

# The Portland limestone--calcined clays at 5°C

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**Abstract:** The effect of calcined clays of the swelling type, on Portland limestone cement at 5°C is studied. Local clays were thermally activated by burning one hour at 900 °C and ground to a Blaine of 2842 (cm<sup>2</sup>/g). The pozzolanic reactivity of the activated clays was defined chemically and according to ASTM C311/C311M-13. Portland limestone cement was prepared by replacing 30% CEM I 42.5 N by limestone powder. 10 and 20% of limestone were further replaced by the calcined clays. Parallel series of mortars specimens pre-cured for 28-day long as well as for a short period of one day, were immersed in water and sulfate solutions at 5°C for time up to 90 days. Compressive strength and length change were measured for the samples.

The results show that replacement of limestone with calcined clays improves the compressive strength and the expansion of Portland limestone cement mortars in water and sulfate solutions. Ettringite was detected in the expanded mortars and no thaumasite formed. The results are interpreted in terms of the mechanism of thaumasite formation.

## Introduction

The production of Portland limestone cements is of technical and economic advantages. The European standards EN 197-1 and the Egyptian specifications ESS 4756-1 allow up to 35% limestone (by weight) in CEM II/A and CEM II/B.

The weakness of Portland limestone cement lays in its susceptibility to the thaumasite form of sulfate attack. The use of calcined clays as pozzolanic material in cement is known as early as the beginning of the twentieth century [1]. Research on the pozzolanic reactivity of the activated clays was carried out few decades ago [2]. However, the importance of the calcined clays was recently recalled [3, 4] and its inclusion in Portland limestone cement has attracted the attention. Most of the published work, however, focuses on metakaolin as calcined clays but the performance of lower grades clays represents as well, an interesting subject for the present state research [5, 6].

The present study aims to find out the effect of calcined clays of the swelling type, on the susceptibility of Portland limestone cement to the thaumasite form of sulfate attack.

## Experimental

CEM I 42.5 N was used as a reference cement (R1). Its oxide composition was measured by means of X-ray fluorescence equipment Philips Type X-CEM. (Table 1). Its C<sub>3</sub>A and C<sub>3</sub>S contents as evaluated by Bogue equation were 6.85 and 67.36 % respectively. The Blaine surface area of the cement was 3086 (cm<sup>2</sup>/g).

Commercial limestone was supplied from the market. Its chemical composition is given in Table 1. The limestone was finely ground in a ball mill for 120 minutes, the fineness of the ground material was 3654 (cm<sup>2</sup>/g) Blaine.

Table 1: The chemical composition of cement and limestone (%)

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	Cl
CEM I 42.5 N	19.03	4.85	3.55	62.37	1.99	0.37	0.17	2.79	0.07
Limestone	1.01	0.34	0.21	55.78	<0.01	<0.01	<0.01	0.13	0.02

The clay-sample was supplied from a red brick factory. Its X-ray diffraction patterns shown in Figure 1 indicate the presence of moderate amount of montmorillonite (M) and kaolinite (K). The main phases composing the sample are quartz (Q) and feldspar (F). Calcite (Cc) is detected with a medium concentration relative to quartz.

