A NEW CEMENT WITH HIGH RESISTANCE TO STRONG SULFATE ATTACK

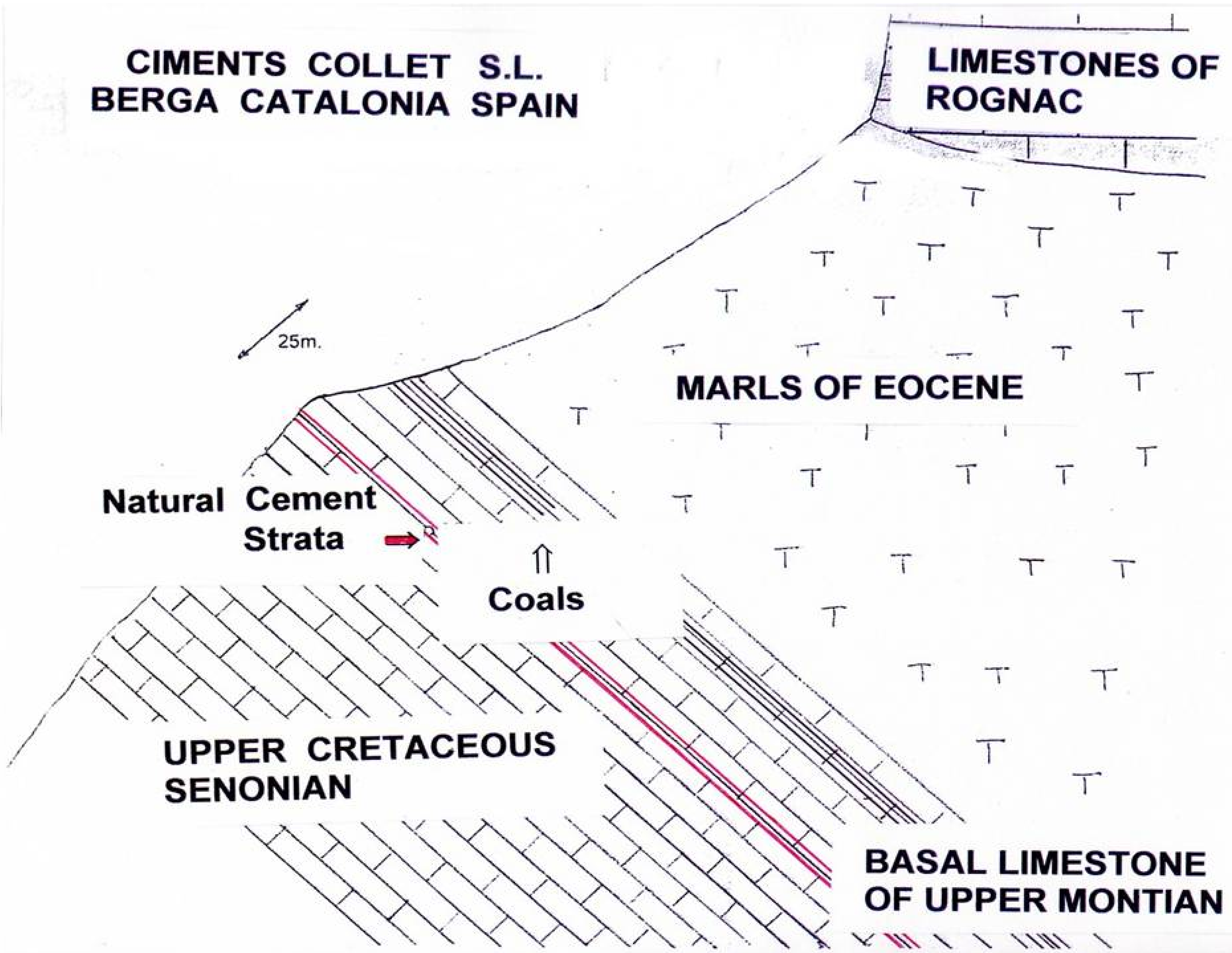
by F.GOMÀ and M. VICENTE

NEW DISCOVERY:

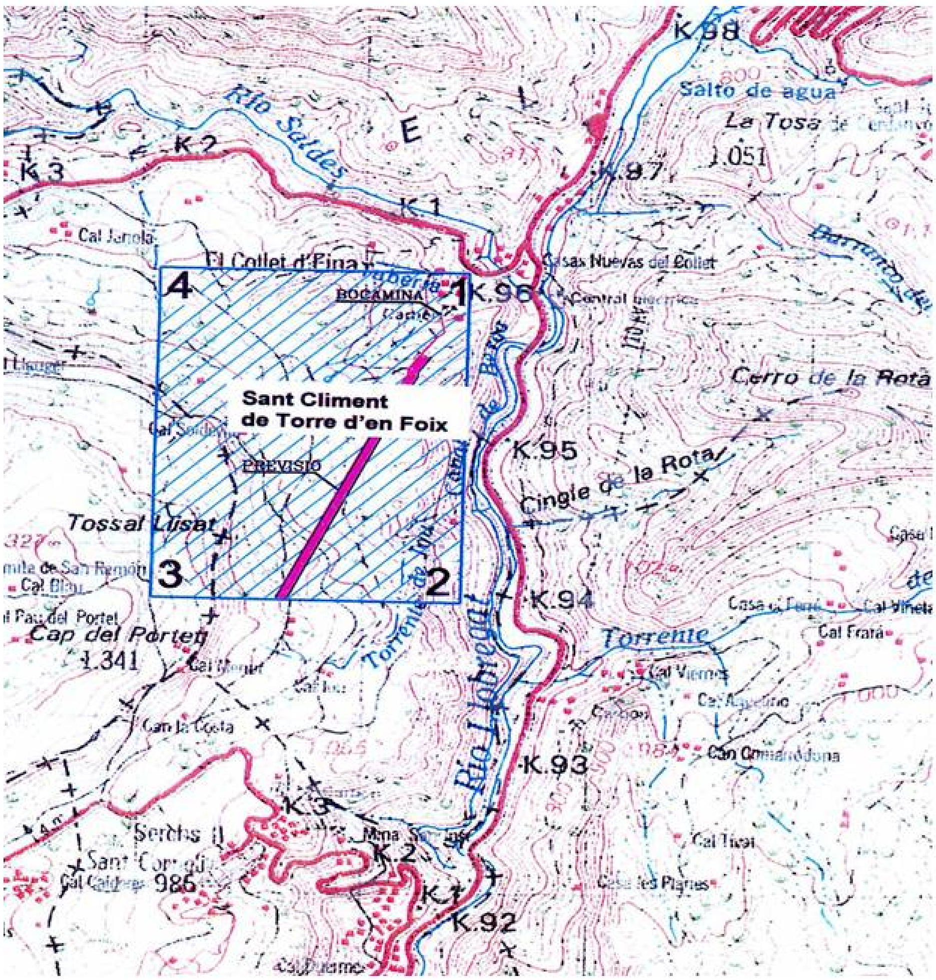
A NEW SPECIAL CLINKER COMPOSITION WITH LOW CLINKERABILITY TEMPERATURE THAT PRODUCES A CEMENT HAVING HIGH RESISTANCE TO STRONG SULFATE ATTACK

GEOLOGICAL SITUATION OF NATURAL MATERIAL

This special composition can be found in certain existing Geological strata in Basal Limestones of Upper Montian

