

**Composition of a Cement Having High Resistance to Strong  
Sulfate Attack:  
A New Look on News Cements in the Future**

by F.Gomà and M. Vicente

**Synopsis:** Certain naturally occurring materials, that proceed from cretaceous geological strata associated with cretaceous coals, possess uniform chemical composition, which is similar to raw mixes for making normal portland cements with only one difference, that it has 3 % of  $\text{SO}_3$ . When these materials are burned at low clinkering temperature between 1,100 and 1,200°C, they produce non expansive naturals cements with characteristics and properties technically significant, and these, are examined in this paper. This cement belongs to the sulfoaluminates cements series having low  $\text{SO}_3$  content and low  $\text{C}_2\text{S}$ . This material, If after normal curing with water for 28 days, further curing by immersion in a strongly aggressive 5 % sulfate solution is carried out, it will be seen to possess total resistance to the sulfate attack and that compressive strength increases during several months until values close to those of normal portland cements are obtained.

Finally, a raw composition is proposed of the component materials and clinkering conditions at low temperatures for the production of a new type of cement that it's suggested as other possibility in the future of the cementitious materials. With the incorporation of this new type of cement, when its parameters and behaviour in structures is established, it would be possible to obtain a significant reduction in gas emissions within more sustainable development and to have a high sulfate resistant cement for use in situations where there is extreme sulfate aggression.

To the question "Portland Cements: is anything new on the horizon"? Perhaps, one answer could be: "this tipe of new cement suggested, in the system  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-SO}_3$ , might be the beginning of an other new binder for the next milenium with a environmentally "sustainable cement manufactures and witout sulfate attack problems

**Keywords:** Calcium sulfoaluminate cements, low energy cements, sulfate attack.

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## INTRODUCTION

Natural cements with uniform raw chemical composition have been found in certain Cretaceous geological strata associated to cretaceous coals as in "torre de Foix", Vallcebre in Berga, Catalonia, Spain, that possess chemical compositions which are similar to raw mixtures for ordinary portland cements with a noticeable difference that it's content 3 % of SO<sub>3</sub>. When these materials are calcined at low temperatures, between 1,000 and 1,200°C, ( temperature of the kiln, no really of the material) they display technical characteristics and properties, unknown up to now, and these are examined in this paper. The work reported in this paper is part of an extensive study to investigate whether the ettringite formation as a major component of the C-A-H phases in the products of a hydrated cement could be an alternative binder. In the sulfate resistance tests performed using the micro-cube technique by the described aggressive solution attack (1) and prism 40X40X160 mm., in accordance with the 196-1 EN standard, it was found that they possess very high resistance to sulfate attack.

The mortar samples, after curing in the usual manner, and maintained in highly aggressive 5% sulfate solutions, underwent a progressive increase in compressive strength; reaching values of up to 45 Mpa from between six months and one year, and which have since been under observation for more than two years to the present date. This means that, in this case, the aggressive solution unexpectedly behaves as a curing solution which contributes extrinsic sulfate to the formation of secondary ettringite as the cause of an increase in strength instead of its destruction. Finally, an interpretation of the secondary ettringite formation mechanism for these cements which do not reveal themselves as being expansive, could lead to new orientations of current knowledge on the resistance of concrete of the normal portland cement to sulfate attack.

## EXPERIMENTAL DETAILS

### Determination of Chemical and Mineral Composition of Clinker of this Natural Cement

A representative sampling was taken of the industrial clinker in which the variation in the major components did not exceed 3%. The chemical composition of the obtained mean sample of clinker was analysed in accordance with current standard EN 196-2 procedures, with the exception of the silica determination which was carried out using a version of the classic gravimetric procedure modified by the author with less standard deviation (2). The results include a representative sample of normal portland cement clinker for comparative reference.