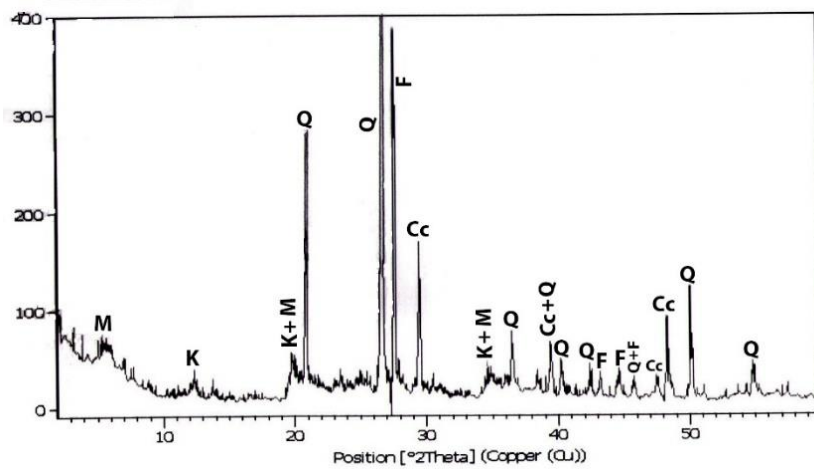


Figure 1: The X-ray diffraction patterns of the as-received clays

The clay-sample was activated by burning one hour at 900°C. Its X-ray diffractogram shows relicts of illite (I) and feldspar (F), beside quartz (Q) as a main phase (Figure 2). A hump is seen between the 2 theta angles 20 to 40°C and indicates the presence of amorphous phase.

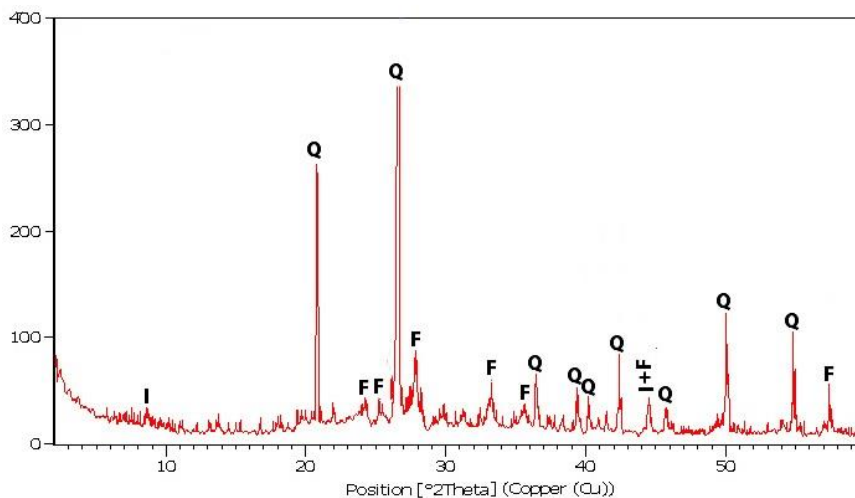


Figure 2: The X-ray diffraction patterns of the calcined clays

The calcine clays was ground 5 hours in a ball mill, the respective powder had a Blaine area of 2842 (cm<sup>2</sup>/g). Its pozzolanic reactivity was performed chemically by measuring the amount free lime remaining after mixing the sample with 20% lime [7], the pozzolanic index was measured mechanically according to ASTM C311/ C311M-13

30% of CEM I was replaced by limestone powder to obtain Portland limestone cement (R2). The limestone was further replaced by 10 and 20% of the calcined clays to get two binders of clay-bearing Portland limestone cement; A20-10, and A10-20 respectively.

The pH of the pastes made of the reference samples R1 and R2 as well as that of the clay-bearing Portland limestone cement was measured on slurries using a water/binder ratio of 5. Readings were taken after 30, 60, 90 and 120 minutes from mixing the binders with water.

The flowability of the mixes was measured by means of the flow table in accordance with ASTM C230 / C230M-14

For the measurement of compressive strength, cubic samples were cast in 50 x 50 x 50 (mm) molds in accordance to ASTM C109. Mortar prisms 25.4 x 25.4 x 285 (mm) were prepared for the measurement of the length change according to ASTM C490-83a.

After demolding a first series of samples were pre-cured 28 days in water at room temperature. The pre-cured specimens were parallelly immersed in water and in 5% hydrated sodium sulfate solution at 5°C. The compressive strength reading was performed after 7, 28, 56, and 90 days and the length change was measured after 56 and 90 days.

To accelerate the rate of sulfate attack on the mortars, a second series of samples were prepared from R2 as well as from the clay-bearing Portland limestone cements (A20-10, A10-20) using a higher water to binder ratio of 0.6. The samples were pre-cured 24 hours only then parallel series were immersed in water at room temperature and in 12% hydrated magnesium sulfate solution at 5°C. Readings were taken after 7, 14, and 28 days.