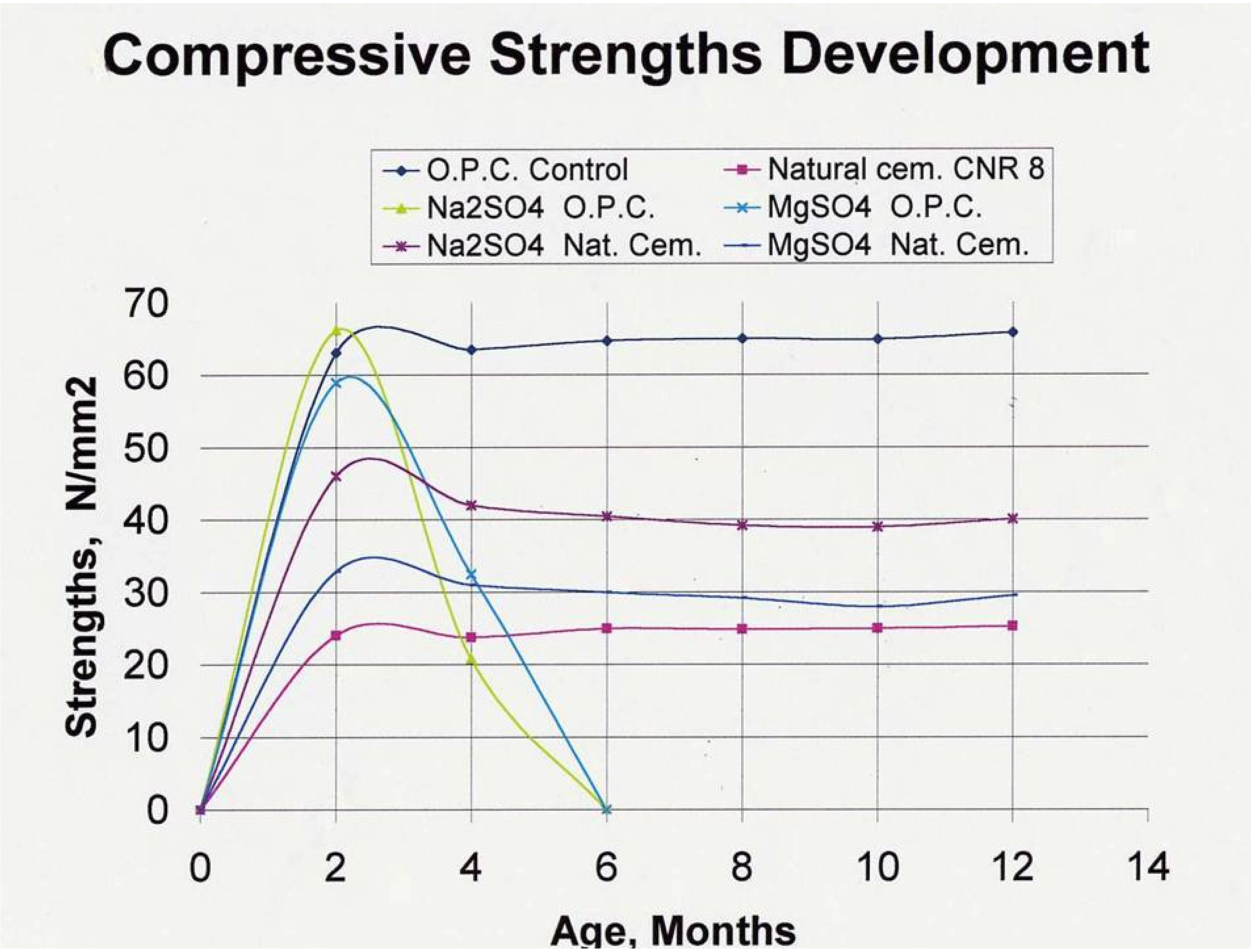

CIMENTS COLLET S.L.
BERGA CATALONIA SPAIN
LIMESTONES OF
ROGNAC
25m.
MARLS OF EOCENE
Natural Cement
Strata
Coals
UPPER CRETACEOUS
SENONIAN
BASAL LIMESTONE
OF UPPER MONTIAN

INSIDE A MINE


Sant Climent
de Torre d'en Foix
BOCAMINA
PREVISIO
1
2
3
4
Río Saldes
Salto de agua
La Tosa
1.051
K.98
K.97
K.96
K.95
K.94
K.93
K.92
K.1
K.2
K.3
Cal Janola
El Collet d'Fina
Casas Nuevas del Collet
Cerro de la Rota
Cingle de la Rota
Tossal Llisat
Cal Blau
Cap del Porten
1.341
Torrente
Río Llobregat
Can la Costa
Serchs
985
Cal Viernes
Can Comamodona
Cal Frara
Cal Tirat
Casa les Planes

CHEMICAL ANALYSIS OF THIS COMPOSITIONS

- **Natural Strata Material**
- **Clinker obtained at 1,000 ºC Temperature**



Compressive Strengths Development
O.P.C. Control
Natural cem. CNR 8
Na2SO4 O.P.C.
MgSO4 O.P.C.
Na2SO4 Nat. Cem.
MgSO4 Nat. Cem.
Strengths, N/mm2
0
10
20
30
40
50
60
70
0
2
4
6
8
10
12
14
Age, Months

Porosity Reduction in Post-Cured Immersion

Average Values	Compression Strength N/mm^2	Porosity Volume %
Pure Paste Grain Size 600µm. W/C 0.4 Water-Cured 28d.	25	47
Post-Cured Immersion 5% Na2SO4 1 year	40	34

Composition Comparison Between Natural Clinker and Portland Clinker

Natural Clinker / Portland Clinker

Values as Percentages

	Natural Clinker	Portland Clinker
TiO2	0.24	0.15
SiO2	22.0	20.8
Al2O3	8.9	6.1
Fe2O3	3.0	3.2
CaO	45.3	64.9
MgO	0.82	1.8
SO3	3.0	0.66
Na2O	0.30	0.19
K2O	1.7	0.54
L.O.I.	13.2	1.1

COMPARATIVE PARAMETRES OF THE CLINKERS

	Natural Clinker	Portland Clinker
•Insoluble Residue	14.6	0.50
•Hydraulic Silica	16.0	20.5
•A/s Mol Ratio	2.32	7.25
•CaO Free Lime	1.6	0.80
• Lime Saturation Factor	61.1	96.2

ANALYSIS OF SOLUBLE AND INSOLUBLE FRACTIONS OF RAW METERIAL IN COLD 10% HYDROCHLORIC ACID BY GOMÀ METHOD

- SOLUBLE FRACTION : MATERIALS UNSTABLES AT LOW TEMPERATURE
- INSOLUBLE FRACTION: MATERIALS WITHOUT REACCTION AT LOW TEMPERATURE

Summary Differences of the Natural Cement Presented with Portland Cement

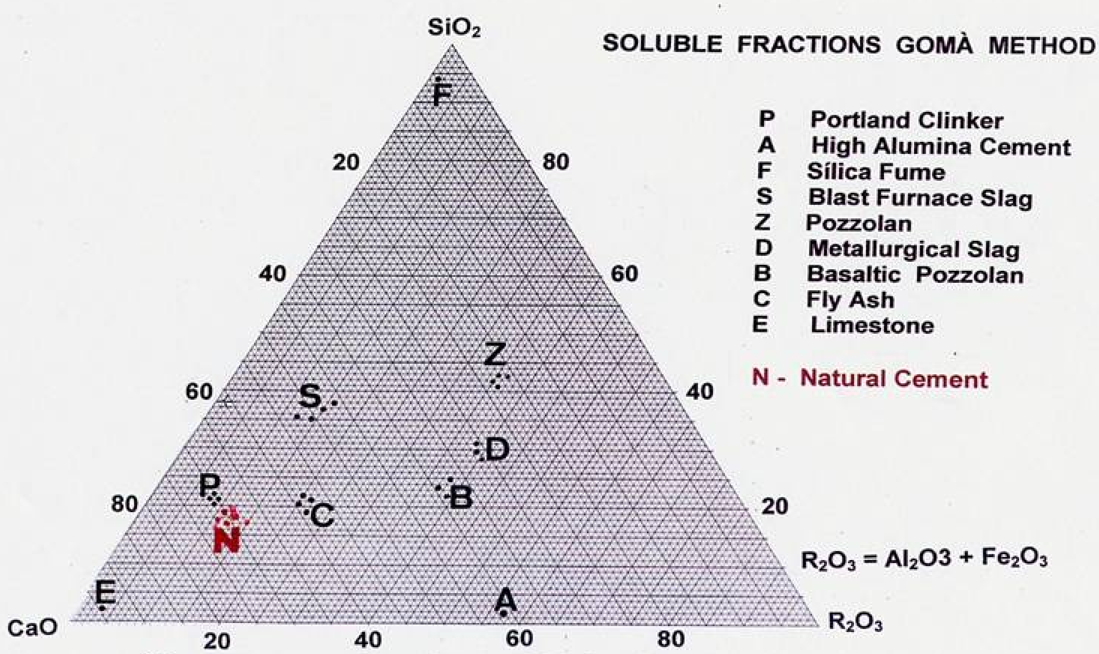
- 3 % SO_3 in Clinker
- Low Content C_2S ; Without C_3S
- Very Low Temperature clinkerization
- Hydrated Phases:

  Ettringite 1 to 2 μm.
  CSH
  CH

ANALYSIS OF CHEMICAL COMPOSITIONS OF THE SOLUBLE AND INSOLUBLE FRACTIONS AS A WHOLE SAMPLE Values as percentages

Soluble Fraction		Insoluble Residue	
TiO_2	0.09	TiO_2	1.2
SiO_2	13.9	SiO_2	60.6
Al_2O_3	6.6	Al_2O_3	16.7
Fe_2O_3	1.6	Fe_2O_3	10.8
CaO	43.8	CaO	3.3
MgO	2.2	MgO	0.80
SO_3	3.2	SO_3	0.20
Na_2O	0.16	Na_2O	1.1
K_2O	1.2	K_2O	3.9
L.O.I.	12.2	L.O.I.	0.20

GRAPHICAL PROCEDURE DESIGNED TO IDENTIFY THE MATERIALS PRESENT

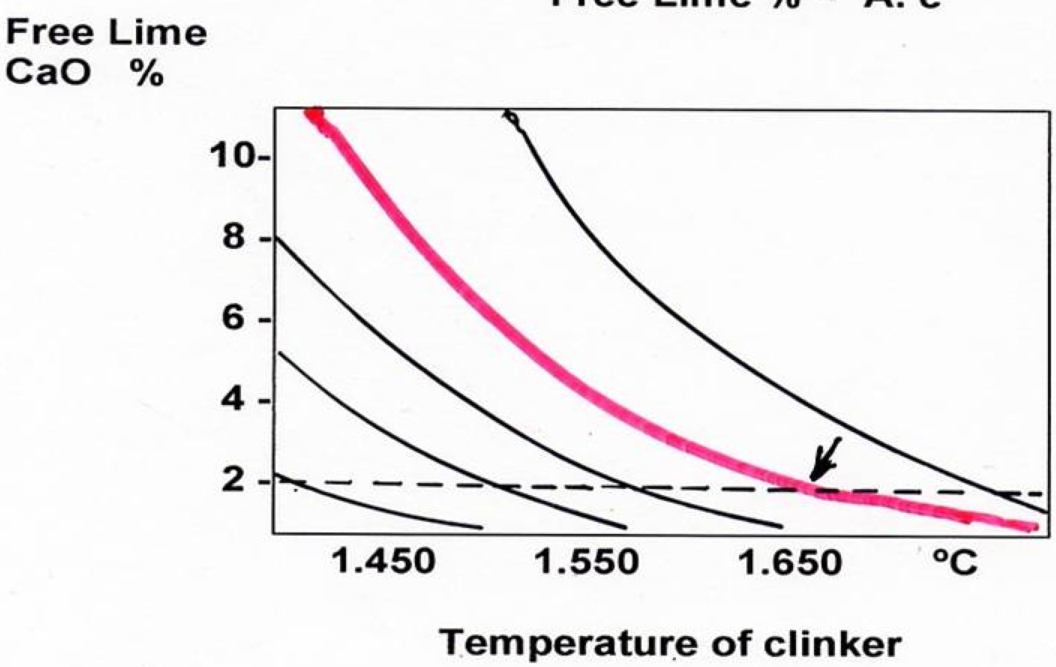


Ternary composition of the soluble fractions

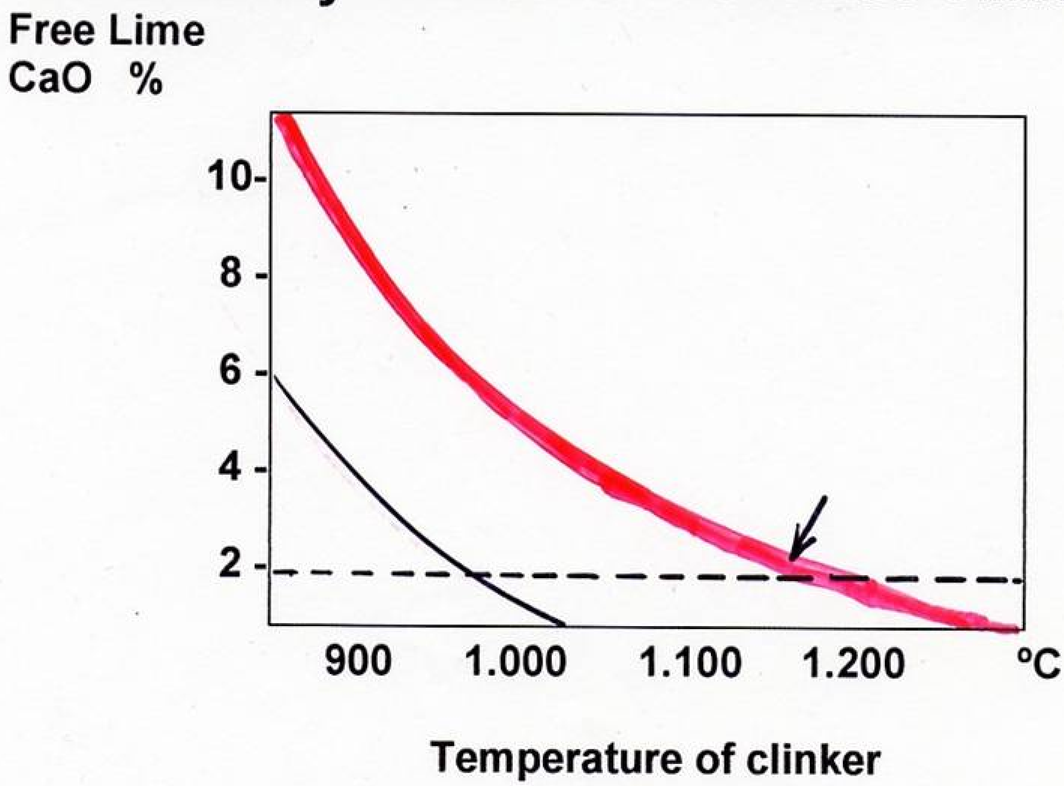
Clinkerability Curves of Portland Clinkers

