, the initial and the final setting times of all samples containing limestone powder or TEA are shorter than the control sample ones. The time intervals are shorter, too.

The combination of both limestone powder and TEA admixtures has a strong effect on setting characteristics of pastes. The paste P₂ (9% limestone powder and 0.6 ml TEA/l water) has the shortest initial setting time, whereas the paste P₁ (7% limestone powder and 1 ml TEA/l water) has the shortest final setting time.

DRYING SHRINKAGE

The total chemical shrinkage during the hydration of cement is due to the smaller volume of reaction products (as calcium silicate hydrate gels and calcium hydroxide) compared with the reactants (alite, belite, celite, water, etc). The total chemical shrinkage equals the external chemical shrinkage until the network of hydration products bridging the not yet reacted cement grains is strong enough to resist the contracting forces. At this point, the external chemical shrinkage rate slows down drastically and the shrinkage versus time curve flattens out. Thereafter, the formation of internal contraction pores, is dominating over the external shrinkage. The total chemical shrinkage, which is the sum of external chemical

shrinkage and the volume of empty contraction pores, is important in the cracking development in the hardened cement pastes, especially when accelerating admixtures are used (Justness et al., 2000)

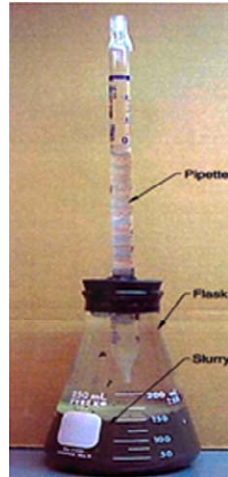


Figure 2: The flask-pipette setup used for the total chemical shrinkage measuring.

In this experimental work the total chemical shrinkage is measured with a flask-pipette setup. A photo of the experimental setup is reproduced in Figure 2. The flask is filled with a known amount of paste and excess water. The pipette on top of the flask is used to read the decrease of water column in ml which, calculated as the mean value from three parallel measurements, is directly the total chemical shrinkage expressed in ml/100 g cement.

The graphical representation of the total chemical shrinkages versus time of cement pastes with w/c ratio 0.35 with and without limestone powder and TEA are shown in Figure 3.

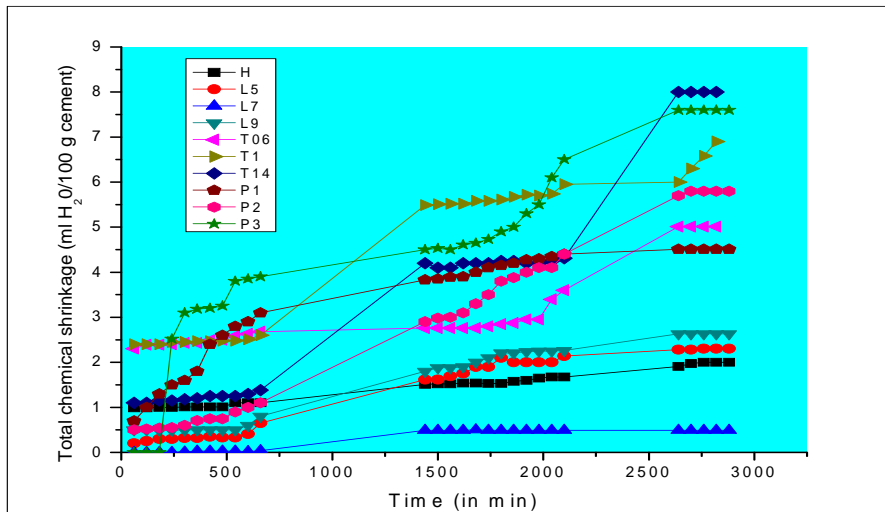


Figure 3: Total chemical shrinkage versus time curves for cement pastes containing limestone cement powder, TEA and the combination limestone powder-TEA compared with the control paste without admixtures.