## Results

Based on the pozzolanic reactivity measurements, the calcined clays were found to react directly with 12% lime, and its 28-day strength activity index was 84.5%. The activated clays was therefore considered to possess good pozzolanic properties as its strength activity index is greater than 75% .

The average pH-value of the slurries was around 12.5 and insured the alkalinity of the blends made of CEM I, limestone, and clays.

Table 2: The effect of calcined clays on the flowability and setting time of the cements

	R1	R2	A10-20	A20-10
Flow diameter (mm)	174.5	180.0	191.5	179.5
Initial setting time (min.)	190	183	189	190
Final setting time (min.)	268	273	275	300

In accordance with the literature [8,9], limestone enhances the flowability of CEM I. The present results show an increase of the flowability of CEM I by ~ 7% (from 174.5 to 180 mm in diameter, Table 2) in presence of 30% limestone. The addition of 10% calcined clays favours the flowability of the limestone cement further and leads to an increase in the diameter to 191.5 mm, but higher replacement ratio decreases the flowability again to attain that of the limestone -free clays.

The initial setting of CEM I is slightly accelerated with limestone replacement and does not vary significantly in presence of clays (Table 2). The final setting time of the cement is, however, obviously retarded by limestone and further by clays replacement.

The compressive strength of the samples cured in water and in 5% sodium sulfate solution for time up to 90-days is shown in Figures 3 and 4. The results indicate a clear improvement in the strength of Portland limestone mortar by replacement of 10% of the limestone by calcined clays (sample A20-10). Higher replacement ratio of 20% (A10-20) shows lower strength in the 56 d samples but improve after 90 d and reaches the value of the specimen with 10% replacement.

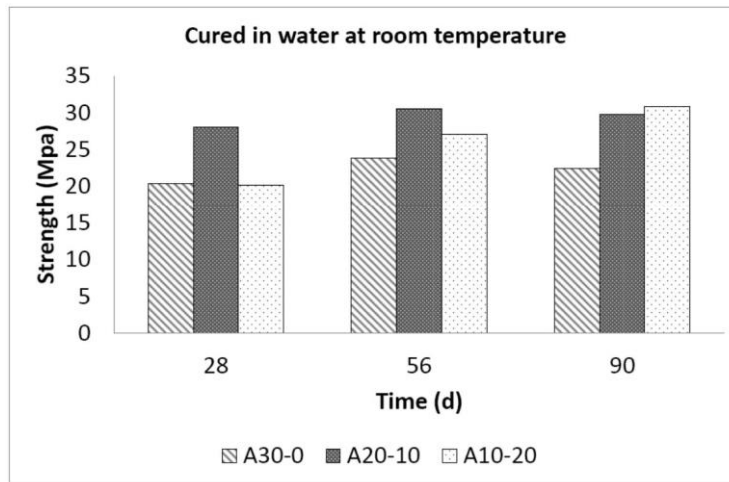


Figure 3: The compressive strength of the Portland limestone mortars with 0, 10 and 20% calcined clays cured in water at room temperature (w/c=0.48)