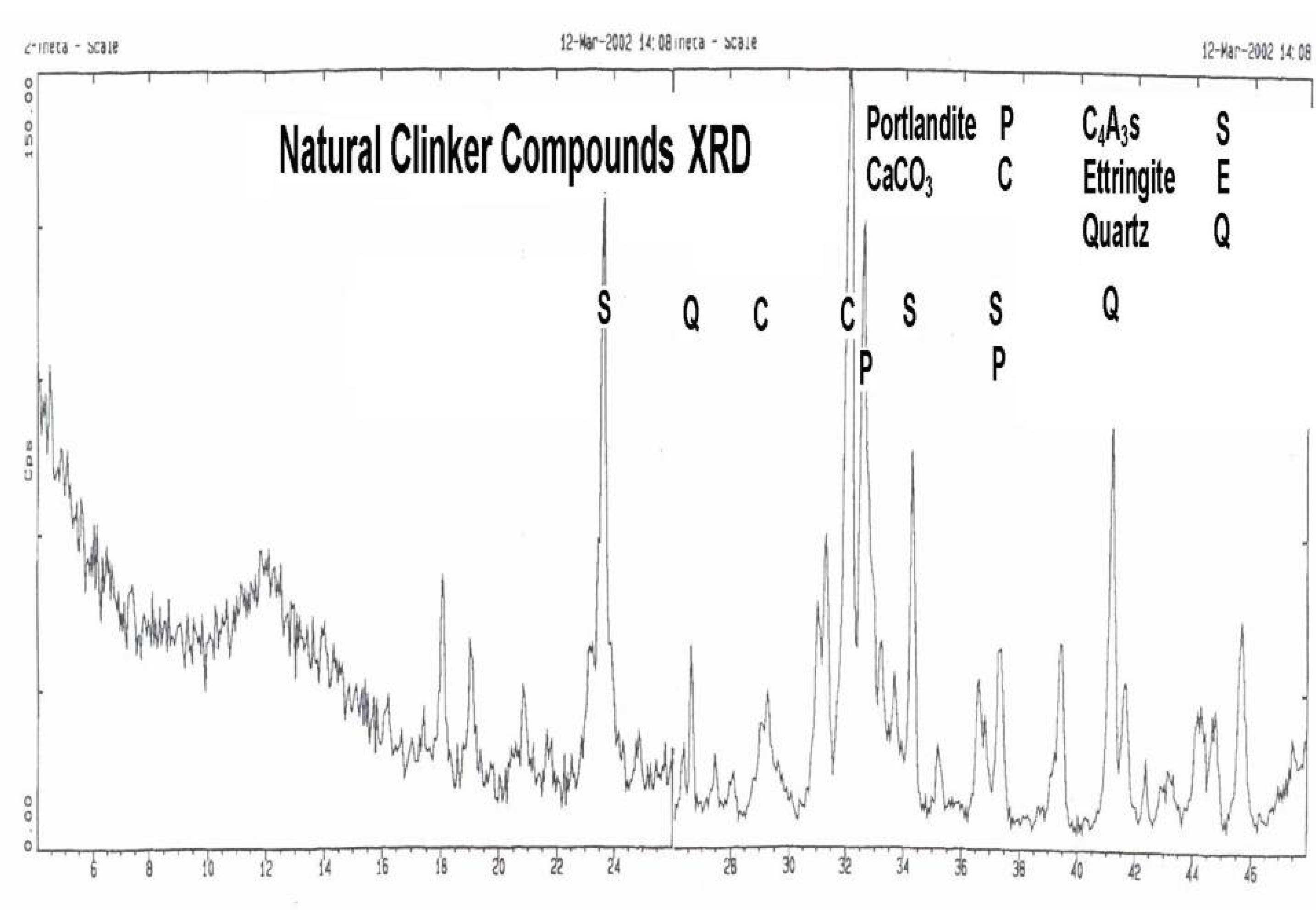
Author's cited method

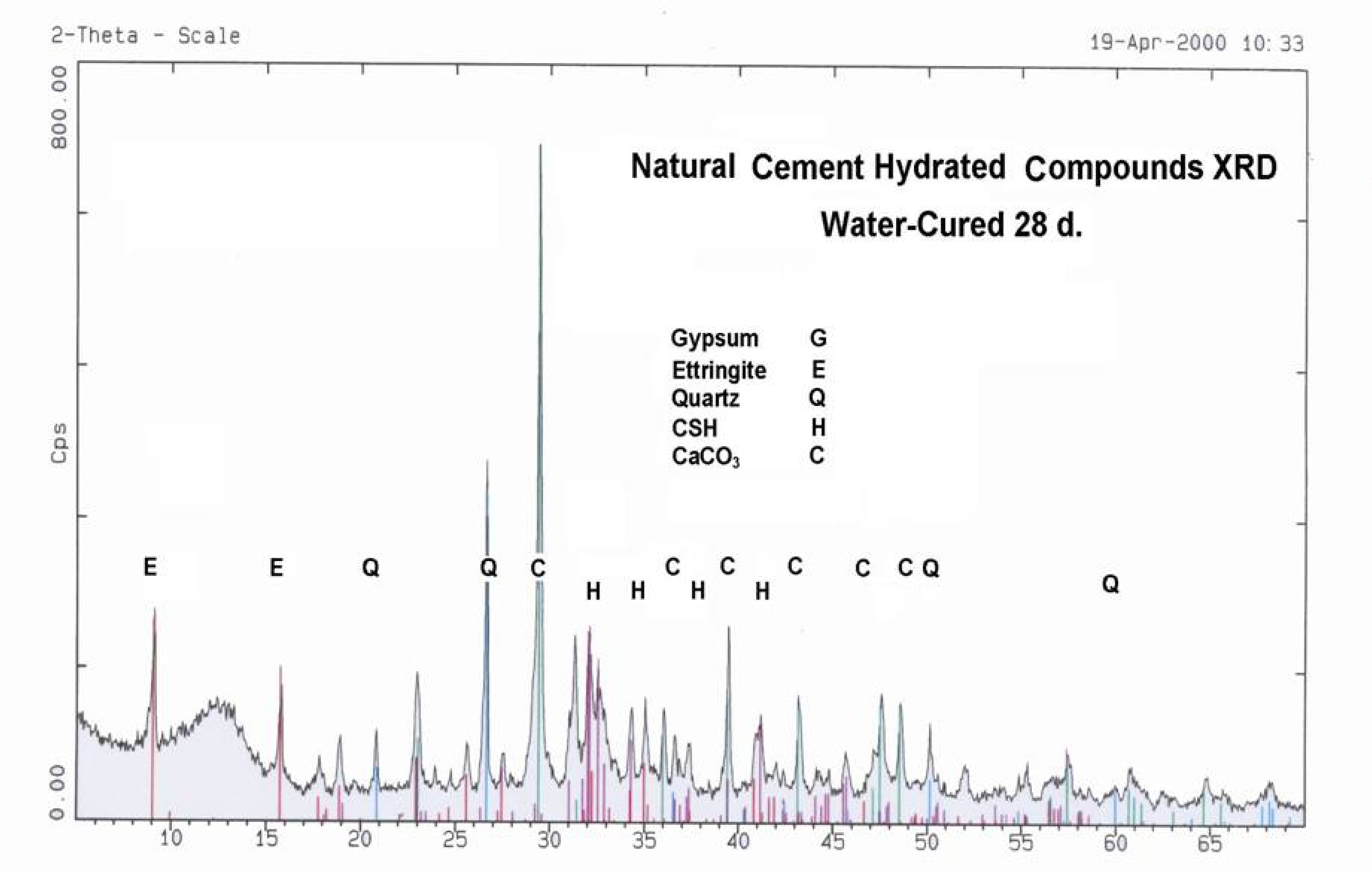
$$\text{Free Lime \%} = A.\, e^{\frac{1.450 - t}{a}}$$

