

**CONFIDENTIAL**

***cost effective GEOPolymeric Cements for  
Innocuous Stabilisation of Toxic EleMents  
(GEOCISTEM)***

***Final technical report***

**From January 1, 1994 - February 28, 1997**

**J. Davidovits, Ph. Rocher, D. Gimeno, C. Marini, A. Rinaldi, S. Tocco**

**April, 1997  
R 39616**



## ***AVERTISSEMENT***

***Le présent rapport a été édité sous une forme acceptée, d'un commun accord, par la Commission européenne et les différents partenaires impliqués techniquement dans la réalisation de ce projet de recherche.***

***De ce fait, la procédure qualité relative à la présentation des rapports BRGM n'a pas été appliquée.***



**BRITE-EURAM BE-7355-93**  
**Contract No. BRE2-CT93-0559**

**COST EFFECTIVE GEOPOLYMERIC CEMENTS**  
**FOR INNOCUOUS STABILISATION OF TOXIC ELEMENTS**



**FINAL TECHNICAL REPORT**

From January 1, 1994 to February 28, 1997

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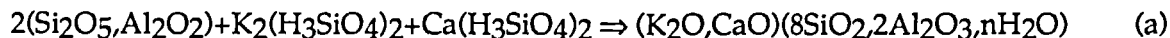
- to commercialise, manufacture, distribute;
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## SUMMARY

Regular geopolymeric advanced binders produced at laboratory scale (costs approx. 3-4 FF/kg) are too expensive for mass application. They comprise three ingredients namely: expensive potassium silicate, calcined kaolinite clay, and cheap blast furnace slag. The chemical reaction



yields a rapid-setting inorganic geopolymeric binder.

The GEOCISTEM project was aimed at manufacturing cost-effectively geopolymeric cements based on this geopolymeric chemistry at a cost in the range of 0.5-0.7 FF/kg. The development of these new geopolymeric cements is based on the replacement of the very expensive K-silicate, with a selection of cheap high alkali volcanic tuffs. The GEOCISTEM project comprises the geological study and mineralogical research of volcanic tuffs aimed at selecting resources providing enough economic potentiality. A series of 10 geological formations from continental Italy, Sardinia, continental Spain and the Canary Islands is selected. The second part of the geology research involves the identification, both quantitative (availability of the resource) and qualitative (suitability of the material), of the best substance to valorize, from an economical, environmental and political point of view. The Consortium selected the SA07 outcrop in Sardinia, Paringianu, near Sulcis. The geological samples are processed either at 1300°C (formation of alkali-melilitic GLASS ( $\text{Ca}, \text{Na}, \text{K}$ )<sub>2</sub>[(Mg, Fe<sup>2+</sup>, Al, Si)<sub>3</sub>O<sub>7</sub>]), or at 800°C (the material being called CARBUNCULUS). Geopolymeric cements manufactured with these geological elements GLASS and CARBUNCULUS are providing up to 80% reduction of the K-silicate part.

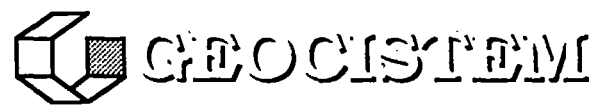
The geopolymeric binders and cements are tested for their use in Waste management applications. One study is to provide inertization of toxic liquid by absorption and subsequent encapsulation. It starts with the study of the absorption capacity data for natural sorbents such as bentonites, zeolites and vermiculites, for removal of heavy metals, arsenic, radioactive elements from concentrated solutions, thermally treated mixed-wastes (organic-inorganic). Best results, with respect to absorption and encapsulation are obtained with Na-modified bentonites that absorb up to 850 g of liquid per 1 kg of bentonite. Pelletisation, coating and inertization is achieved with GEOPOLYMERIC binders and the selected CARBUNCULUS cement. The results are compared with Portland cement coating. The best results are provided by laboratory GEOPOLYMERIC binders, followed by CARBUNCULUS cement, with respect to attrition behaviour.

The unique properties of the expensive Geopolymeric Binders of the Background knowledge are found in this new cheaper cements, namely: high early strength, sulphate resistance, corrosion resistance to sulphuric acid, no Alkali-Aggregate -Reaction, which make them ideal for long term containment. Testing involves comparative sand mortar standard methods with Portland cement (type I 42.5 R from Cementi Buzzi) and CARBUNCULUS cement made with the sample SA07 from Sardinia. A study determines the best possible uses for geopolymeric cements in the cleanup of polluted mine tailings sites (uranium mine tailing at the German WISMUT site), and decantation ponds. Another study deals with regular concrete applications.

Chemistry mechanism is studied by the means of the very powerful NMR Spectroscopy of <sup>29</sup>Si and <sup>27</sup>Al. The resulting structure belongs to the tecto-alumino-silicate Si(Q4) types and the good properties of the CARBUNCULUS cements are essentially those provided by the geopolymeric Base reaction (a). Geological elements are reacting at the interface between Base and grain surface.

Two long-term durability studies for concretes elaborated with these new cements are performed. The first research involves an archaeo-linguistic study based on Latin texts, for example *De Architectura* by Vitruvius, followed by a selection of Roman cements and mortars in Rome and Ostia dating from the 3rd c. BC to the 3rd c. AD. Archaeological analogues are based on the calcic activation of alkali rich volcanic tuffs, with lime. The excess of unreacted lime recarbonates slowly into Ca-Carbonate. In addition to the conventional mineralogical testing of mortars, an NMR Spectroscopy investigation of these cements provides two archaeological Roman cement analogues, dating to the 2nd. c. AD. The second study focuses on geological analogues. Zeolitic analogues are selected and tested for acid resistance and bio-lixivation.

Geopolymeric cement, CARBUNCULUS type, does not require any calcination of calcium carbonate, like it is the case in the manufacture of ordinary Portland Cement. Compared to Portland Cement, Green House gas CO<sub>2</sub> emission is reduced by 80-90% during manufacture. This would mitigate GLOBAL-WARMING.



## **1. Objectives of the Project GEOCISTEM**

## **2. Methodology and Results**

# 1. OBJECTIVES of the GEOCISTEM Project

## Cost effective **GEO**polymeric **C**ements for **I**nnocuous **S**tabilisation of **T**oxic **E**lements

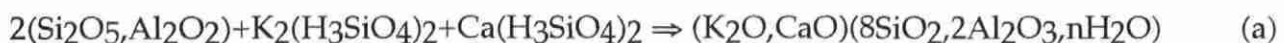
GEOCISTEM addresses essentially problems dealing with major global environmental and ecological concerns, for example the safe and innocuous disposal of toxic and hazardous wastes and mine tailings. It also addresses the mitigation of one of the major Global-Warming «Green-House» gas, carbon dioxide CO<sub>2</sub>.

New cementitious materials, mineral geopolymeric binders, invented and developed in Europe by CORDI-GEOPOLYMERE, had been successfully tested by Canadian and American Institutions (CANMET and EPA) in 1987-1990 [1-2]. Fig.1 and Fig.2 display examples of the results obtained at Ontario Research Foundation (Canada) on the innocuous solidification and stabilisation of nonmetallic and uranium mine tailings.

The rapid hardening geopolymeric binder used in the Canadian research program had compressive strengths higher than 15-20 MPa at 4h-20°C. It involved basically three reactive constituents [3].

- Alumino-silicate oxide (calcined kaolin KANDOXI), (Si<sub>2</sub>O<sub>5</sub>,Al<sub>2</sub>O<sub>2</sub>)
- Potassium disilicate K<sub>2</sub>(H<sub>3</sub>SiO<sub>4</sub>)<sub>2</sub>
- Calcium disilicate Ca(H<sub>3</sub>SiO<sub>4</sub>)<sub>2</sub> (blast-furnace slag)

The chemical reaction



yields a rapid-setting inorganic binder.

Yet these mineral geopolymeric binders are **too expensive** for mass application. So far, their production costs are 15 times higher than ordinary Portland Cement.

**a) The first objective** was to achieve a drastic reduction in the production costs of geopolymeric cements, essentially by replacing the expensive Potassium Silicate. The research project involved the manufacture of a reactive potassium alumino-silicate glass obtained by melting at 1300°C and quenching natural geological materials containing alkali alumino-silicate components, and, in the second part of the project, the manufacture of a

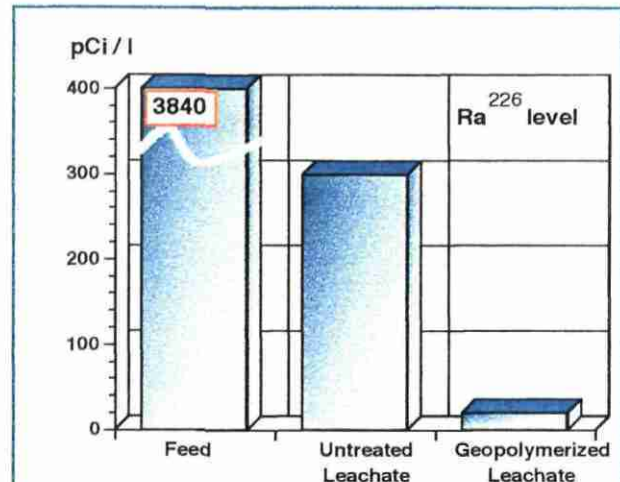


Figure 1: Radium level in uranium waste tailing; acid leaching.