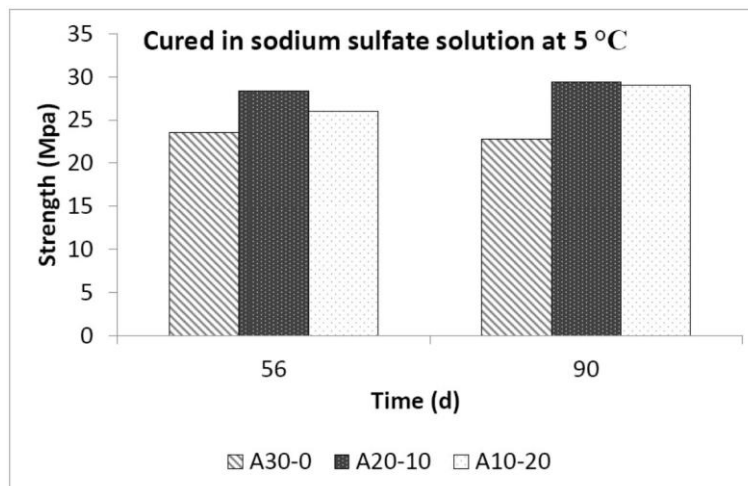


Figure 4: The compressive strength of the Portland limestone mortars with 0, 10 and 20% calcined clays pre-cured 28 days in water at room temperature then immersed in sodium sulfate solution at 5°C (w/c=0.48)

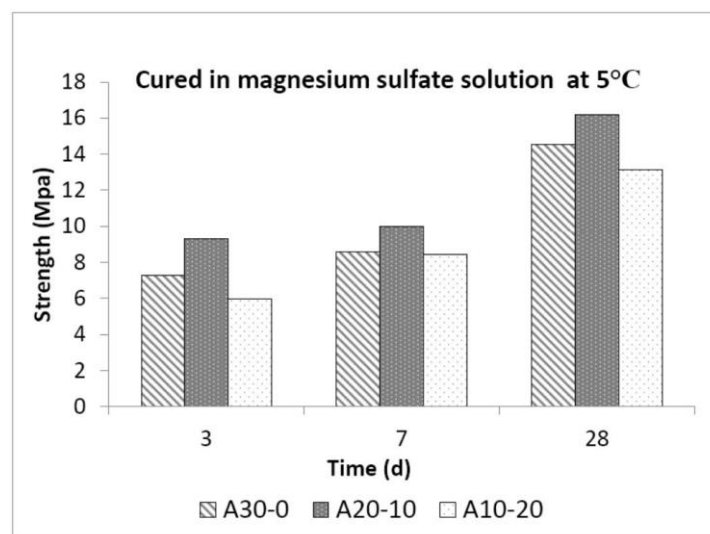


Figure 5: The compressive strength of the Portland limestone mortars with 10 and 20% calcined clays pre-cured 1 day in water at room temperature then immersed in magnesium sulfate solution at 5°C (w/c= 0.6)

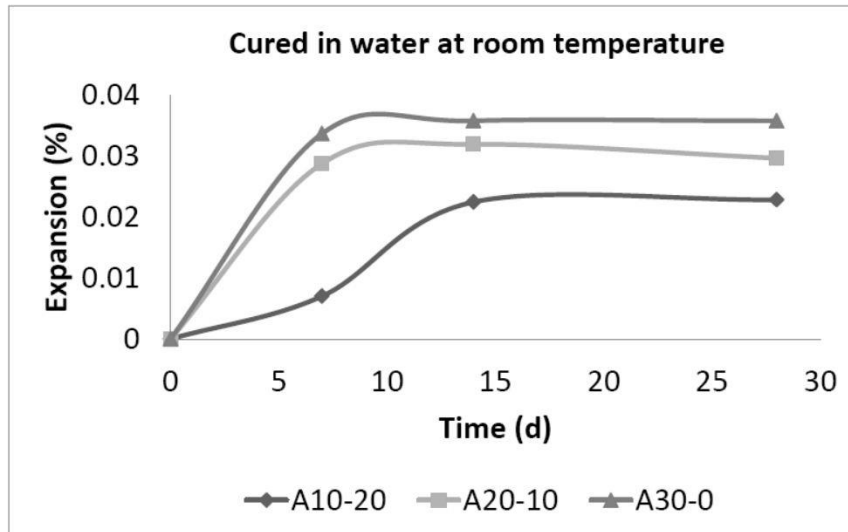


Figure 6: The expansion of the Portland limestone mortar with 10 and 20% calcined clays cured in water at room temperature (w/c=0.6)

The mortars pre-cured for one day and prepared with a water/binder ratio of 0.6 undergo the same improvement in strength with 10% calcined clays upon exposure to 12% magnesium sulfate solution despite the short age of the sample and the markedly lower strength values (Figure 5).