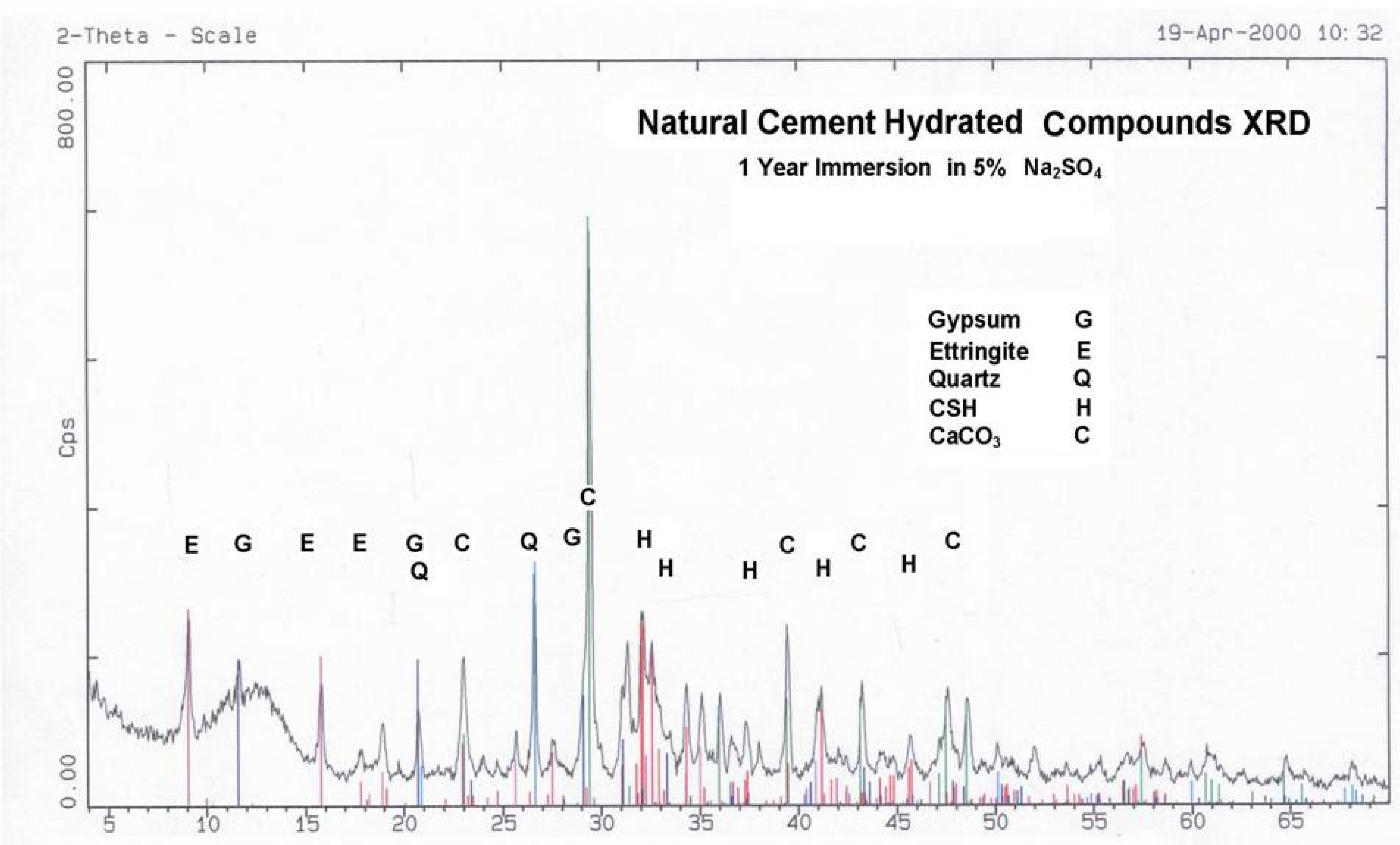


Clinkerability Curves of Non-Alitic Clinker



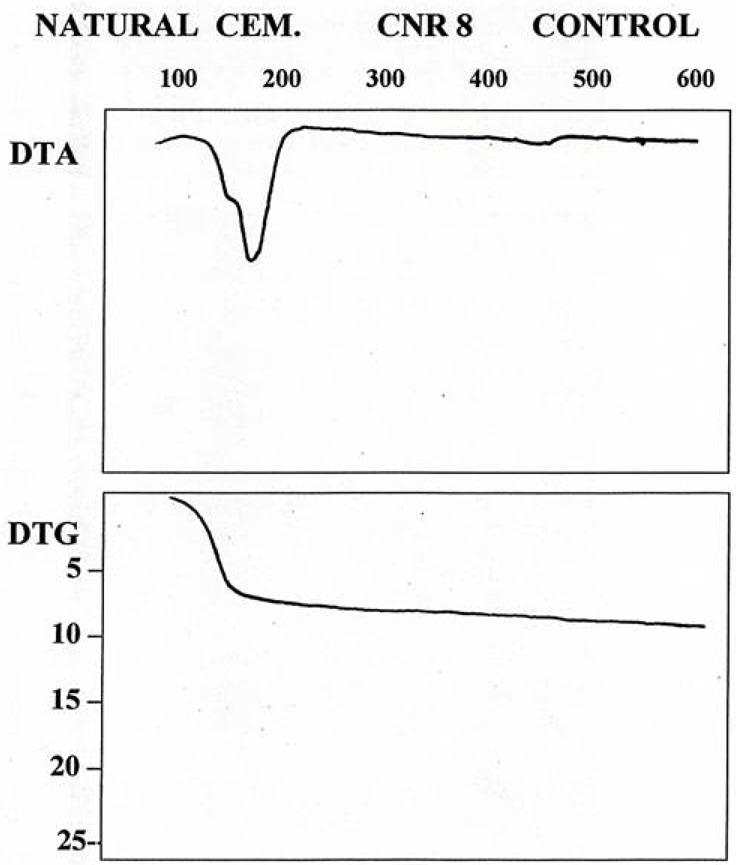

2-Theta - Scale
12-Mar-2002 14:08
Theta - Scale
12-Mar-2002 14:08
Natural Clinker Compounds XRD
Portlandite P
$CaCO_3$ C
C_4A_3s S
Ettringite E
Quartz Q
S
Q
C
C
P
S
S
P
Q
150.00
Cps
0.00
0
6
8
10
12
14
16
18
20
22
24
28
30
32
34
36
38
40
42
44
46


2-Theta - Scale
19-Apr-2000 10:33
800.00
Cps
0.00
Natural Cement Hydrated Compounds XRD
Water-Cured 28 d.
Gypsum G
Ettringite E
Quartz Q
CSH H
$CaCO_3$ C
E E Q Q C H H C H C H C C C Q Q
10 15 20 25 30 35 40 45 50 55 60 65



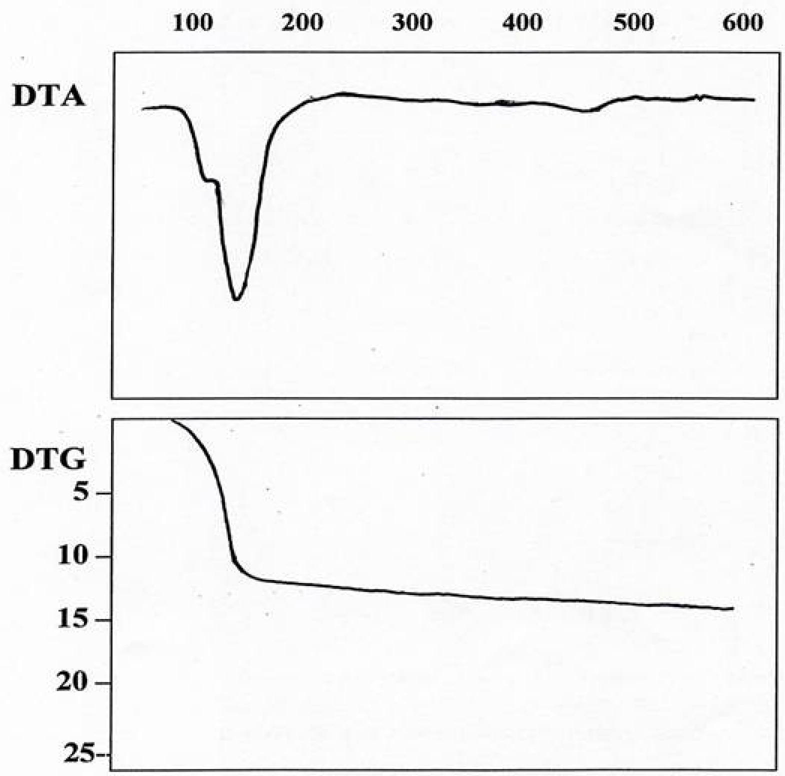
2-Theta - Scale
19-Apr-2000 10:32
Natural Cement Hydrated Compounds XRD
1 Year Immersion in 5% Na_2SO_4
Gypsum G
Ettringite E
Quartz Q
CSH H
$CaCO_3$ C
Cps
800.00
0.00
E G E E G Q C Q G C H H H C H C H C
5 10 15 20 25 30 35 40 45 50 55 60 65

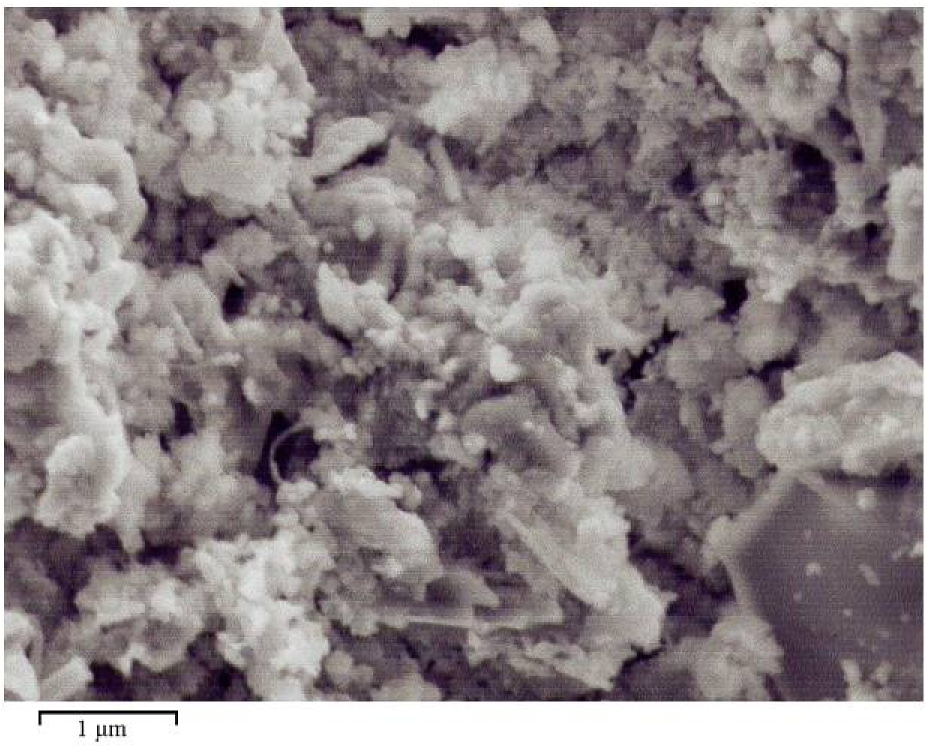
DTA curves of the hydrated cement pastes extracted from the micro-cubes