It is evident that, except L₇, the total chemical drying shrinkage (after 48 hours) of pastes containing limestone and TEA, are higher compared with the control paste (the one without admixtures). Assuming that chemical shrinkage approximately is proportional with the degree of hydration, results that in these cases the degree of hydration is higher than that of the control paste. Probably, the reason for this effect is the better dispersion and breaking of cement grains in pastes containing admixtures. The setting times represented in the Figure 2, show the same trend of accelerating effect caused by adding limestone and TEA.

From the Figure 3, it is clear that the final total chemical shrinkage is higher for the pastes containing TEA (pastes T) and for those containing both limestone and TEA (pastes P). But the profiles of curves of external chemical shrinkage versus time for the P pastes in Figure 3 are different from those of T pastes. For the P pastes the very early chemical shrinkage are lower than the control paste, whereas for the T pastes the very early chemical shrinkage are higher than the control paste. For this reason mixes with only TEA might be more prone to form drying shrinkage cracks.

MECHANICAL STRENGTHS AT 7TH AND 28TH DAY

Test results of compression and flexure strengths at 7th and 28th day for the hardened mortars produced with each mortar mix (with and without admixtures), are represented at the Figures 4 and 5.

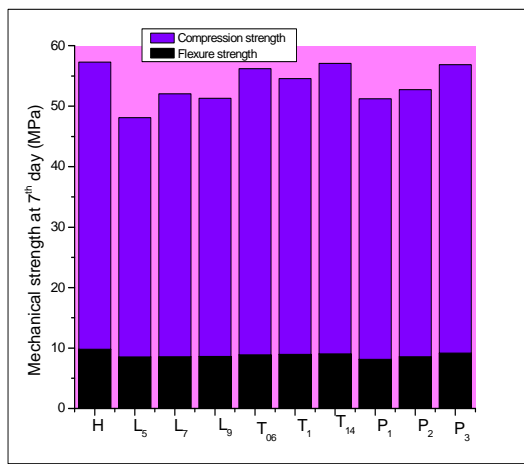


Figure 4: The compressive and flexure strength at the 7th day for the hardened mortars produced with and without limestone and TEA.

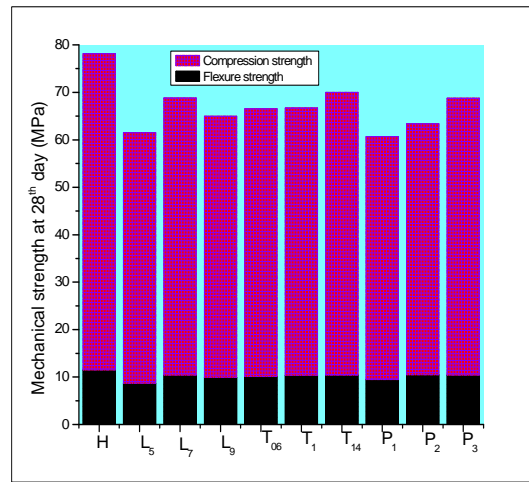


Figure 5: The compressive and flexure strength at the 28th day for the hardened mortars produced with and without limestone and TEA.

Test results represented in the Figures 4 and 5 show that the hardened mortars containing limestone or TEA have mechanical strengths at 7th and 28th day

lower than the reference sample (CEM I + 0 % additive). Nevertheless, it is evident that the presence of both limestone and TEA (Samples P) in mortar mixes improves the strength development. At 7th day the mortar produced with the paste P₃, has mechanical strength higher than other mortars containing limestone or TEA. The value of compressive strength at 7th day for sample P₃ is nearly the same as the value for the control sample. Also, the mechanical strengths at 28th day of the sample P₃ are higher then the case when limestone powder or TEA are used separately.

RESISTANCE TO FROST DAMAGE

After 50 cycles freeze/thaw, there was no important mass change for hardened mortars produced with and without limestone and TEA.