The positive effect of the clays replacement is further observed in the length change of the same mortars pre-cured for one day. The expansion curve is lowest in the sample with 20% limestone replacement with calcined clays immersed in water (Figure 6) as well as in 12% magnesium sulfate solution (Figure 7).

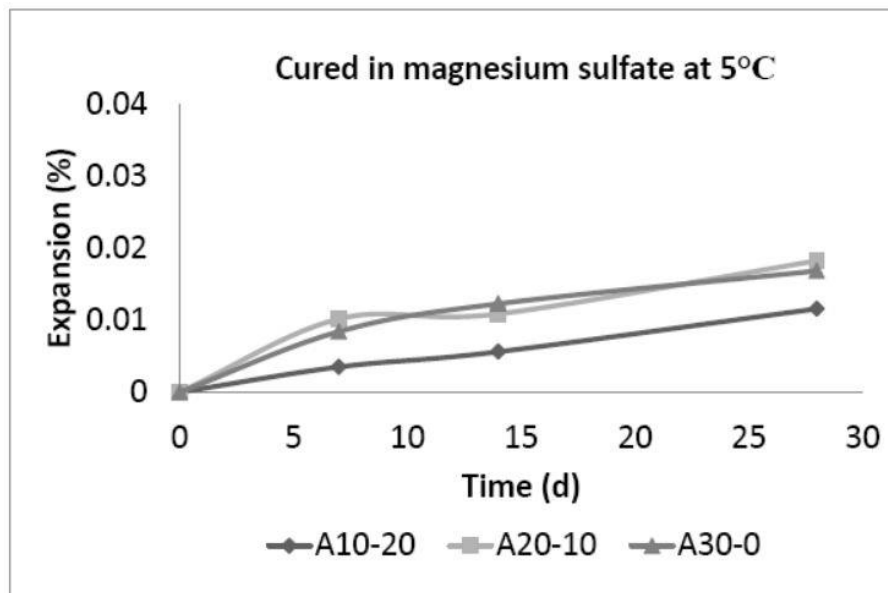


Figure 7: The expansion of the Portland limestone mortar with 10 and 20% calcined clays pre-cured for 1 day in water at room temperature then further cured in magnesium sulfate solution at 5°C (w/c=0.6)

Gypsum phase precipitated on the mortars exposed to sulfate solution without the occurrence of cracks or deterioration phenomena.

The X-ray diffraction patterns of the mortar samples with 10% replacement cured 28-days in magnesium sulfate solution indicated the formation of ettringite, The ettringite phase was detected

as well in the 90- day specimen made of 10% clay and cured in sodium sulfate solution. Typical patterns are illustrated in Figure 8. The thaumasite phase did not formed under these conditions

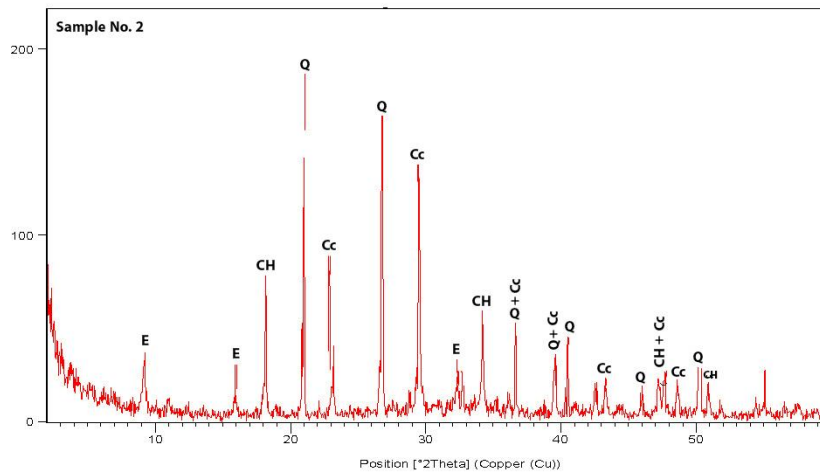


Figure 8: The X-ray diffractogram of the Portland limestone mortar with 10% calcined clays (w/c=0.6) pre-cured for 1 day then cured 28 days in magnesium sulfate solution at 5°C

## Discussion

The tendency of Portland limestone cement to thaumasite form of sulfate attack limits its use. The thaumasite formation is proved to be dependent on the solubility of lime and CO<sub>2</sub> which increases by low temperature [10, 11].