DTA curves of the hydrated cement pastes extracted from the micro-cubes cured in agressive dissolutions

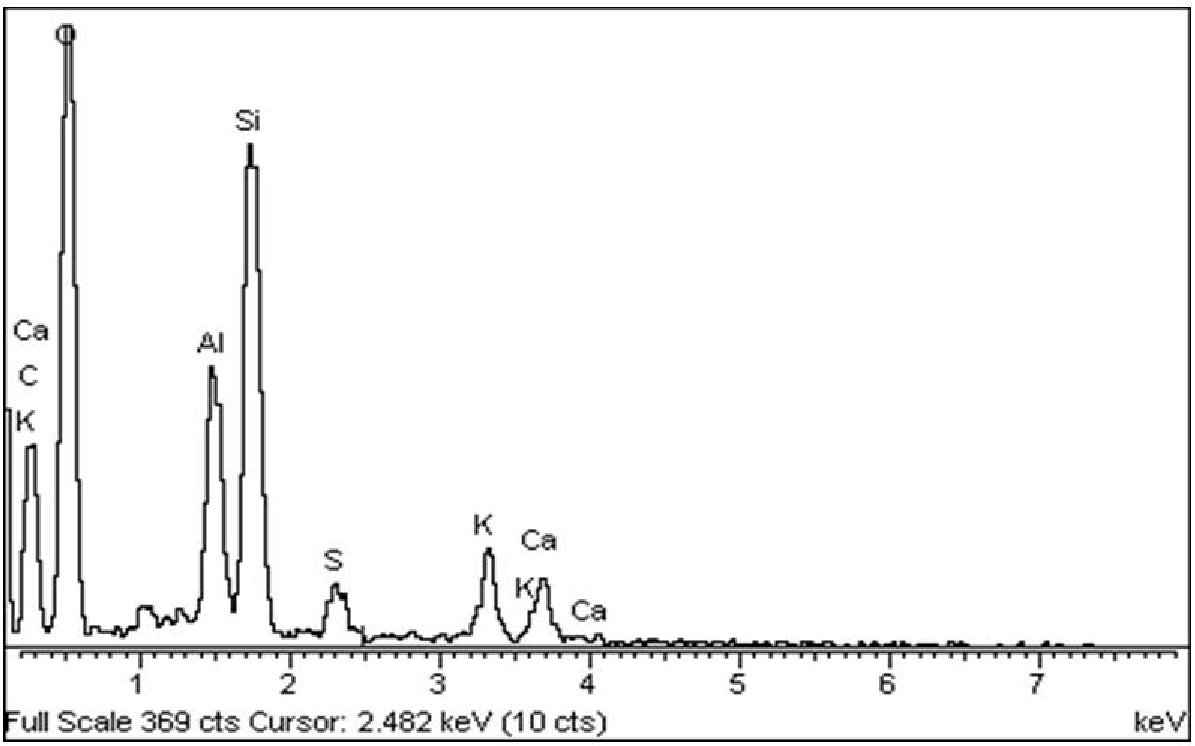
NATURAL CEM. CNR 8

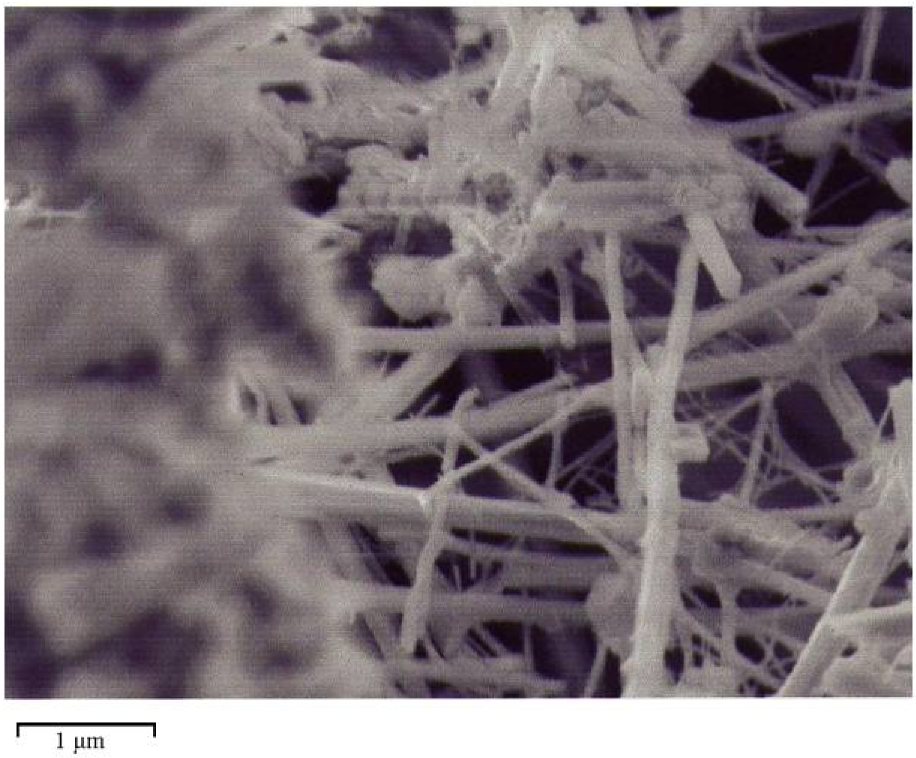




Scanning Electron Micrographs of Hydrated Pastes Water cured 28d

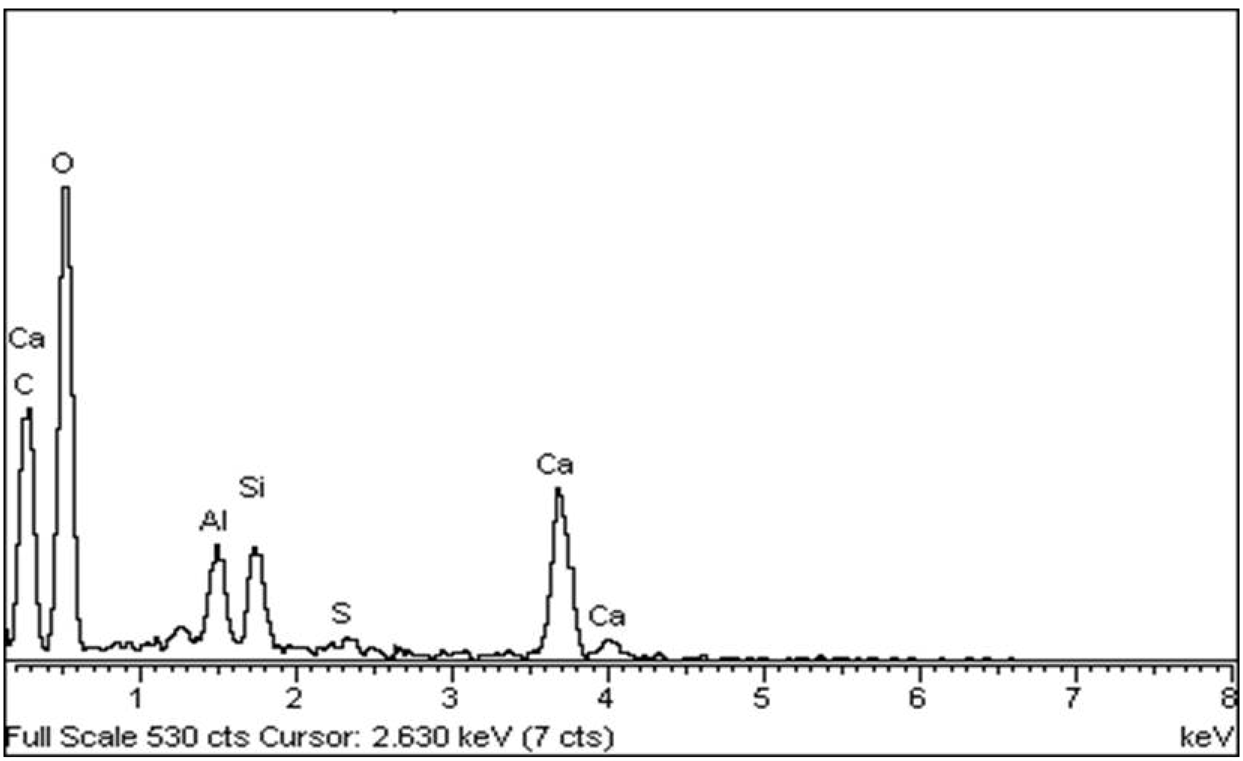
EDAX Dominant cryastal shape detection

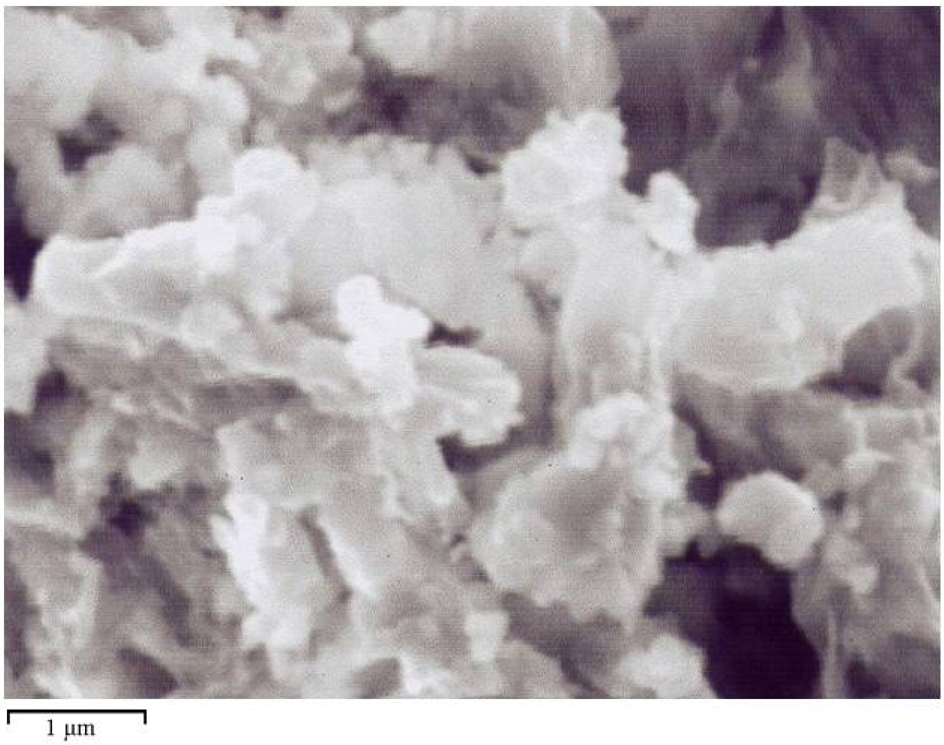




Scanning Electron Micrographs of Hydrated Pastes Water cured 28d

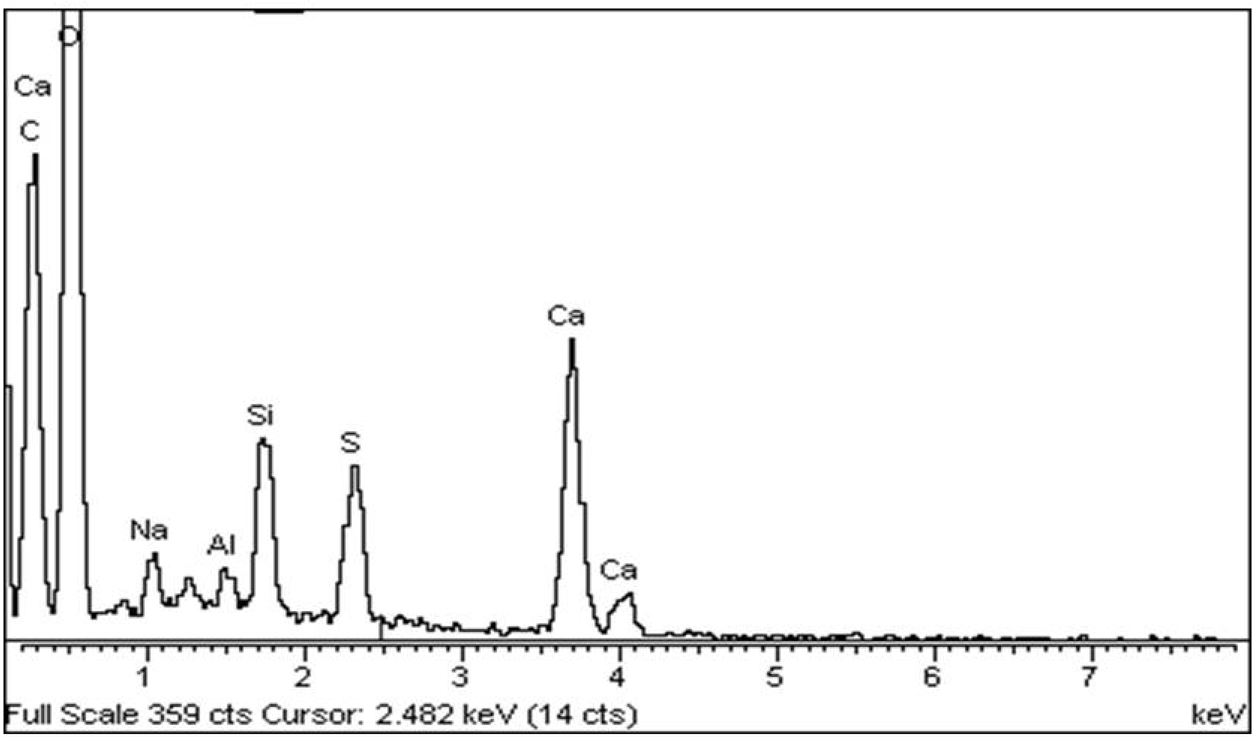
EDAX Dominant cryastal shape detection

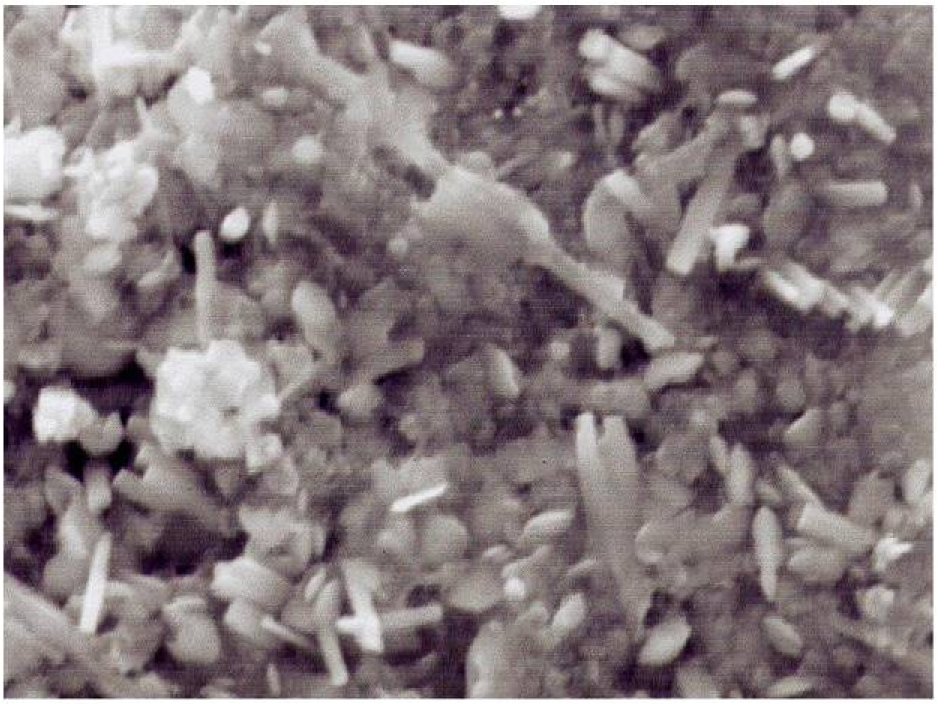




Scanning Electron Micrographs of Hydrated Pastes 1 year immersion 5% Na_2SO_4

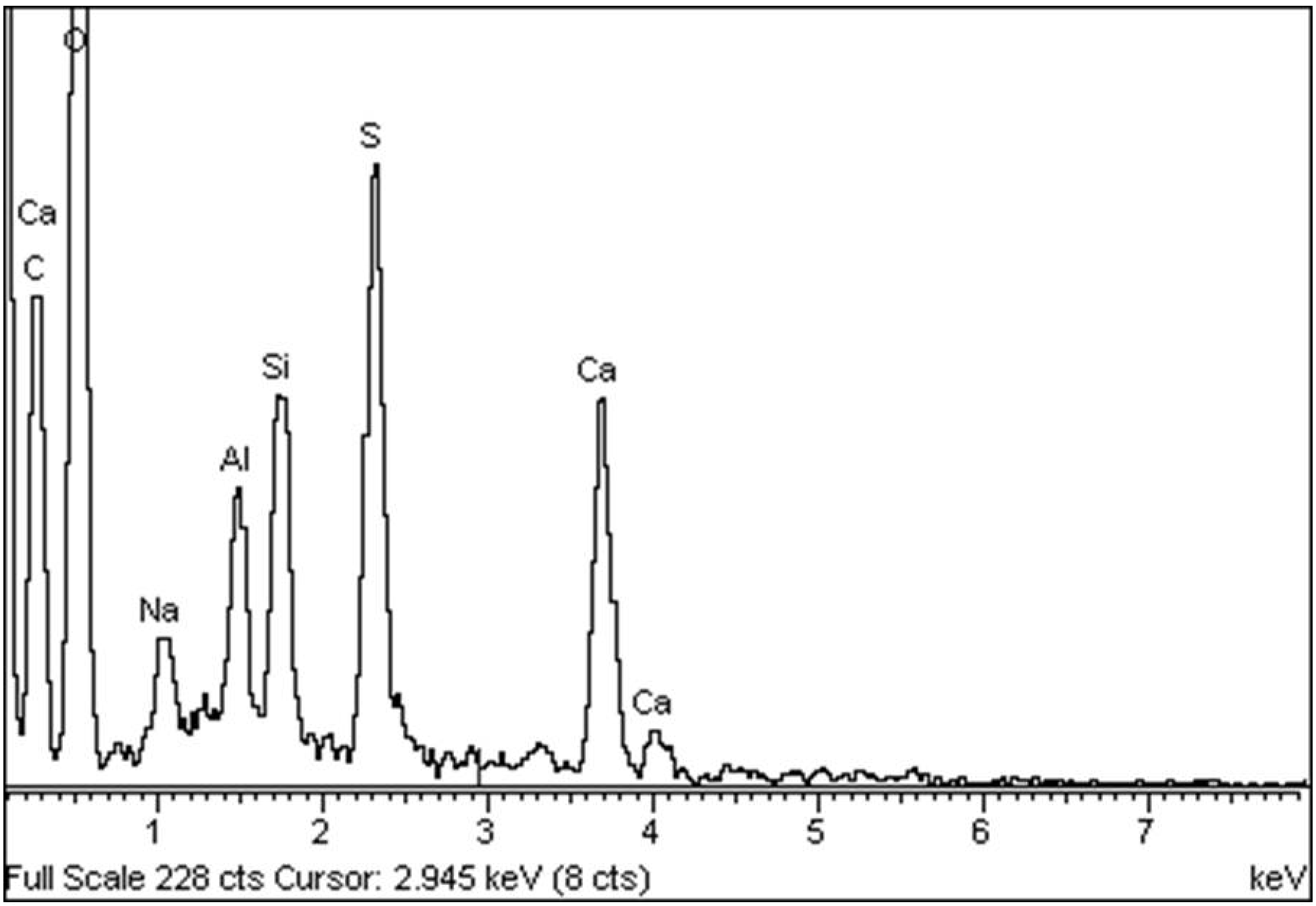
EDAX Dominant cryastal shape detection