The natural cement clinker under study was calcined at a temperature of 1,200°C in a vertical kiln and its composition had a Kstll "British Lime Saturation Factor" of 61.1%; silica ratio  $\text{SiO}_2/\text{Al}_2\text{O}_3+\text{Fe}_2\text{O}_3$  1.85 and the  $\text{SO}_3$  content in clinker was 3.0% whereas that of the normal portland cement clinker, used as a reference, was 96.1%; silica ratio  $\text{SiO}_2/\text{Al}_2\text{O}_3+\text{Fe}_2\text{O}_3$  2.23 ; the  $\text{SO}_3$  content in clinker was 0.3%. The analysis results are shown in Table 1. The clinkerability temperature of the raw mix of this normal portland clinker, taken as a reference, was evaluated using the author's procedure and was determined to be 1,625°C , near to the technical limit is 1,650 °C (3), whereas the natural cement clinker, which was calcined in a vertical kiln at 1,200°C with a temperature of clinkerability that is very much lower, about 1,000 °C, produced a free lime value of less than 2%, with decarbonation degree of the 76 % . The energy consumption is therefore, considerably lower including level of pollution.

### Clinker Finishing and Mechanical Strengths

The portland cement clinker sample was ground with added gypsum in order to obtain 3.0%  $\text{SO}_3$  in the resulting cement, together with a fineness equivalent to a cumulative value of 95%, which would pass through a 63-micron sieve, which are the usual conditions normal portland cement nowadays. Three series of micro-cubes 20X20X20 mm., and three series of prisms 40 x 40 x 160 mm, in accordance with the 196-1 EN standard, with a W/C of 0.5 and an C/S of 1:3, with standardised sand, were prepared and cured by immersion in water at 20°C. Test samples from one of the series were used for determining the compressive strength and the test samples of the other two, previously cured in water, for post curing attacks in aggressive solutions of 5% sodium sulfate and 5% magnesium sulfate respectively.

The cement obtained from the natural cement clinker was ground, with the special conditions for technical use as a masonry cement, to a fineness equivalent to an accumulative value of 82%, which passed through a 63-micron sieve, and had a maximum particles size of 600 microns as is indicated in Table 2. Any additives were added, but only 0.4 %, over the cement weigh, of the citric acid, were used to delay setting and hardening by 30 to 40 minutes in order to mould under suitable conditions. This was used to prepare another three series of 20 x 20 x 20 micro-cubes, and three series of prisms 40 x 40 x 160 mm, in accordance with the 196-1 EN standard, of pure paste with a W/C of 0.4, which were similarly cured in water at 20°C. After 28 days of water curing, they were all tested for compressive strength. After 28 days of water curing, one series of each type of mortar and cement were immersed in aggressive solutions of 5% sodium sulfate and 5% magnesium sulfate respectively both saturated with  $\text{Ca}(\text{OH})_2$ . In all these samples, the compressive strength was periodically determined during a period of two years. These results are shown in Fig. 1.

### **Hydration Specifications and aggressive attacks conditions**

All the specimens and micro-cubes were hydrated at 20°C in water, chamber-cured for 24 hours, removed from the moulds and immersed in de-ionised water at 20°C in order to carry out prior water curing up to 28 days.

They were then placed in aggressive solutions of  $\text{Na}_2\text{SO}_4$  at 5 % and  $\text{MgSO}_4$  at 5 %, respectively saturated with  $\text{Ca}(\text{OH})_2$  on a long-term basis for up to two years, after which the XRD patterns for the samples were determined and the results are given in Fig. 2, in values  $K\alpha\text{Cu}$ . Scanning Electron Micrograph and EDAX were determined and the results shown in Figs. 3. In order to establish any variations occurring to the physical parameters of the material in the pure paste specimens with natural cement due to the aggressive treatment, the physical parameters were determined in accordance with the standard ASTM C-642 method using cement paste micro-cubes which had been cured for 28 days in water and, at the end of this period, placed into the aggressive solution treatment period. The results are given in Table 2.

### **DISCUSSION OF RESULTS**

The experimental facts which we established in our work are described as follows: after water curing, the natural cement having the described composition and specifications, has a strength of between 12 to 15 MPa when tested as a pure paste under the described granulometric conditions and with a W/C of 0.4. When the specimens were previously cured in water for 28 days and then exposed to highly aggressive water containing 5% sodium sulfate and/or 5% magnesium sulfate both saturated with calcium hydroxide  $\text{Ca}(\text{OH})_2$  at 20°C, they undergo a progressive increase in compressive strength during between six and twelve months, which can reach 40 to 45 MPa.