MICROSTRUCTURE OF HARDENED CEMENT PASTES

The hardened (at 28th day) mortars samples H, L₉, T_{1.4} and P₃ microstructure is examined and XRD patterns are represented respectively in Figures 6, 7, 8 and 9.

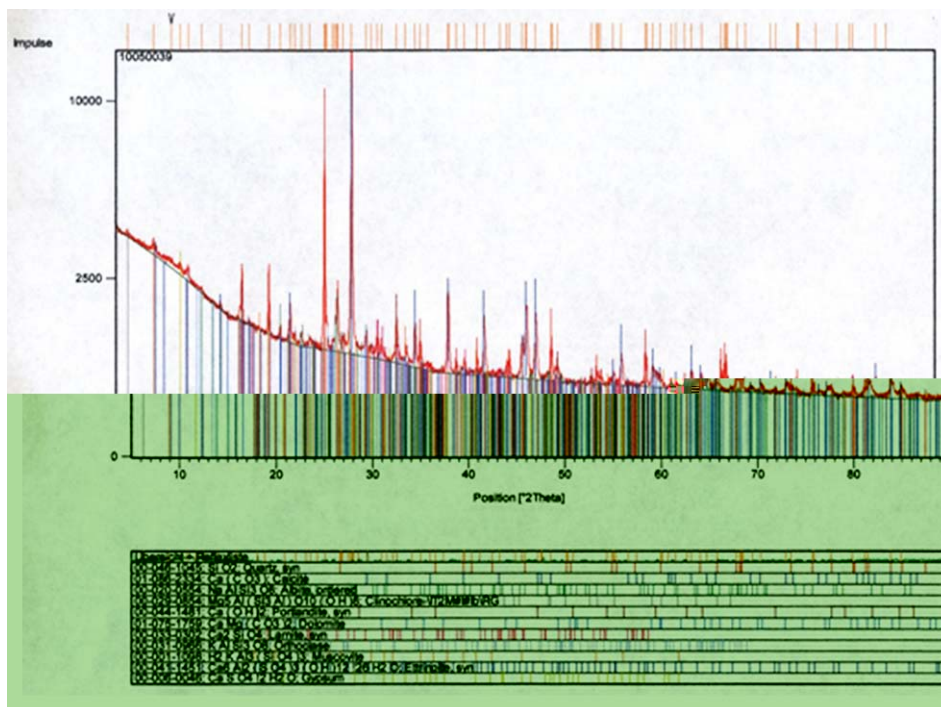


Figure 6: XRD pattern of cement paste H without admixture.