Recent studies carried out on pure system of sodium silicate and ettringite at 7°C highlighted the role of pH on the mechanism of the thaumasite formation [12, 13]. Low pH value of 9.5 initiated by bubbling CO<sub>2</sub> gas to the mix at 7°C leads to an intermediate phase which accords with the literature [14]. The X-ray diffractogram of the intermediate phase proved to be composed of carbonated ettringite and silicate phases which show an infrared shoulder around 1030 cm<sup>-1</sup>. (Figure 9 a ,b). The intermediate phases transform to thaumasite upon rising the pH-value to 12.5 by supplying lime water (Figure 10).

Aragonite was detected in the carbonated phase. Its presence indicates that the bubbling process have created a localized pressure suitable to form the high-pressure calcium carbonate polymorph. Under these conditions of highly localized pressure, the octahedral silicon might have formed with the residual OH ions in the mix. This arise at low temperatures where atomic and molecular vibrations are relatively slow. The [Si(OH)<sub>6</sub>]<sup>2-</sup> groups formed is distorted because the carbonate ions delocalize the high charge of the strongly polarizing Si ion [14].

The supply of lime offers a strong nucleophilic agent to silicon already polarized by the carbonate ions and is further polarized by the OH<sup>-</sup> ions. This results in bonding the lime with the octahedrally polarized silicon and the formation of thaumasite. The identification of an octahedral silicon in the amorphous phase by NMR shall support this theory.

It is interesting to know that the thaumasite formed despite the low concentration of sulfate which only source is ettringite [12, 13]. This would rise the question of whether a destructive and nondestructive thaumasite exist depending on the concentration of sulfate in a way analogous to the previous finding of sulfate deficient ettringite which becomes harmful with the excess of the sulfate supply [15, 16].

The present work indicates that activated clays improves the performance of Portland limestone cement in water and sulfate solution. This takes place in mortar cured for 28 days in water as well as in mortars of higher porosity prepared with a w/binder ratio =0.6 and cured for 1 day only at room temperature.

The improvement is due to lowering lime concentration due to the pozzolanic reaction of the activated clay and the increased CSH phases formed in the system. Thaumasite attack in this system is not expected to appear because of the relatively slow carbonation process in samples totally

immersed in water or in sulfate solutions which is not enough for the formation of the intermediate phase and the consequent rise of pH by the excess supply of lime.