No expansion or degradation phenomena were observed in any of the cases and the levels of strength attained remained constant during observation of up to two years. This progressive increase in strength occurred at the same time as the physical parameters were modified, with a reduction in porosity of some 13 to 15% in the sodium sulfate solutions and noticeably less, 11 to 13%, in the magnesium sulfate solutions. X-ray diffraction confirmed that the amount of ettringite and C-S-H from  $C_2S$  formed are present as the dominant phases.

### **Background to this Fact Found in the Literature**

The natural cement clinker under study have incorporated 3 % of  $SO_3$  and by this reason we have therefore compared it with the clinkers and cements of the  $CaO-SiO_2-Al_2O_3-SO_3$  system. There are background studies into these types of clinkers/cements (4-7). These show that obtained compressive strength values are comparable to those of natural portland cement and that the ettringite is either controlled or is not produced. The common factor in these clinkers is the fact that the dominant phases are  $4CaO.3Al_2O_3.SO_3$ , and  $C_2S$  and produce the ettringite and CSH phases respectively as a hydrolysis product. Among which, the produced cements from clinkers with  $Al_2O_3/SO_3$  molar ratios close to 1.3, in which the compressive strength (tests carried out in accordance with the JIS R 5201 standard), produced a value of 59 MPa at 28 days. The authors used Scanning Electron Micrograph techniques to determine that this ettringite has a crystallisation of 1 to 2  $\mu m$  within hardened mass having a large specific surface area that has undergone a total porosity loss in volume in function of time up to 28 days with mercury porosimeter monitoring.

Our research has enabled us to confirm that the reduction of the porosity is due to the formation of secondary ettringite in the natural cement studied by the determination of the usual physical parameters in accordance with the ASTM C-642 standard, with the results demonstrating a marked reduction as shown in Table 3, and the crystals size of ettringite are less than 2 $\mu m$ . Figs 3. The obtaining of high resistance on a level of that provided by portland cement was also observed by other authors ( 8 ), who obtained an increase in compressive strength, based on sulfo-aluminates, together with the formation of ettringite. These reached the same levels as portland cements after some four months with an asymptotic growth up to six years later, together with stable concrete during twelve to sixteen years in constant immersion.

In spite of these good results, none of the preceding authors have proposed any type of cement from this class as an alternative to normal portland cement for structural construction ( prior database)

## **Expansive Behaviour of the Ettringite Formed in this Class of Cements**

The cited background studies, carried out using these types of clinkers or cements belonging to CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-SO<sub>3</sub> system were focused on obtaining cements with controlled expansion for specific applications. The expansion conditions in clinkers for expansive cements have been examined with the conclusion that low free lime and low chalk content are required (4). The common factor in these cements is the fact that the dominant phase are the secondary ettringite and CSH phases from C<sub>2</sub>S as a hydrolysis products. As has been demonstrated that when the formation of ettringite is micro-crystalline of 1 to 2 microns and the free lime content is low, then expansion is not produced (7), and confirmed in this paper. It must be emphasised that this is an important difference that the sulfate accion in our investigation have extrinsic origen and under the conditions of the tested natural cement clinker did not reveal any expansion during the secondary ettringite formation and this has been confirmed by x-ray diffraction. This leads to the conclusion that the ettringite formation, in this class of natural cement investigated, produces high strength without any degradation or expansive effects.