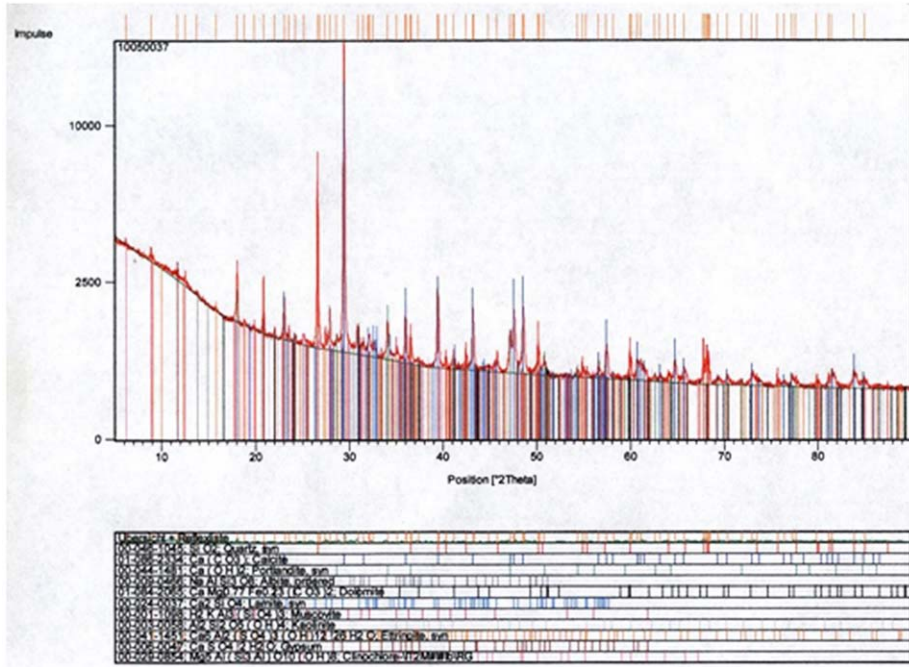


Figure 7: XRD pattern of cement paste L9; only limestone powder added.

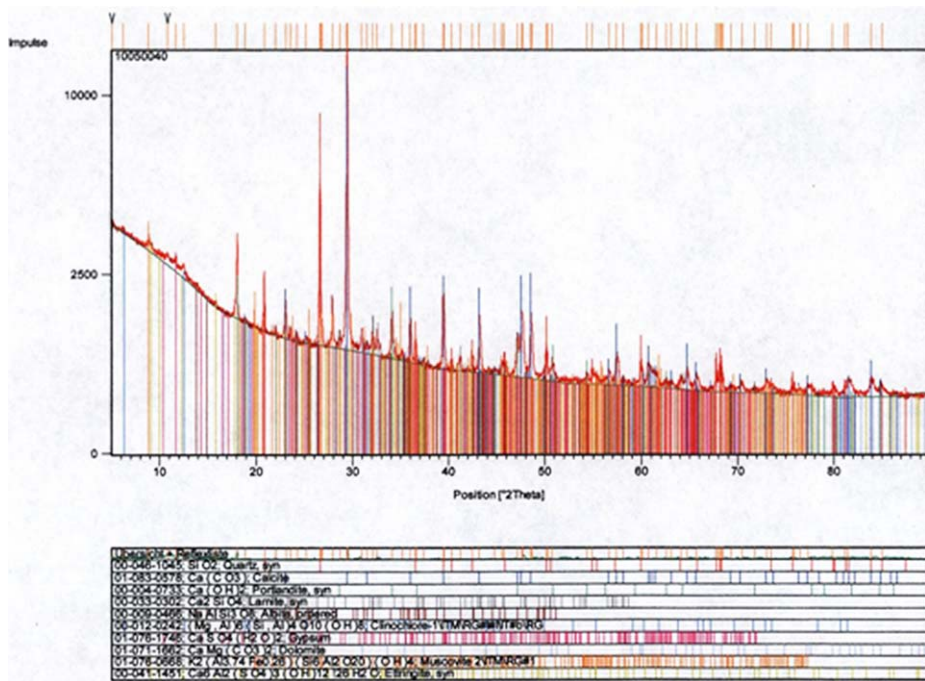


Figure 8: XRD pattern of cement paste T1.4; only TEA added.