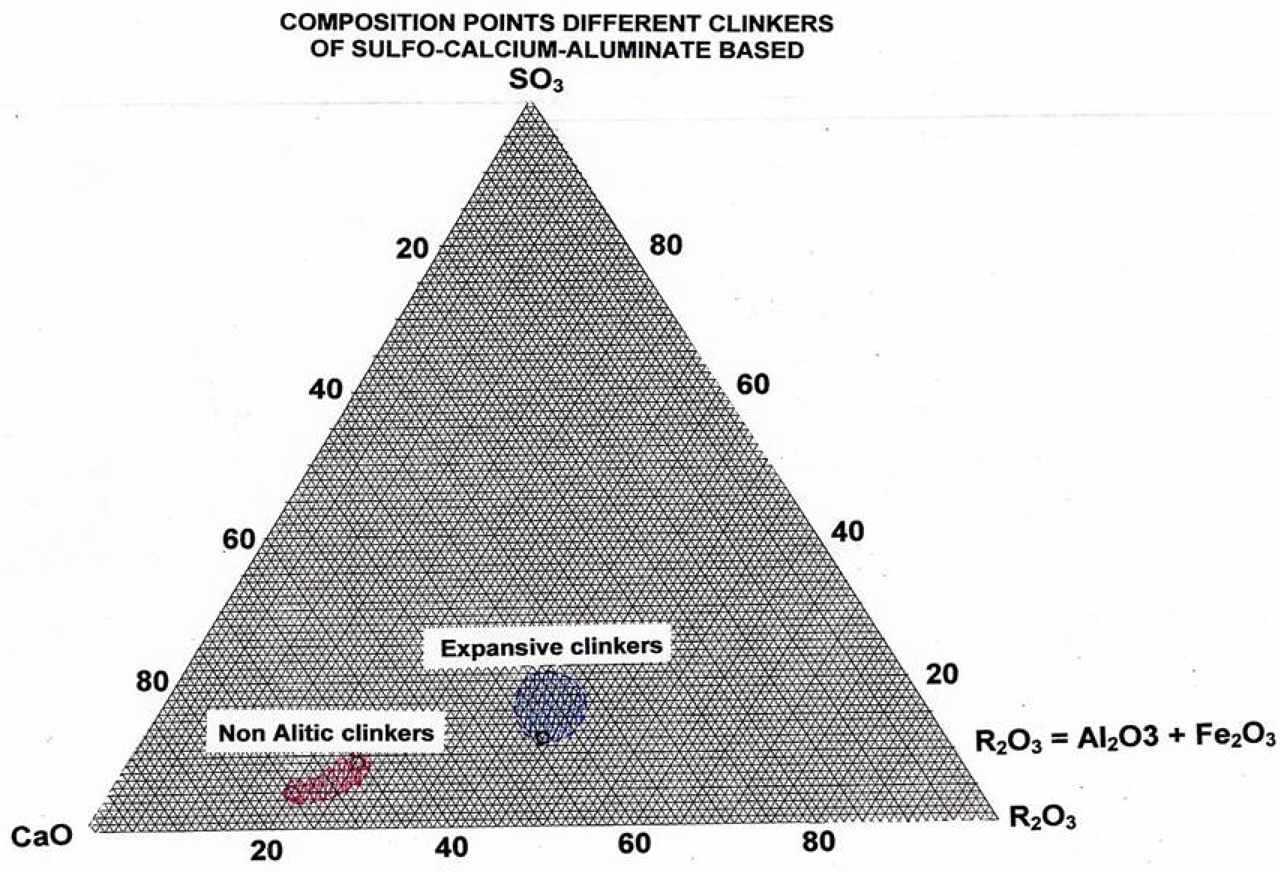


1 μm

Scanning Electron Micrographs of Hydrated Pastes 1 year immersion 5% Na_2SO_4



O
S
Ca
C
Si
Ca
Al
Na
Ca
1
2
3
4
5
6
7
Full Scale 228 cts Cursor: 2.945 keV (8 cts)
keV


COMPOSITION POINTS DIFFERENT CLINKERS
OF SULFO-CALCIUM-ALUMINATE BASED
SO_3
20
40
60
80
80
60
40
20
Expansive clinkers
Non Alitic clinkers
$R_2O_3 = Al_2O3 + Fe_2O_3$
CaO
R_2O_3
20
40
60
80

CONCLUSIONS

- A new cement having a composition very close to that of a Portland cement, with a 3% SO_3 content in raw mix and a low clinkerability temperature of 1,000 to 1,150 ºC instead of 1,600 to 1,650 ºC of the Portland clinker may be produced.

- The 1 –2 μm secondary ettringite formation does not manifest itself as expansive when the amount of the C_2S is low and there is no C_3S and the increase in compression strength may allow a new type of alternative usage cement to be produced.

- Its most significant application is its use in situations of strong aggression due to high sulfate concentrations.

- 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 structures with real volumes, is justified, and will enable a specific standard for its use to be established by the Standards Committees.

- To the question "Portland Cements: is anything new on the horizon?" Perhaps one answer could be: "this type of suggested new cement might be the beginning of another new binder for the next millennium with environmentally sustainable cement manufacture and without sulfate attack problems"