This fact shows that the secondary ettringite in these types of cements appears without any expansion and is the cause of the compressive strength, leads us to a new interpretation of the destructive mechanisms produced by the secondary ettringite formation in portland cement and to which we shall now refer to, with a brief review of the literature on the evolution of its interpretations

### **A Brief Literature Review**

In the 40s, the U.S. Road Administration commenced a field study, based on "The durability of concrete in service", into the state of real structures affected by sulfate attack and those which were not (9). The discrepancies which were found between the actual results and those predicted by the laboratory placed even more emphasis on the need to review the causes. As from the 50s, a large number of researchers have contributed to the establishment of various causes associated with the ettringite formation which explains the destruction of concrete due to sulphate attack and which may be summarised as follows: a C3A content in excess of 5% as a general criterion from the beginning; the expansive forces produced by osmosis (10); the topo-chemical formation of ettringite (11); the influence of pH on expansion (12); the absorption of water by the poorly crystallised ettringite, and the loss of strength of the CSH phases when the pH is reduced and the disappearance of the CH phase (13); the

need and/or concomitant micro-cracking of the concrete in presence of water as defended in his holistic view (14). The introduction of the osmosis process as being the most significant generalized cause of expansion has been accepted. Osmotic pressure implies the formation and existence of a semi-permeable membrane, which is caused by the existence of alkaline silicates coming from Newkirk phases and which exists in all portland cements to a greater or lesser degree, and the eventual presence of small amounts of clay material in the concrete aggregates aids this membrane formation (15). Recently, in traditional concretes or mortars by comparing these ettringite formations with those produced in portland mortar and concrete, were able to obtain information through SEM observations of micro-structures" in the C-S-H phases. Two different manifestations in the hydrated C-S-H phase masses, a light grey internal one, called the inner C-S-H product that surrounds the non-hydrated clinker grains, together with another darker mass or outer product, or non-differentiated product housing the formation of secondary expansive ettringite which is produced over time with mortar or concrete having the original sulfate ions, both intrinsic and extrinsic. These authors reached the conclusion that ettringite crystallisation takes place inside the outer exterior C-S-H phase micro pores and that this is associated with the expansion phenomenon (17).

In summing up, there is a large number of controversial contributions for the interpretation of the behaviour of conventional concrete without active additions in which there does not appear to be any single generalised prevalent conclusion, in spite of being ever-closer to a more thorough understanding. Diamond (16) has concluded that the cements having high early strength have high  $C_3S$  and  $C_2S$  content and produce a general tendency for the concrete to crack more easily under lower levels of creep and higher drying shrinkage and thermal shrinkage. As this micro-cracking increases, the concrete penetrability increases and the durability decreases

### **New Contributions to Critical Aspects**

There are still certain critical aspects and suggestions from the author to this updated summary. The conditions for ettringite formation in both cement types are really quite different. The most active phase in portland cement during hydrolysis is the C-A-H, so that it is well-known that the  $C_3S$  and  $C_2S$  do not commence to hydrolyse until after the first two days, forming a binder network once of the C-S-H after the primary ettringite has been produced. The C-S-H gel develops much more resistance than that produced by the ettringite for two reasons, first, because it is present in greater amounts 75% of ( $C_2S + C_3S$ ) against 20% of aluminates, and secondly because the C-S-H gel is a colloid with a smaller range of particle size, together with great cohesive power due to its large specific surface area of between 21.000 and 25.000  $cm^2/g$ , which it strengthened by the polymerisation action of the silica.

In accordance with our own criteria, it seems understandable that the primary ettringite is not expansive in any type of portland because it forms within the first 48 hours, in other words, before the C-S-H gel is formed. There is always space available to hold the primary ettringite. When the hydrated cement is 80% hydrated at 28 days of curing, the C-S-H gel formation is almost complete. The ettringite which then forms due to intrinsic or extrinsic attack or because of Delayed Ettringite Formation (DEF) is the secondary ettringite which crystallises within the indeterminate outer C-S-H phase, with a higher level of cohesion, which is rigid, together with the possibility of having formed semi-permeable membranes capable of creating osmotic pressure etc, and which is therefore expansive. In natural or sulfo-aluminate-based cements, and certain ones from the  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-SO}_3$  system, expansion is not produced because the  $\text{C}_2\text{S}$  content is very low and  $\text{C}_3\text{S}$  is non-existent. The resistance of these cements to sulfate attack therefore seems understandable and this, together with the growing formation of secondary ettringite, increases these levels of resistance to those of portland cements as we pointed out in our research. In Table 2, one can see how the total porosity of the samples attacked by sulfate disolutions has been decreased.