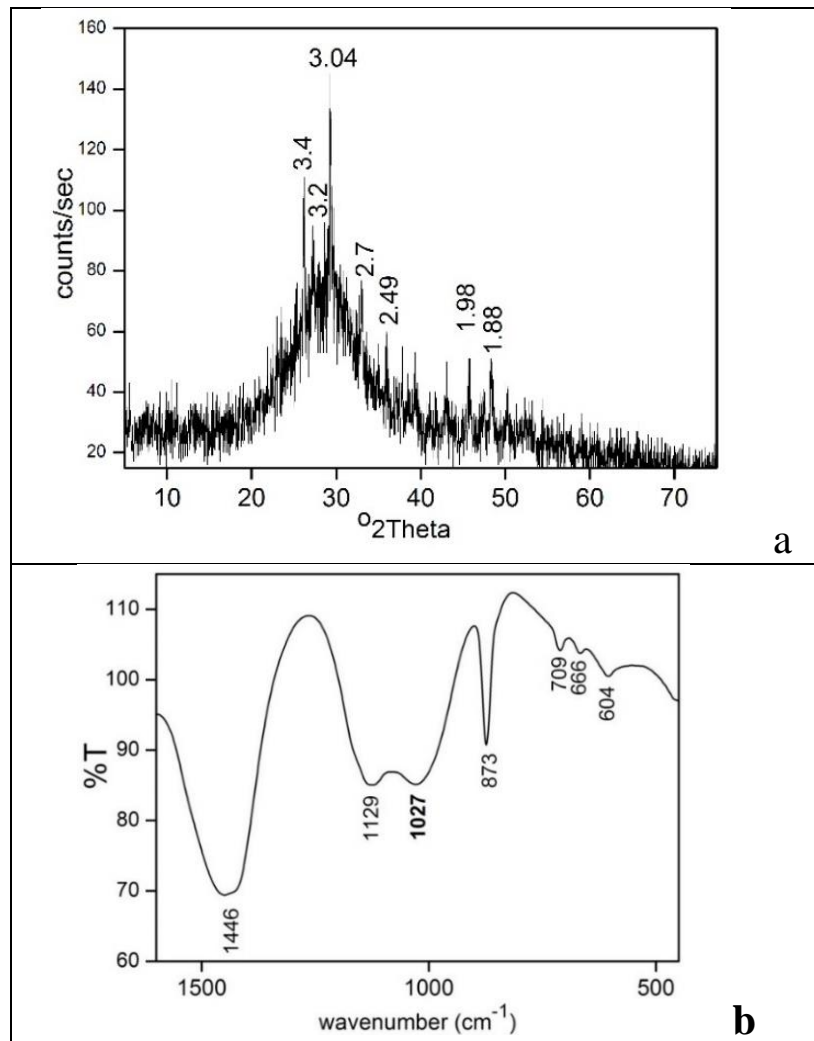


Figure 9: a) The X-ray diffraction patterns, b) the infrared spectrogram of the intermediate phase formed through the carbonation of sodium silicate/ ettringite mix at 7°C, pH 9.5

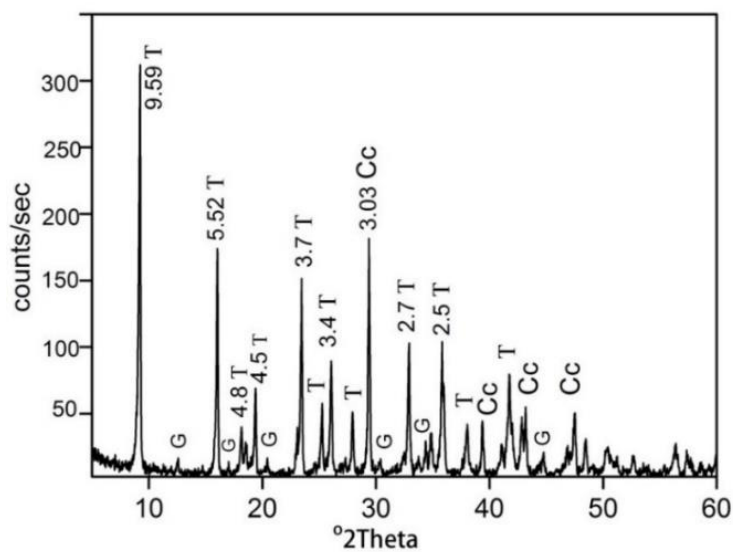


Figure 10: The X-ray diffraction patterns of the thaumasite formed from increasing the pH value of the intermediate phase to 12.5 by adding lime water at 7°C



## Summary

- Low grade clays activated at 900°C for 1 hour possess good pozzolanic properties
- Replacement of limestone by calcined clays in Portland limestone cement improves its resistance to sulfate attack. It leads to better compressive strength and lower ettringite expansion
- The thaumasite formation is conditioned by the formation of an intermediate phase composed of carbonated ettringite-silicate phases at pH 9.5 then its re-exposure to lime and the re-rise of pH value to 12.5 at ~7°C. The thaumasite formation is delayed in samples completely immersed in sulfate solution which weakens the carbonation process.
- Clays reduces the amount of lime needed to form the thaumasite salt

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