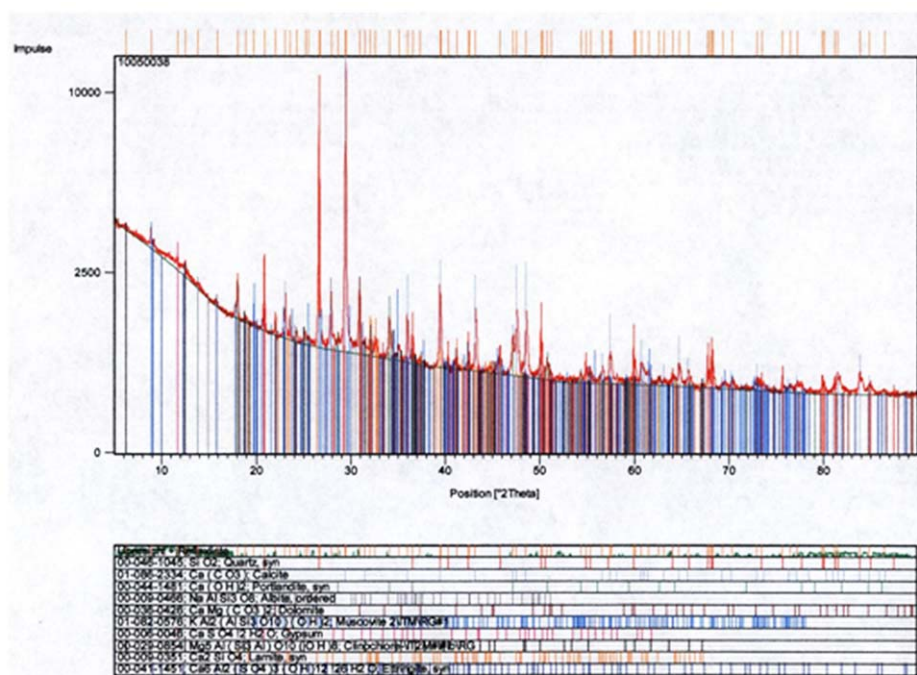


Figure 9: XRD pattern of cement paste P₃; both limestone powder and TEA added.

The main minerals amounts present in hardened samples are shown in the Table 4.

Table 4: The amounts in % of the main minerals in the hardened mortars at the 28th day.

Mineral content (%)	H	L ₉	T _{1.4}	P ₃
Calcite	35.67	41.06	42.42	37.81
Ettringite	3.83	5.10	4.88	3.61
Portlandite	4.42	4.82	6.02	5.09

It is evident that in the samples with both limestone powder and TEA the amount of ettringite is lower compared with L₉ and T_{1.4}. This low content of ettringite, which is almost the same as of the control paste, shows that the combination of both limestone powder and TEA have a positive effect in the hardening of Portland cement paste.

The SEM images of cement pastes with and without limestone powder and TEA are represented at the Figure 10.