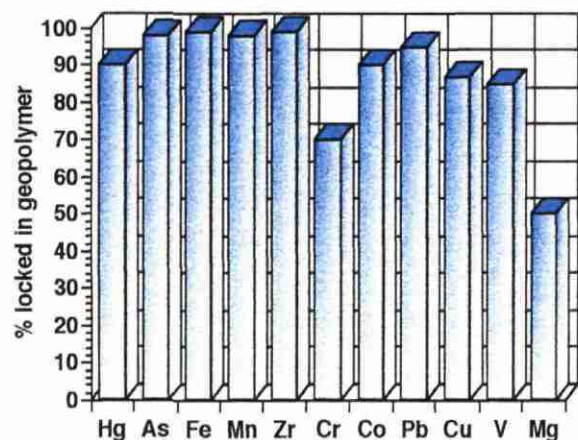


Figure 2: Efficiency of geopolymeric binders acid leaching

reactive geological filler obtained by calcination at 800°C of the same geological samples.

Table 1 presents the costs paid by CORDI-GEOPOLYMERE at the beginning of the GEO-CISTEM project (1993) for quantities in the 1 Tonne range. The expected costs are those which were foreseen at the end of the project.

*Table 1: Costs of the main ingredients*

Ingredients	amount/ Tonne	present cost	expected cost
Alumino-silicate oxide	0.35	1150 FF	255 FF
Potassium disilicate	0.35	1950 FF	310 FF
Calcium disilicate	0.30	150 FF	50 FF
total for 1 tonne	1.00	3250 FF	615 FF

**b) The second objective** was to test these acid resistant geopolymeric cements for safe and innocuous disposal of toxic and hazardous wastes and mine tailings (nonmetallic, metallic, uranium mines). Their unique properties, which include high early strength, freeze-thaw resistance, sulphate resistance, and chemical corrosion resistance, make them ideal for long term containment [4].

The behaviour of geopolymeric cements (zeolitic in nature) is similar to that of zeolites and feldspathoids; they immobilize hazardous materials within the geopolymeric matrix, and act as a binder to convert semi-solid wastes into adhesive solids. The pollutants become locked into the three dimensional geopolymeric framework. Geopolymeric containment has been shown to greatly minimize the leaching of iron, cobalt, cadmium, nickel, zinc, lead, arsenic, radium and uranium, even in **aggressive acidic medium** (Fig. 1 and 2).

**c) The third objective** deals with the testing of low-CO<sub>2</sub> emission cement. The production of these acid resistant geopolymeric cements does not require any calcination of calcium carbonate, like it is the case in the manufacture of ordinary Portland Cement, which involves the calcination of limestone. The GEOCISTEM project demonstrates that it is possible to create new cements with low-CO<sub>2</sub> emission during their manufacture, to **minimize the «Green House» Global-Warming**. [5]

## 2. METHODOLOGY and RESULTS

### 2.1 Starting Point

From unpublished fundamental research carried out by GEOPOLYMERE during the development of high-performance cements in USA, we came to the conclusion that alkali-melilite glass, which was strongly accelerating the hardening of portland cements, could replace the expensive potassium silicate ingredient in geopolymeric cements. With selected geological raw materials, there should be possible to manufacture glasses with 50-80% of alkali-melilite (Ca,Na,K)<sub>2</sub>[(Mg,Fe<sup>2+</sup>,Al,Si)<sub>3</sub>O<sub>7</sub>]; cf. Background Patents in [6].

The improved manufacturing process and the replacement of expensive potassium silicate by geological materials could open a market in the waste management industry, which was closed due to the very high costs of raw materials. In addition, this new cement minimizes also CO<sub>2</sub> gas emission and mitigate GLOBAL-WARMING.

### 2.2 Project Methodology

The project methodology comprised the achievement of two complementary targets:

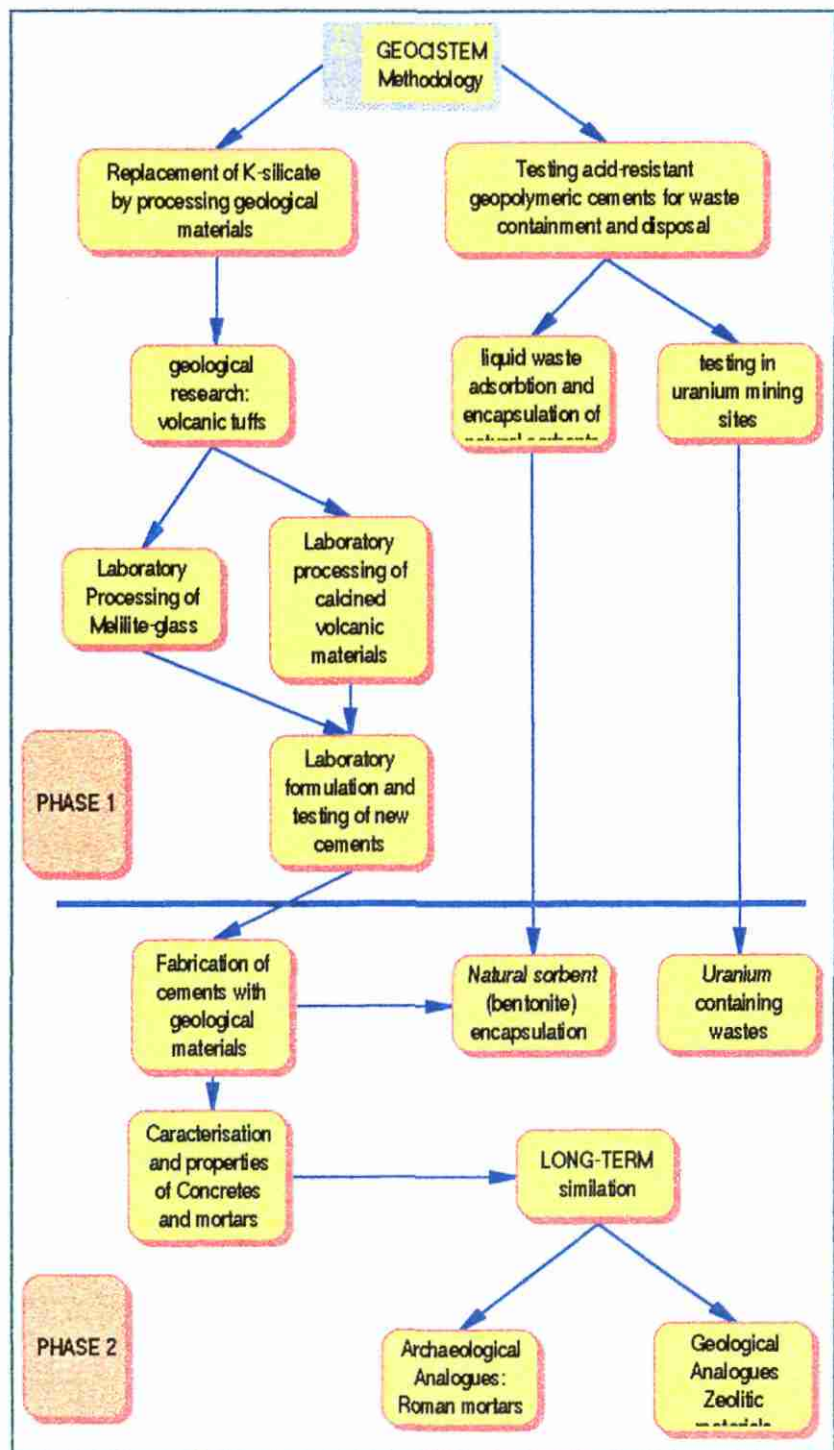
1) the replacement of K-silicate, by processing geological materials with very high K<sub>2</sub>O content.

2) the testing of these acid resistant geopolymeric cements for safe containment and disposal.

Both subprojects were run simultaneously. They comprised following main research tasks:

#### Subproject 1: Cement.

- geological study and mineralogical research
- laboratory processing of the two major ingredients: MELILITE-Glass and CARBUNCULUS calcined volcanic tuff.