From our point of view, the main problem of expansion by sulfats attack in normal portland cement would appear to be one of a lack of compatibility in the binding systems in the C-A-H and C-S-H phases so that the sulfate pathology generates the rigidity in the C-S-H formation. The natural cement under study therefore, is not only resistant to sulfate attack, but, attains compressive strength similar to normal portland cements in the medium and/or long term. It also includes the pozzolanic additions that forms a micro-porus structure (opens spaces) within the C-S-H gel mass that in which ettringite is able to crystallise and prevents the excessive formation of semi-permeable membranes.

Meta-kaolin or alumino-silicates which are calcined above  $800^\circ\text{C}$ , such that only amorphous masses of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  are formed, have been demonstrated as being especially useful as pozzolans. The natural cement under investigation was calcined at low temperature and contained an average value of 15% silicates material, that produces amorphous oxides by burning effect.

The conclusions reached concerning the applications of this type of cement appear to lead towards the opening of a new road forward in the research into new cements which are immune to sulfate attack, possess high compressive strength, involve much lower energy costs and a very significant reduction in pollution.



## CONCLUSIONS REMARKS

Naturally occurring materials with a uniform composition very close to that of a normal portland cement, with a 3% SO<sub>3</sub> content, and calcined at a low temperature of 1,150 to 1,200 °C produced a new type of cement similar to natural cement which is resistance to attack by 5% sodium sulfate solution.

Compared to the normal portland cement, the medium and long-term compressive strengths of the natural cement increased until approaches to both values through the formation of secondary ettringite on sulfate exposure.

The ettringite formation did not manifest itself as expansive when the amount of the C<sub>2</sub>S is very low and there is no C<sub>3</sub>S. Its most significant application is for use in exposure conditions where there is high concentration of sulfates.

The increase in compressive strength may allow a new type of alternative cement to be created with a notable reduction in energy costs, together with very significant reduction in levels of pollution.

The commencement of an extensive study, both in the laboratory, in order to determine all its physical-chemical parameters, and through work in the field on actual structures is recommended and justified for development of technical data base for development standards by the standards committees.

To the question “Portland Cements: is anything new on the horizon”? Perhaps, one answer could be: “this type of new cement suggested, in the system CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-SO<sub>3</sub>, might be the beginning of another new binder for the next millennium with an environmentally “sustainable cement manufactures and without sulfate attack problems””

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**Table 1 - Chemical Composition of the Binders**

	Natural Clinker			Portland Clinker
	Whole Sample	Soluble Fraction as Whole Sample (18)	Insoluble Residue as Whole Sample	
TiO <sub>2</sub>	0.24	0.09	1.2	0.15
SiO <sub>2</sub>	22.0	13.9	60.6	20.8
Al <sub>2</sub> O <sub>3</sub>	8.9	6.6	16.7	6.1
Fe <sub>2</sub> O <sub>3</sub>	3.0	1.6	10.8	3.2
CaO	45.3	43.8	3.3	64.9
MgO	0.82	2.2	0.80	1.8
Na <sub>2</sub> O	0.30	0.16	1.1	0.19
K <sub>2</sub> O	1.7	1.2	3.9	0.54
SO <sub>3</sub>	3.0	3.2	0.2	0.66
L.O.I. 550° C	0.5	-	0.1	0.80
L.O.I. 950° C	11.7	-	0.1	0.32
Insoluble Residue (18)	14.6	-		0.50
Lime Saturation Factor KstII	61.1	91.7		96.1
SR SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> +Fe <sub>2</sub> O <sub>3</sub>	1.85	1.70		2.24
AR Al <sub>2</sub> O <sub>3</sub> /Fe <sub>2</sub> O <sub>3</sub>	2.97	1.50		1.91
Molar Ratio Al <sub>2</sub> O <sub>3</sub> /SO <sub>3</sub>	2.32	1.38		7.25
Free Lime CaO	1.6	-		0.8
Degree of Decarbonation	76	-		-
Bogue Potential Compounds				
C <sub>3</sub> S				60.
C <sub>2</sub> S				16
C <sub>3</sub> A				11
C <sub>4</sub> AF				10