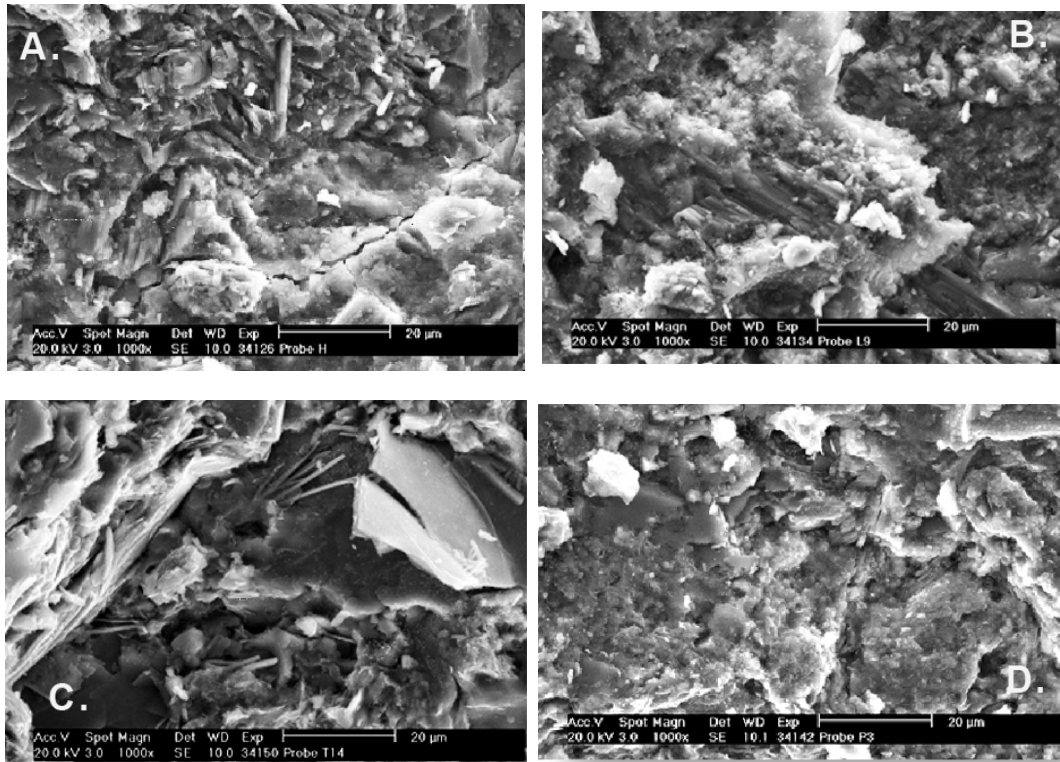


Figure 10: SEM image of hardened control Portland cement paste H (above left), Portland cement paste L₉ containing limestone (above right), cement paste T_{1.4} containing TEA (below left), cement paste P containing both limestone and TEA (below, right).

The micrographs show clear difference in the microstructure of the hardened cement pastes with and without limestone powder and TEA. The hardened cement pastes with both limestone and TEA, seems to be denser than the other hardened pastes.

The test results of thermal analyses are represented at the Figures 11-14. In each Figures there are shown two curves, one represents the results of Differential Scanning Calorimetry (DSC) and the other the results of Thermogravimetric analysis (TG).

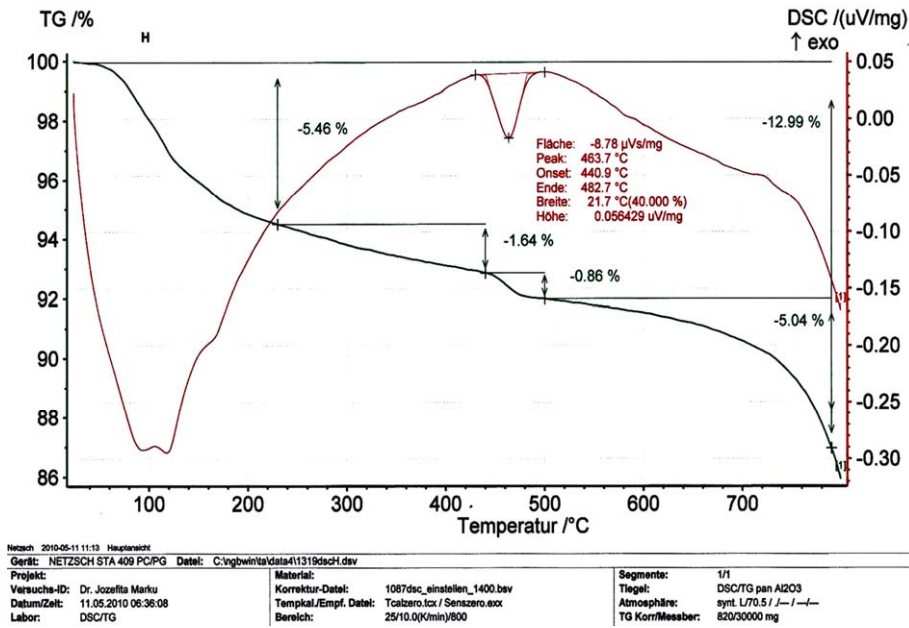


Figure 11: TG and DSC curves of Portland cement control sample (H).