- elaboration of durability tests and long-term durability diagnosis.

#### Subproject 2: Hazardous Waste treatment

- geopolymeric cement formulation for toxic waste encapsulation
- geopolymeric cement formulation for acid-resistant concretes and uranium mining sites treatments.
- absorption technology of toxic elements on mineral sorbents.

#### **2.2.1. Geological studies: Tasks GEOPROSPEC-1 and 2**

The project task relating to the «geology and characterization of volcanic tuffs» involved Partners B.R.G.M., Cagliari University and Barcelona University.

CORDI-GEOPOLYMERE had recommended to search for materials with the highest  $K_2O$  content, or the highest  $Na_2O+K_2O$  content, if possible in the 10% by weight range. The first Geological study GEOPROSPEC 1 located the European Regions where the geological resources required for the manufacture of alkali-melilite glass could be found. It dealt with regional geological investigations and rough characterization of the materials.

GEOPROSPEC 1 determined the quantitative character of the resources - only the potentially economic deposits were selected - and investigated promising targets from a qualitative standpoint, bearing in mind the technical specifications (especially chemical composition).

The second phase, GEOPROSPEC 2, was dedicated to a more precise qualitative determination of one resource, which was selected by the Consortium for its technical and industrial potential. It is located in South-Western Sardinia and corresponds to volcanic tuffs belonging to the Paringianu Unit. This step involved detailed geological investigations with fine characterization of the materials; more precise determination of the location, amount and purity of the geological samples.

The main objective of the «geological/resource» part of the project was the identification and characterization of suitable European resources qualified for the manufacture of geopolymeric cements, from a quantitative and qualitative point of view. The exploration was undertaken in several volcanic regions where volcanic tuffs have a very wide composition range. The geological study was performed in 3 different EU Member states: Italy, Spain and Greece.

The geological and mineralogical research detected and located several suitable raw materials in a great number of countries (EU Member states and non EU Member states) for the industrialisation and mass production of the geopolymeric cements.

#### **2.2.2. Replacement of K-Silicate by processing Volcanic Tuffs: Task GPCEMENT**

Task leader: CORDI-GEOPOLYMERE

Based on the Background Patents # FR 90 15144, 93 13770/ PCT/FR 91/00689 (WO 92/04298) [6], this major project task involved the research related to the processing of 2 major ingredients. From the 3 ingredients necessary for geopolymeric cement formulation only the third, blast-furnace slag, was not processed.

- The first ingredient called «KANDOXI» for KAolinite-Nacrite-Dickite-OXide ( $Si_2O_5, Al_2O_2$ ), results from the calcination of kaolinitic species such as kaolinite, nacrite

or dickite, and occasionally halloysite.

- The second ingredient MELILITE  $(Ca,Na,K)_2[(Mg,Fe^{2+},Al,Si)_3O_7]$  is obtained through vitrification of selected alkali-geological volcanic tuffs.

KANDOXI manufacturing relates to calcination of kaolinitic clays. The research has determined a simple testing method necessary to select the most reactive aluminosilicate oxide  $(Si_2O_5,Al_2O_3)$  essentially different from  $(2SiO_2,Al_2O_3)$ . Quality criteria is an optimum amount of Al cation in (IV-V) coordination detected by  $^{27}Al$  MASS-NMR Spectroscopy [7].

MELILITE-glass manufacturing involved the fabrication of an alkali-melilite glass, or slag having following expected formula  $(Ca,Na,K)_2[(Mg,Fe^{2+},Al,Si)_3O_7]$ . The research has defined vitrification, cooling, activation, to achieve highest reactivity and alkalinity. Given the need to develop a reactive alkali-melilite glass capable of reacting like soluble alkali silicates, whilst satisfying the constraint of low cost, the feasibility of obtaining a geopolymeric cement as efficient as those produced on small scale with chemical ingredients, had to be established. The fabrication of alkali-melilite glass cannot be carried out in regular rotary cement kilns, due to the alkali attack of the refractory lining. Equipment similar to those used in the manufacture of enamels or glazes or regular glass were planned for testing.

During the ongoing of the project, before the end of Phase 1 and MidTerm, it was discovered that, instead of vitrifying the volcanic tuffs, a simple calcination at lower temperature (800°C) yielded a material suitable for the making of geopolymeric cement. This material was coined CARBUNCULUS (in relation with the archaeological Long-Term study described below).

### **2.2.3. Application of geopolymeric cement for waste management: Task WASTEMANAGNT** This task is subdivided in two Sub-tasks BARRIER and TOXIC ABSORP

#### Sub-task 3.1 BARRIER

Task leader: CORDI-GEOPOLYMERE, with sub-contractor WISMUT GmbH and HEIDELBERGER ZEMENT (both from Germany).

BARRIER has determined the best possible uses for geopolymeric cements in the cleanup of contaminated mine tailing sites (uranium mine tailing, metallic and nonmetallic mine tailing), and decantation ponds. Tests were carried out with expensive laboratory geopolymeric binders and tested for their physico-chemical properties.

#### Sub-task 3.2 TOXIC ABSORP

Task leader: LAVIOSA

It developed an Absorption technique aimed at saturating natural sorbents with concentrated solution of hazards, heavy metals. The target was to determine which mineral sorbents such as natural bentonites, zeolites, provided the highest absorption capacity to toxic elements: heavy metals, arsenic, radioactive elements.

The best resulted saturates were selected for subsequent encapsulation with laboratory geopolymeric binders, and tested for their physico-chemical properties, toxicity of leachates, innocuity. The encapsulated and solidified samples, made with expensive laboratory geopolymeric binders, were the reference data-base for task TOXIC ENCAPS set forth in Phase 2, which used the new geological cement CARBUNCULUS.

### **2.2.4. Geopolymeric Cement formulation for toxic waste encapsulation:** **Task TOXIC ENCAPS**

Sorbent encapsulation techniques were developed and cement formulations based on the new geological cement CARBUNCULUS prepared for this task. Granulation, pelletisation,

and bulk solidification in blocks were tested.

### **2.2.5. Geopolymeric Cement formulation for acid resistant concrete:**

#### **Tasks CEMENTMANUFA/CONCRETE**

Task leader: CORDI-GEOPOLYMERE with sub-contractor CEMENTI BUZZI (Italy).

It involved the processing of geopolymeric cement formulations for toxic waste stabilisation. The research has determined the basic properties of concretes elaborated with these new cements. The technical approach consisted on a series of tests on mortar bars in order to determine mechanical, physico-chemical properties and durability (alkali-aggregate-reaction, sulphate resistance, chemical corrosion with acids).

The task CONCRETE involved developing geopolymeric concretes to be used in the construction of acid-resistant geological barriers, cappings and walls for radioactive contaminated uranium mining site.

### **2.2.6. Elaboration of durability tests and long-term durability diagnosis: Task LONGTERM**

This task dealt with the better understanding of long-term durability. It is difficult to predict extended durability on the basis of operating experience, laboratory experimentation and prototype testing. Therefore, extrapolation of data collected from ancient man-made materials (cements) with similar chemical make-up and structure, and natural geological analogues was used. The research involved geological, chemical and archaeological aspects by comparing durability of natural geological analogues and also understanding the chemical make-up of ancient Roman cements and mortars.

The geological and mineralogical research was performed by BRGM and Cagliari Univ., the chemical and structural research by CORDI-GEOPOLYMERE (with sub-contractor NAMUR Univ.), and the archaeological study by sub-contractor CAEN Univ.

This part of the research addressed also the pre-normative aspect of the project.

## **2.3 Summary of the Results**

### **2.3.1. Cost Effective acid-resistant cement**

The objectives of the programme were the fabrication of alkali-melilitic glass  $(Ca,Na,K)_2[(Mg,Fe^{2+},Al,Si)_3O_7]$  with selected geological raw materials, and mineral additives such as calcium carbonate. Vitrification at temperatures ranging from 1200°C to 1350°C were performed in a laboratory kiln. After several incidents (overfusion of samples, destruction of the refractory lining), the vitrification of geological samples was nor longer carried during the second part of the project.

This decision was also supported by the fact that it was discovered that calcination at 800°C, instead of vitrification at 1300°C, provides also very good results with respect to the strength developed after 28 days (see GP-CEMENT). The material calcined at 800°C is coined «carbunculus» because of its similarity with the calcined pozzolan which, according to the Roman architect Vitruvius, was the basic material of the good Roman mortar [8] (see the task LONGTERM 1).