	Natural Clinker	Normal Portland Clinker
Fineness		
% passing 250 $\mu\text{m}$ .	85	100
“ 88 “	62	99
“ 63 “	47	95
Compressive Strength MPa		
R <sub>2</sub>	8.5	34.3
R <sub>28</sub>	11.3	63.1

**Table 2 – Physical Properties of the Binders**

	After Water 28 d. Cured	After 1 year Na <sub>2</sub> SO <sub>4</sub> 5% Cured	After 1 year MgSO <sub>4</sub> 5% Cured
Absorption After Immersion %	32.7	20.4	22.9
Bulk Specific Gravity cm <sup>3</sup> /g	1.45	1.67	1.55
Apparent Density cm <sup>3</sup> /g.	2.78	2.53	2.45
Volume of Permeable voids %	47.7	34.0	35.5

**Table 3 - Physical Properties of Natural Cement Pastes W/C 0.4**

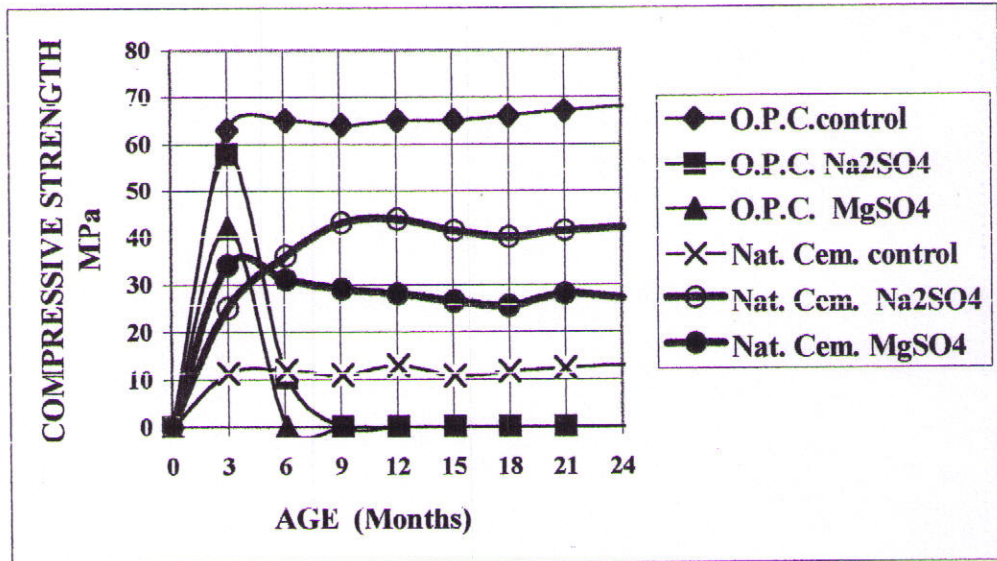
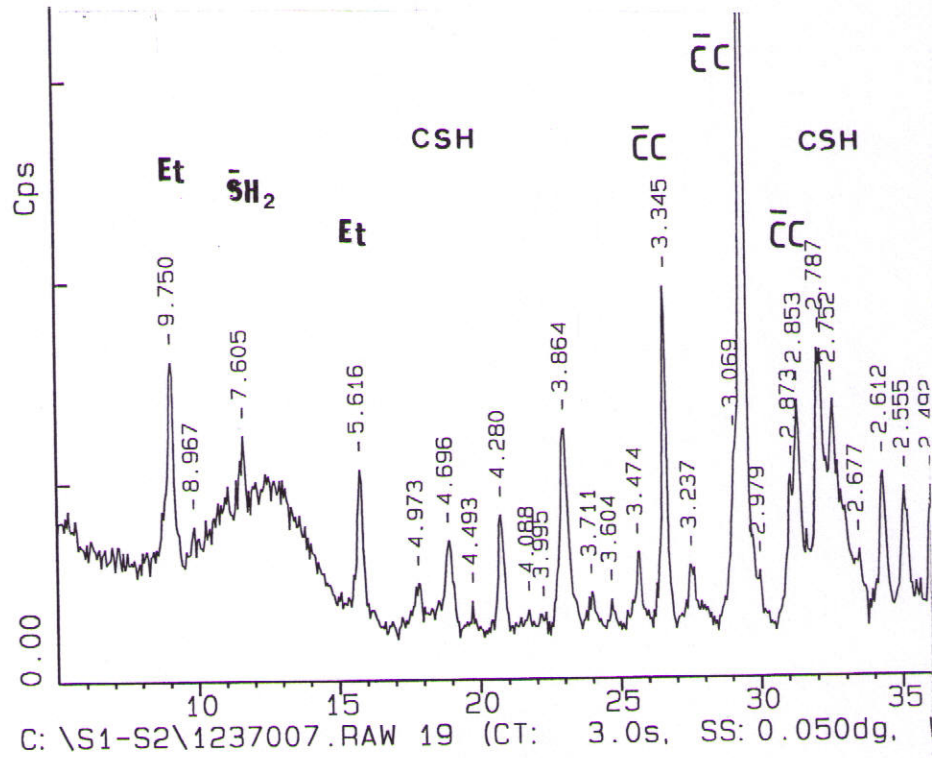