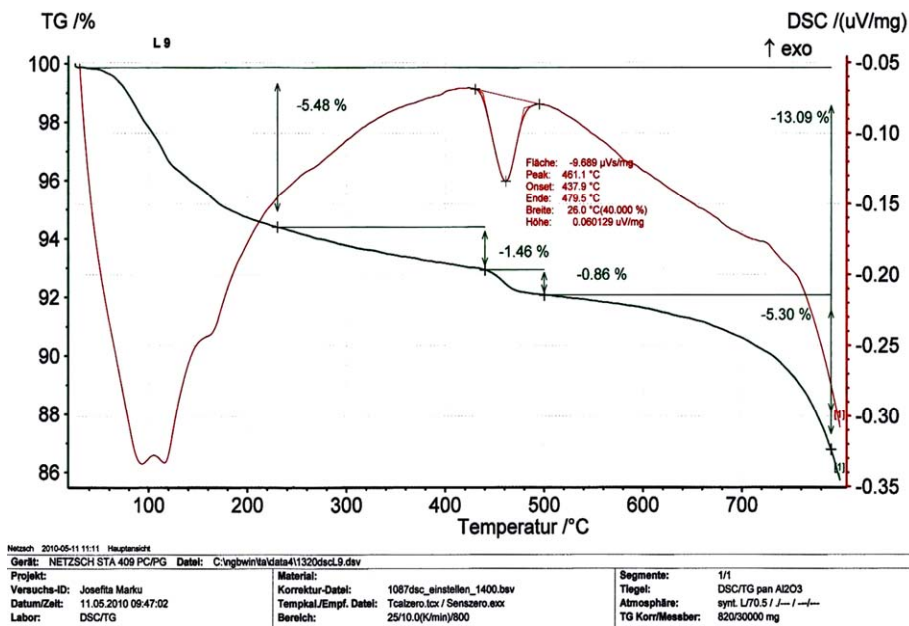


Figure 12: TG and DSC curves of Portland cement sample containing limestone powder (L₉).

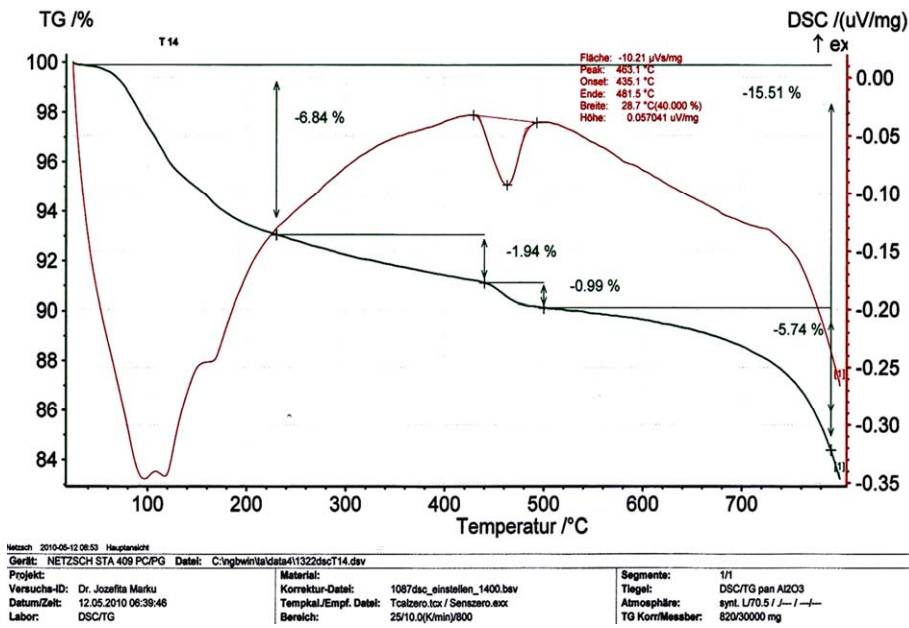


Figure 13: TG and DSC curves of Portland cement sample containing TEA (T_{1.4}).