Two manufacturing processes have been worked on:

⇒ **Alkali-melilitic glass** (first part of the task):

- grinding, blending with calcium carbonate, later with lime CaO
- melting at 1250°C-1350°C, 4-6 hours
- quenching, drying
- fine grinding, grain size <50µm; 50%<10-15µm

⇒ **Carbunculus** (calcination at 800°C) (second part of the task):

- grinding
- calcination at 800°C, 3 hours
- fine grinding, grain size 50%<10-15µm

The structural make-up of the «glass» and the «carbunculus» was investigated with MAS-NMR Spectroscopy [9, 10]. Comparative study was made with the Italian volcanic tuff LA01.

**LA01 «melilite» glass, vitrified 1350°C:**

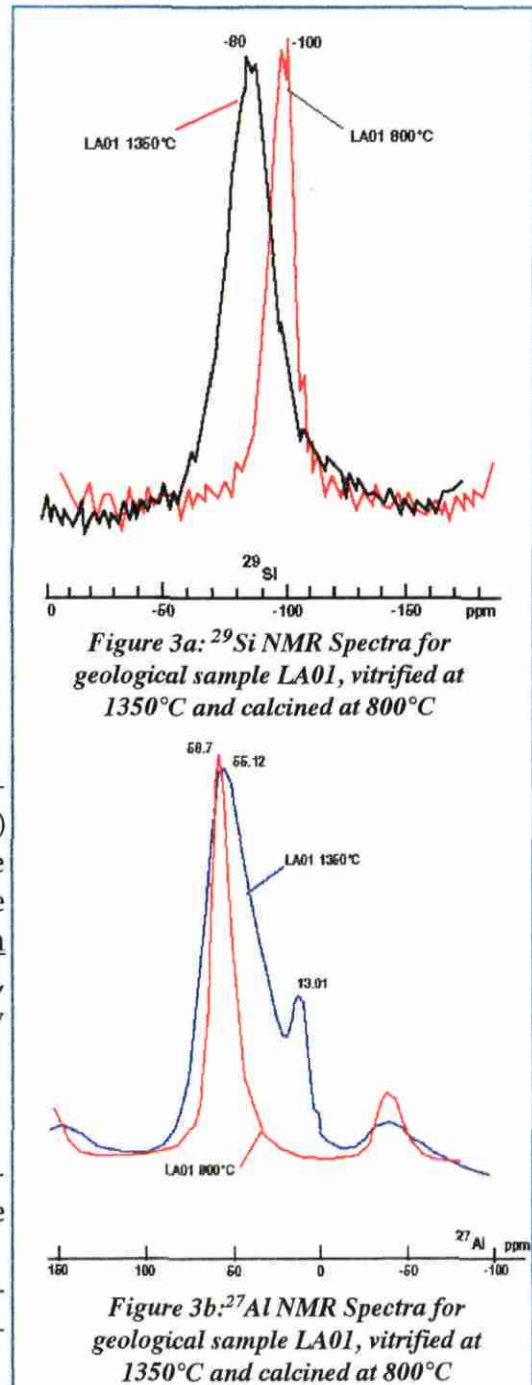
**29Si spectrum (Fig.3a):** resonance peaks in the range -75, -90ppm, but with an additional broad spectrum up to -95ppm. This suggest a complex structure involving low-molecular and high-molecular silicate structures, from Si(Q0) (monosilicates), Si(Q1-Q2), (chain silicates), Si(Q3) (chain branching sites), and also Si(Q4) (three dimensional cross-linked silicates, tecto-alumino-silicates).

**27Al spectrum (Fig.3b):** two major resonance peaks at 55 and 13 ppm corresponding to Al(IV) and Al(VI) sites, respectively. The Al(IV) is typical for Al(Q4Si) sites related to the original tecto-alumino-silicate structure of the LA01 sample. The Al(VI) suggest a structure of the glassy hornblende type (?), resulting from the depolymerisation of the framework under the action of CaO. This spectrum does not fit with the expected melilite structure, which should not display any Al(VI) sites but only Al(IV) sites.

**LA01 «carbunculus», calcined 800°C:**

**29Si spectrum (Fig.3a):** resonance peaks in the range -95,-100ppm characterising tecto-alumino-silicate structures, i.e. Si(Q4) sites.

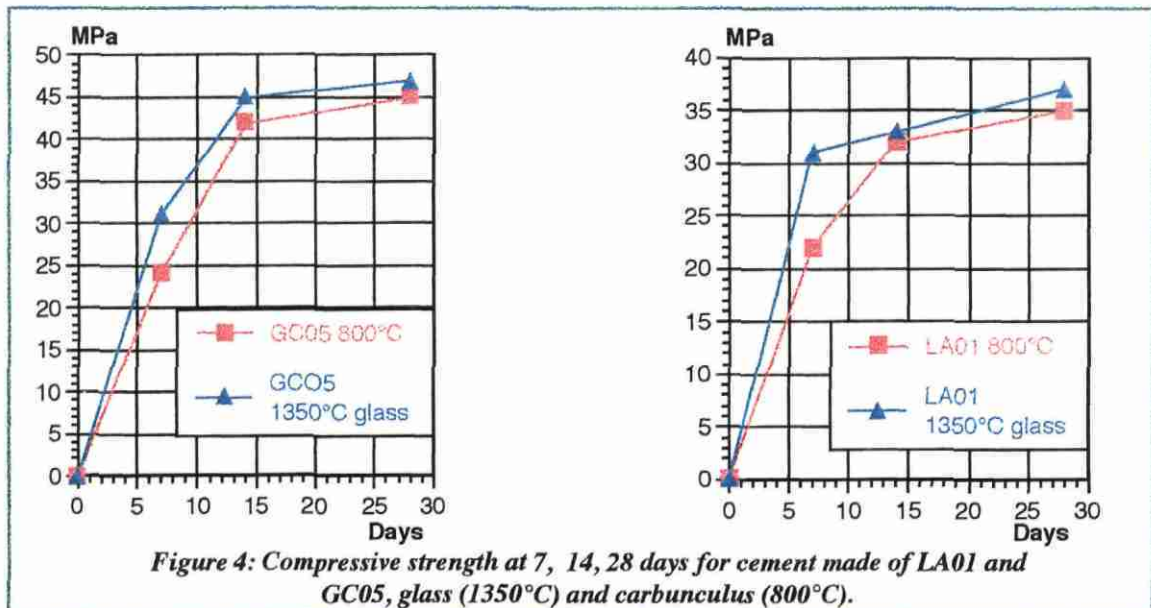
**27Al spectrum (Fig.3b):** resonance peak at 58ppm typical for Al(IV) in Al(Q4Si) sites, i.e. tecto-alumino-silicates.



**Conclusion:**

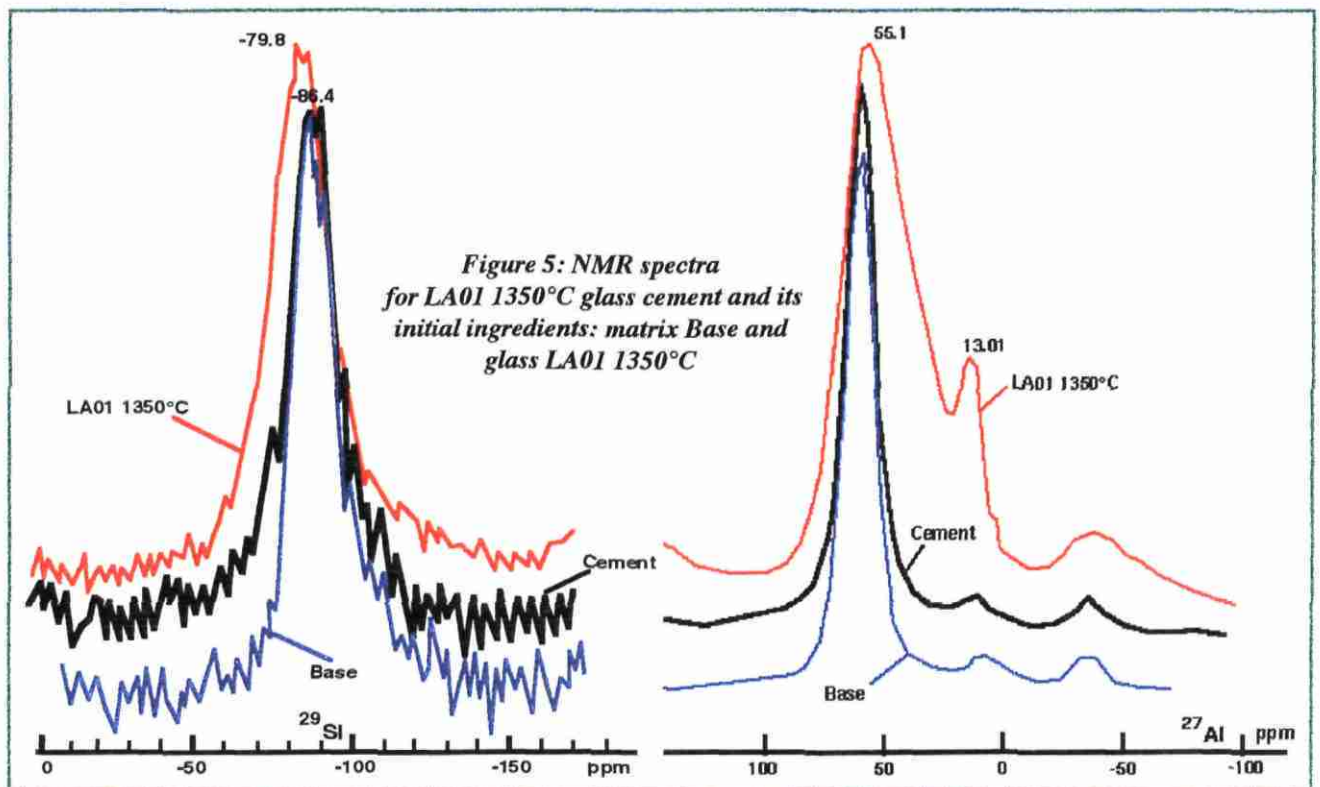
The name that was given initially to the glassy material, namely "MELILITE", no longer conforms to the molecular structure (hornblende type?) obtained by 1350°C-vitrifying and water-quenching of volcanic tuffs. Therefore, and in order to avoid any wrong interpretation of this research, the adjective "melilite or melilitic" is no longer used in the description of the geopolymeric cements manufactured with this glass.