Fig. 1. Compressive Strength versus time

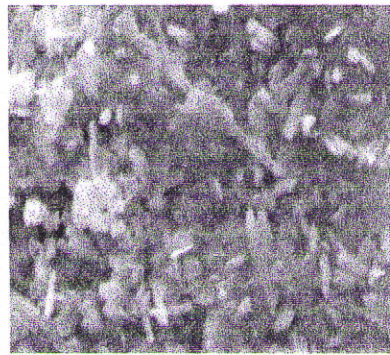


2θ Cu K

Et = ettringite,  $\bar{S}H_2$  = gypsum,  $\bar{C}C$  calcium carbonate

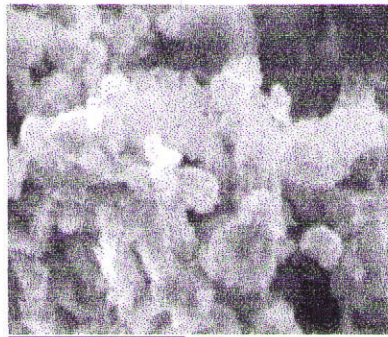
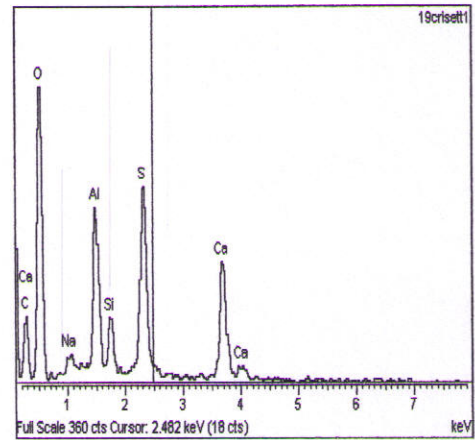
CSH = calcium silicate hydrates

Fig. 2 X-ray patterns of natural cement pure paste attacked 1 year with Na<sub>2</sub>SO<sub>4</sub>



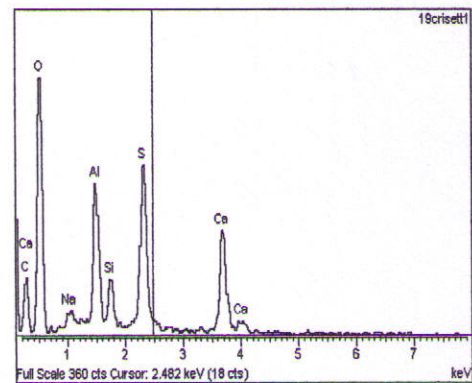
6 μm

a)



6 μm

b)



**Fig. 3 Scanning Electron Micrograph and EDAX**

**Pure paste 1 year attacked  $\text{Na}_2\text{SO}_4$  5 %**

**a) Ettringite dominant phase**

**b) CSH dominant phase**