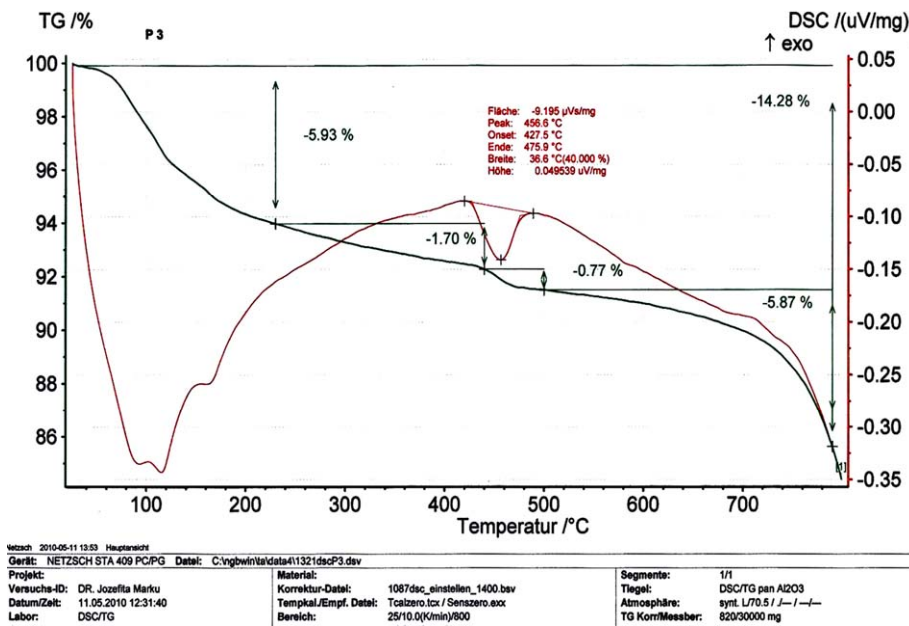


Figure 14: TG and DSC curves of hardened cement sample containing both limestone powder and TEA (P).

It is obvious that the profile of curves of the four samples hardly differ from each other. Two significant endothermic peaks around 100°C and 460°C are observed in these curves.

The endothermic peak around 100°C is mainly due to the dehydration of CSH. The endothermic peak at around 460°C corresponds to the decomposition of Ca(OH)₂. This peak intensity is the highest in sample T_{1,4} containing only TEA and the lowest in the control sample.

Less content of portlandite, Ca(OH)₂, in hardened samples is evidence of the formation of hydrates with high CaO:SiO₂ ratio, but in our experiments, it happens only for the control paste. This fact indicates that the limestone powder and TEA added separately or together do not influence the decrease of the content of Ca(OH)₂, which is the weakest component of the Portland cement.

CONCLUSIONS

Based on the experiments' results, it is concluded that:

- Adding of limestone powder as partial substitute of Portland cement shortens the setting times and the interval between initial and final setting time of the fresh mortar pastes.

- Adding of TEA as chemical admixture with the mixing water shortens the setting times and the interval between initial and final setting time of the fresh mortar pastes.

- Adding of limestone powder or TEA as admixtures in mortar mixes, decreases the mechanical strengths compared with Portland cement mortar.

- Adding of both admixtures, limestone powder and TEA in combination, affects strongly in the decrease of the setting times and in the increase of the total chemical shrinkage. At the same time, the mechanical strengths are comparable with those of Portland cement mortar.

- The increase of mechanical strengths (up to the level of control sample) of hardened mortars produced with Portland cement and both admixtures, limestone powder and TEA in combination, compared with those of mortars produced with Portland cement and each of the admixtures separately, is more likely to be due to the increased mortar density and lower content of ettringite rather than the decrease of portlandite.

- The best mix proportion among those experimented resulted to be the combination P₃, with dosage of 5% limestone powder and TEA concentration of 1.4 ml/l mixing water. This combination of admixtures accelerates the setting times and increases the total chemical shrinkage but with less possibility of drying shrinkage cracks formation and consequently with less reduction of mechanical strengths.

- The use of TEA – Limestone combination as admixture in cement and mortar production, besides the improvement of mortar production cost and characteristics, have a notable impact in the environment protection because of partially substitution of the Portland cement with limestone and the recycling of wastes containing TEA.

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