In terms of the measured compressive strength, the glass cement develops its strength more rapidly than does the carbunculus (800°C) cement. However, at 28 days, the strengths for both systems are in the same range; see in Fig. 4 the comparative results for LA01 and GC05 geological samples.



**Glass cement 1350°C: (Fig. 5)**

Both NMR spectra indicate that the cement results from a chemical reaction between the Base and the glass (LA01 1350°C). The cement spectra are similar to those for the matrix Base, suggesting a regular geopolymeric framework



**Carbunculus cement 800°C: (Fig. 6)**

Both NMR spectra indicates that carbunculus cement comprises two separate phases. The matrix Base does not dissolve the «carbunculus» phase. Both ingredients, matrix Base and «carbunculus», react only at the interfaces, yielding high strength. This confirms previous data pertaining to the Background knowledge [11, 12]

From the study of NMR spectra, it becomes clear that glass cement is very different

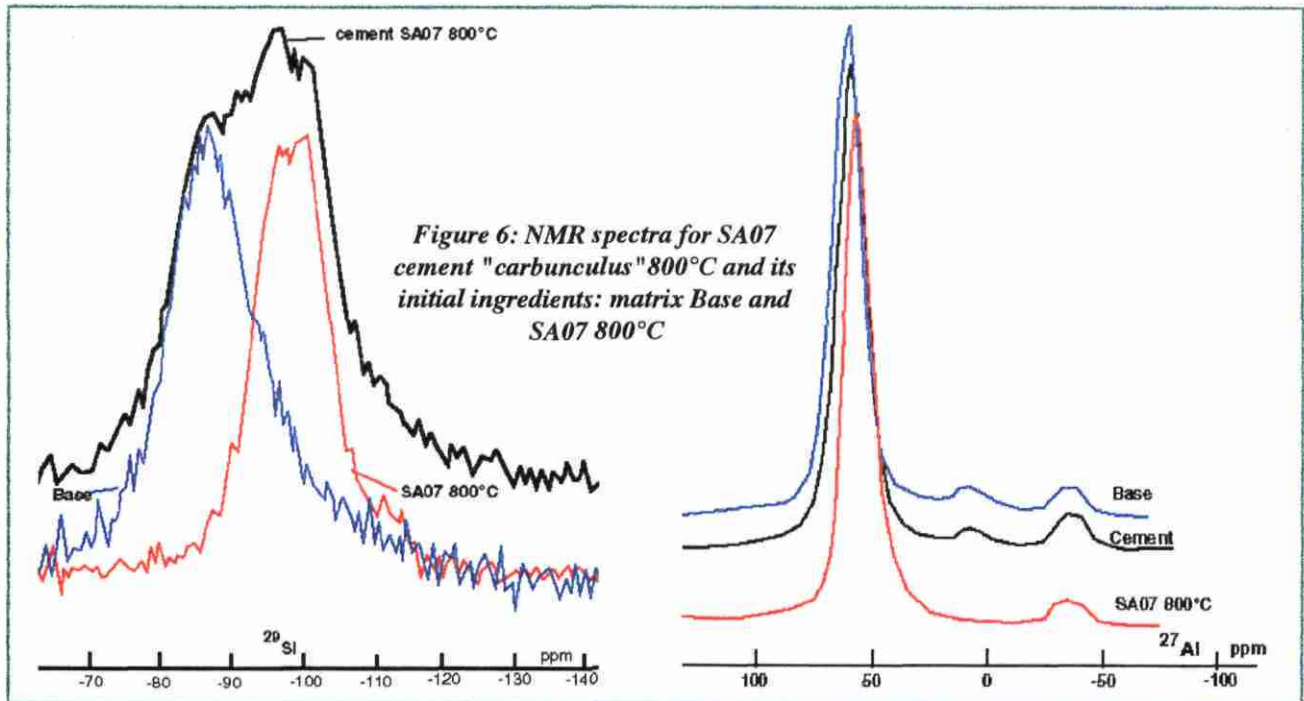
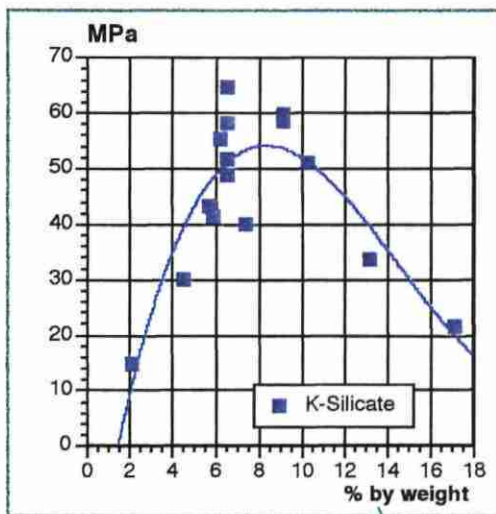


Figure 6: NMR spectra for SA07 cement "carbunculus" 800°C and its initial ingredients: matrix Base and SA07 800°C

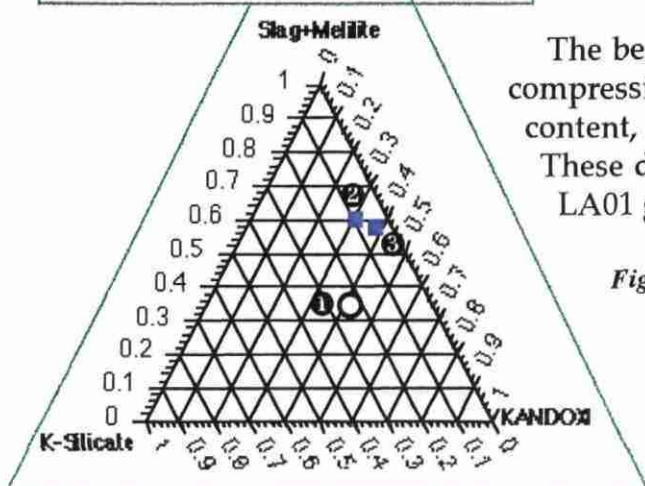


from «carbunculus» cement. (see further NMR spectra, LA01, SA07, GC05, in the ANNEX).

The work set forth in the Workprogramme was aimed at reducing subsequently the amount of potassium silicate currently part of geopolymeric cements (standard cement).

For practical applications, the K-silicate content would range between 4-9%, down from 25%, with an optimum around 8% by weight, as displayed in Fig.7.

Figure 7: Relationship between K-Silicate content and 8 day compressive strength for geopolymeric cement.



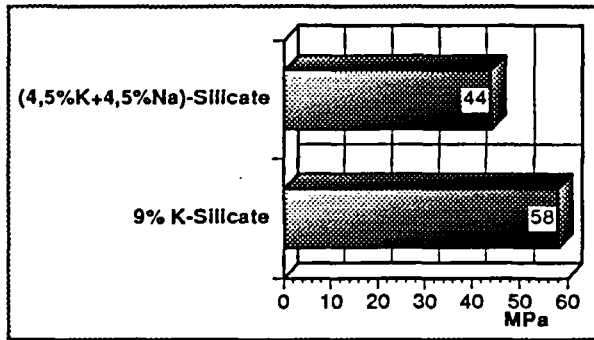
The best results for «glass» cements, in terms of 8 day compressive strength >30 MPa, for the lowest K-silicate content, are plotted in the ternary diagramme of Fig.8. These data were obtained with glass cement based on LA01 geological samples.

Figure 8: Ternary composition diagramme for «glass» cements with 8 day compressive strength >30MPa:

- 1) = standard geopolymeric cement
- 2) = best of GEOPOLYCEM
- 3) = best of PZ-GEOPOLY

(see in the ANNEXE for definition of this terms)

For applications which require 8 day compressive strength not greater than 30 MPa, the K-silicate content can be reduced by 80-85% of the initial content.



K-Silicate could be replaced with some amount of cheaper Na-Silicate. Fig. 9 shows that a 50% replacement of K- by Na-Silicate induces a sensitive decrease of the 8 day compressive strength.

Figure 9: Replacement of K-Silicate with Na-Silicate (50% replacement) in «glass» geopolymeric cement comprising initially 9% by weight of K-Silicate; 8 day compressive strength.

## Conclusion for task GPCEMENT

A total of 140 formulations has been tested (70 in 1994 and 70 in 1995). The task has demonstrated the feasibility of manufacturing the new «glass» cement (vitrification at 1350°C of volcanic tuffs). However, vitrification requires the whole melting of the material, which resulted sometimes in the destruction of the ceramic lining of the kiln. The industrial manufacture of this type of cement would be similar to that of the smelting of alkali-glass, i.e. would require industrial equipments very different from those used in manufacturing regular Portland cement. A simpler method, namely calcining volcanic tuffs at 800°C, instead of vitrification, provides interesting results. The cement obtained in this way, called «carbunculus», is very easy to manufacture; the equipment are currently used in mineral processing plants. The good properties of the CARBUNCULUS cements are essentially those provided by the geopolymeric Base reaction (a). Geological elements are reacting at the interface between Base and grain surface, see also in the Background knowledge.

Tab.2 displays the evolution of the geopolymeric cement formulations and Tab.3 the expected production costs at the start and the end of this programme

Table 2 : Cement formulations, % weight dry.

	Beginning of the programme	end of 1994	end of 1995
Kandoxi	42	31	25
K-silicate	25	9	9
iron slag	33	13	23
glass	0	47	0
carbunculus	0	0	43

Table 3: Estimated production costs for 1 tonne of «Carbunculus» cement (K-silicate costs at the end of 1995 are purchased costs, and at the end of 1996, estimated production costs)

	Beginning of the programme	end of 1995 expected cost	end of 1996 expected cost
Kandoxi	1380 FF	88 FF	88 FF
K-silicate	1392 FF	501 FF	160FF
iron slag	165 FF	115 FF	115 FF
carbunculus	0 FF	150 FF	150 FF
total for 1 tonne	2937 FF	854 FF	513 FF

## 2.3.2. Large scale geological resources

### 2.3.2.1. Volcanic tuffs

Explorations in Phases 1 and 2 of Task GEOPROSPEC 1 were carried out in 6 regions and 10 representative samples sent to GÉOPOLYMÈRE (see Table 4). In addition to the locations studied, **Sardinia, Central Italy (Latium, Toscana), South-East Spain, Canary Islands**, phase 3 of GEOPROSPEC has determined the potentiality of the resources for Greece, especially in Macedonia and Samos (see Fig. 10). Literature studies suggest interesting potential resources in other European regions.

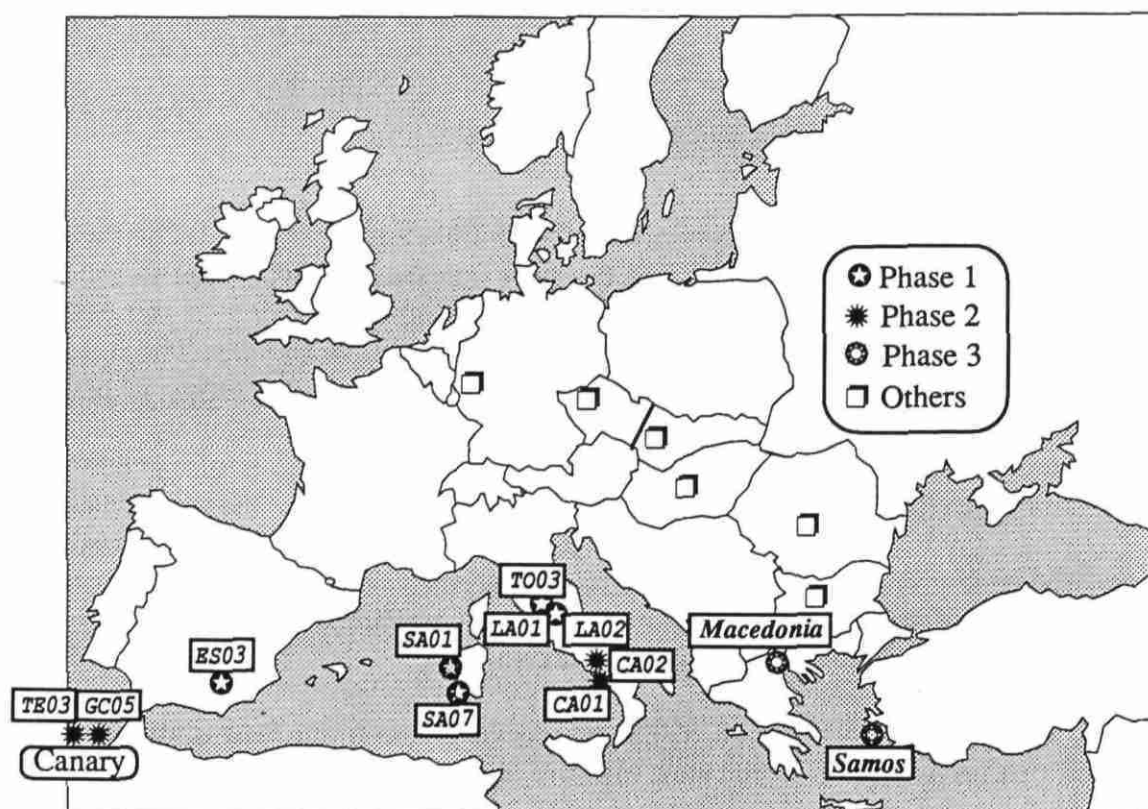


Figure 10: Potential European geological resources for GEOCISTEM

Table 4: Origin of selected samples in Phases 1, 2 and 3

Country	Region	Nature of the rock	Name of sample
Italy	Centre-west Sardinia	andesitic lava	SA01
Italy	South-west Sardinia	ashy tuff	SA07
Italy	Latium	ignimbrite	LA01
Italy	Latium	zeolithic tuff	LA02
Italy	Toscana	pumice	TO03
Spain	Murcia	lamproitic lava	ES03
Italy	Campany	volcanic tuff (yellow)	CA01
Italy	Campany	ignimbrite	CA02
Spain	Gran Canaria	ign. (ash+pumice)	GC05
Spain	Tenerife, Canary	pumice	TE03
Greece	Kilkis, Macedonia	altered pyroclastite	
Greece	Karlovassi, Samos	tuff and ash	

The Greek samples are very rich in  $K_2O$  and good candidates for geopolymeric cement.

For the Task GEOPROSPEC 2 , the Consortium selected the ashy tuff SA07 of South-West Sardinia as representative for a potential industrial application.

**Additional sampling** of the Paringianu Unit (Fig. 11) was performed on 20-30 samples. A summary of 12 samples (samples # SA10 to SA20) provides following mean constitution:

Oxides. ....	weight %
L.O.I. ....	0,70 to 4,41
$P_2O_5$ .....	< 0,05
$SiO_2$ .....	71,00 à 75,36
$Al_2O_3$ .....	12,61 à 13,89
$Fe_2O_3$ .....	0,57 à 1,91
$CaO$ .....	0,26 à 0,34
$MgO$ .....	< 0,20
$Na_2O$ .....	3,66 à 4,66
$K_2O$ .....	4,84 à 5,19
$TiO_2$ .....	0,11 à 0,13
$MnO$ .....	< 0,02 à 0,04

The outcrop is very homogenous. 50 kg of a new sample, called SA20, were sent to Géopolymère. SA20 is a blend of samples SA18 and SA19.



*Figure 11: The GEOCISTEM team visited the Paringianu site on September 27, 1996. From the left: Frédéric Davidovits (Caen), Domingo Gimeno (Barcelona), Philippe Rocher (BRGM), Carlo Marini (Cagliari), Athos Rinaldi (Laviosa), Joseph Davidovits (Géopolymère), Sandro Tocco (Cagliari), Michel Laval (BRGM), Luigi Buzzi (Cementi Buzzi), Jean Claude Toussaint (Commission, Brussels).*

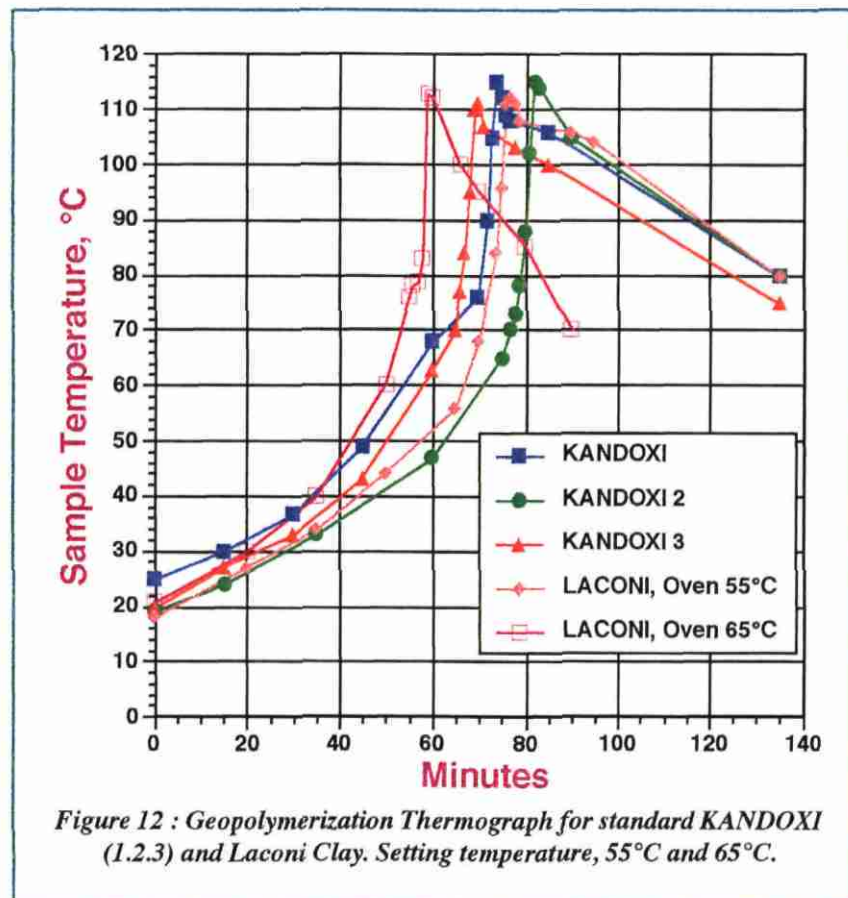
### 2.3.2.2. Kaolinitic Clay resource in Sardinia:

The second geological material needed in geopolymeric cement formulation is calcined kaolinitic clay, or KANDOXI.

Three Kaolinitic Clays from Sardinia were tested for their reactivity, according to the Thermographic method developed in Task KANDOXI. The reaction of calcined kaolinite with potassium silicate is strongly exothermic. Non-reactive material does not exhibit this exothermicity. Examples of Thermographs for current commercial KANDOXI are displayed in Fig. 12 (KANDOXI 1, 2, 3). The selected kaolinitic clays were calcined 3 hours at 750°C.

Mara clay	does not harden, within 8 hours at 60°C
Nurallao clay	hardens, after 7 hours at 60°C
Laconi clay	hardens, within 2 hours at 60°C

The Thermograph of the Laconi clay is displayed in Fig.12. It is identical with those of commercial KANDOXI. It represents a good local resource for the geopolymeric Cement, in



**2.3.3. Cement with very low CO<sub>2</sub> emission**

In order to provide complementary information for the selection of the geological sites, with respect to CARBUNCULUS cements, new series of tests were carried out on all geological materials, either natural (not calcined at all) or calcined at 800°C. A total of 20 CARBUNCULUS cements formulations (10 with natural, 10 with calcined materials) were tested for compressive strength at 28day (80 samples).

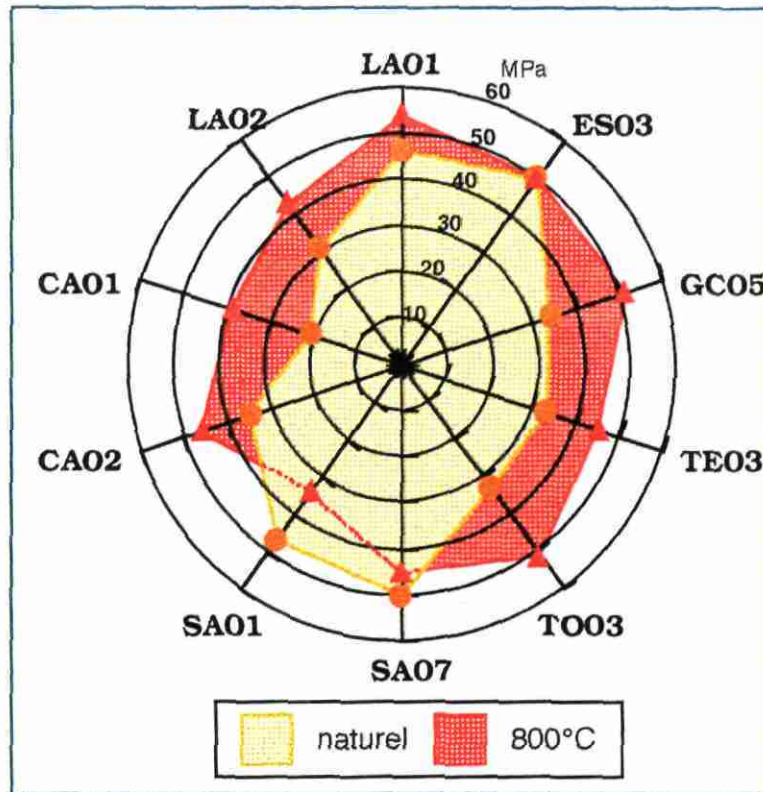


Fig.13 shows that, in general, as expected, calcination does increase the compressive strength. However, detailed study of the results are providing following clues:

Fig.13 shows that, in general, as expected, calcination does increase the compressive strength. However, detailed study of the results are providing following clues:

- a) for LA02, CA01, CA02, TO03, GC05, calcination increases the strength by 50% to 100%.
- b) for LA01, calcination increases the strength by 25%.
- c) for ES03 and SA07, calcination does not increase the strength.
- d) for SA01, natural material has a higher strength.

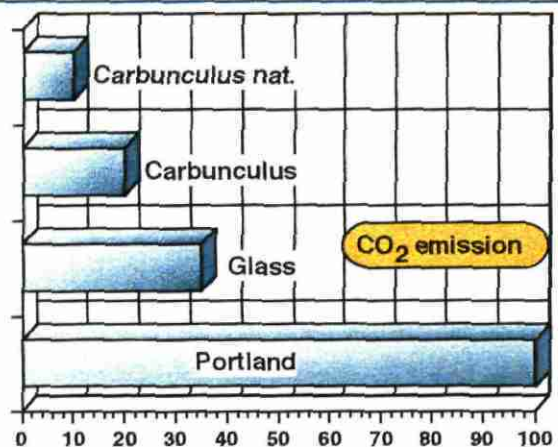
Figure 13: 28 day compressive strength of CARBUNCULUS cements with natural and 800°C calcined geological materials.

Tab.65 and Fig. 14 show some interesting data on energy cost and CO<sub>2</sub> emission for Portland cement, glass cement and carbunculus cement.

Table 5 : Comparison between energy needs and CO<sub>2</sub> emission, during manufacturing, for various cement types, assuming Portland = 100

Cement type	Manufacturing temperature	Energy consumption	CO <sub>2</sub> emission
Portland	1450-1500°C	100	100
Glass	750°C-1350°C	64 (-36%)	35 (-65%)
Carbunculus	750-800°C	40 (-60%)	20 (-80%)
Carbunculus nat.	750°C	30 (-70%)	10 (-90%)

Figure 14: Comparison between CO<sub>2</sub> emission during manufacture, for various cement types, assuming Portland = 100



### 2.3.4. Absorption and Encapsulation of hazardous liquids on bentonite

The experimental studies performed by LAVIOSIA CHIMICA MINERARIA consisted of three separate phases, as summarised below:

Phase I- Compare adsorption capacities with capacities of other absorbents

Phase II- Pelletization of sorbents with commercial geopolymeric binders.

Phase III- Toxicity Characteristics Leaching Procedure (TCLP) Characterization

#### Phase I: absorption capacity

A percolate solution leaching out of a Land Fill of type B located near Livorno has been used for these preliminary tests. **114 absorption tests** (64 more than planned) have been carried out, so far, on commercially available sorbents ranging from cheap bentonite types to very expensive active coal. Following sorbents have been tested:

- Clays: bentonite, smectite, attapulgite, sepiolite; natural and synthetic zeolites, talc and pumice.
- Treated minerals: activated clays and coals, pillared clays (too expensive)
- Expanded products: vermiculite, perlite and clay

Additives, organic ingredients were used: PAA, CMC and similar. A selection of representative data is displayed in Table 6.

*Table 6: Absorption capacity in grams per kilogram of sorbent (percolate solution).*

#	Sorbent	type	granulated	Absorption
44-82	Bentonite	clay	yes	150
78	Bentonite BP CP	clay	yes	360
107	Bentonite BP 70%	clay	yes	800
114	Bentonite BP 83%	clay	yes	750
20	Urasite	volcanic tuff	yes	400
17	Vermiculite	expanded	no	1500
21	Argilla APA	bentonite	yes	600
23	Cleansol	expanded perlite	no	2000
97-98	Pumice		no	450
19	Attapulgite	clay	yes	450
36-37	Active coal	coarse	no	800

#### Results:

- Expanded clays, vermiculite and perlite are the best sorbents, providing 2000 g of liquid absorption per 1000g of material. But this liquid is not chemically bounded, even after encapsulation.
- Hard smectites (bentonites) are good absorbents, 500 g/1000g of material, chemically bounded.
- Hardened powdered Bentonites have higher absorption capacity, 750 g/1000g. The granules (2 to 10 mm) are hard enough for subsequent encapsulation procedure.

#### Phase II: pelletization of sorbents and Leachate (Phase III)

The encapsulation technique has been tested with two geopolymeric binders supplied by GÉOPOLYMÈRE: the binder GEOPOLYMITE GP140 and the cement PZ-GEOPOLY and later with the geological CARBUNCULUS cement SA07. The resulting material was of two types:

- pellets
- blocks

**41 encapsulation tests** have been carried out so far. The coating is performed in a fast blade mixer with 20g of geopolymeric binder added to 100g of sorbent. The coated granules are dried 1 hour at 80°C.

Leaching values have been performed with the Triaxial Penetrometer equipment, with distilled water. As expected, expanded minerals, vermiculite (#17, 94), cleansol (#23, 95), pumice (#97), are very easily leached out, whereas bentonite types minerals and urasite retain the cations.

Representative results of tested materials are displayed in Table 7.

*Table 7 : Leaching and mechanical properties of encapsulated material (see in ANNEXE)*

Sample #	Sorbent	Geopolymer	bloc	pellet	leaching	attrition	R. compr.
8/I	urasite	GP 140	-	yes	0.10 ppm	-	-
11/I	vermiculite	GP 140	-	yes	10.50 ppm	-	-
13/I	pumice	GP 140	-	yes	15.20 ppm	-	-
27/I	cleansol	GP Z	yes	-	9.80 ppm	-	-
31/I	vermiculite	GP Z	yes	-	3.80 ppm	-	-
38/I	bentonite	GP Z	yes	-	0.19 ppm	-	-
39/I	bentonite	GP 140	-	yes	0.19 ppm	4%	-
41/I	bentonite	GP 140	yes	-	0.19 ppm	-	>20 MPa

*Phase III: encapsulation (pellets and blocks) of bentonite sorbents with the new «carbunculus» cement*

Encapsulation performed on best saturated bentonite pellets with GEOPOLYMITE binders (GP140 or GPZ), CARBUNCULUS cement SA07 and three different types of Portland cements are displayed in Tab. 8. None of the cements behave like geopolymeric materials. The CARBUNCULUS cement SA07 shows good results with respect to attrition test but is weak as far as the making of blocks is concerned. This is due to a relatively high demand in water content, which slows down the setting of the cement. None of the Portland cements provide sufficient attrition values. The attrition value should be lower than 10%.

*Table 8: Mechanical properties of Encapsulated Bentonite pellets with Geopolymeric materials and Portland Cements(Buzzi, Sacci, Italcementi)*

	Attrition (granules)%	Leaching ( heavy metal)	Compressive Strength (5 day)
GEOPOLYMITE GPZ	3	0.15 ppm	>25 MPa
CARBUNCULUS SA07	7	0.30 ppm	3 MPa
BUZZI tipo B (pronto)	16.5	0.50 ppm	13 MPa
SACCI (pozzolanic)	24	0.40 ppm	7 Mpa
ITALCEMENTI (pronto)	18	0.30 ppm	>25 MPa

### 2.3.5. Acid resistant concrete for uranium mining sites

#### 2.3.5.1. Concrete for metallic mine tailings

The discussions with WISMUT (Germany) and Geopolymere's cement partner (Heidelberger Zement) have determined the possible uses for geopolymeric cements in the safe cleanup of contaminated mine tailings sites (uranium mine tailing). The mineralogy of the local aggregates for the site of Ronneburg (Thüringen) is given in Table 9:

Table 9: Mineralogy of the local Ronneburg aggregates (% range)

Quartz	Mica	Kaolinite	Dolomite	Calcite	Chlorite	Pyrite	Hematite	Phosphorite	Organic
11-58	3-54	3-15	1.5-57	0.5-22.5	1-25	0.5-7	1-3	0.3-3	0.8-9.5

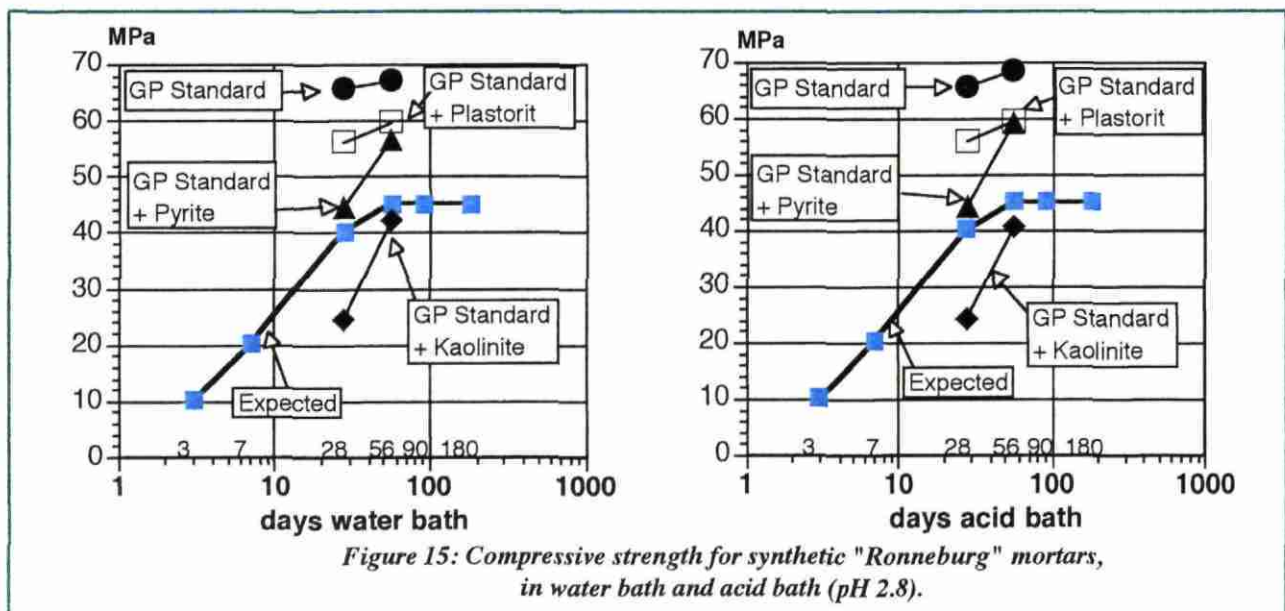
Tests have been carried out with laboratory geopolymeric binders from type PZ-GEOPOLY and tested for their physico-chemical properties with a synthetic aggregates comprising:

- Kaolinite 10-15%
- Pyrite 7%.
- Mica+chlorite 5%

The tests series were split into 2 phases. Phase 1, performed in GEOPOLYMERE laboratory, has determined the basic properties of sand mortars containing these ingredients. Phase 2 performed in GEOPOLYMERE Cement subcontractor (Heidelberger Zement) consisted on a series of tests on mortar bars (synthetic «Ronneburg aggregates) in order to determine mechanical, physico-chemical properties and durability (chemical corrosion) in acidic medium, pH=2.8, after 28 days and 56 days in water bath and/or acid bath. Following mortars were tested (see Fig.15):

- GP Standard: mortar with normed sand aggregate
- GP standard + Pyrite: the sand contains 7% by weight of pyrite powder
- GP standard + Kaolinite: the sand contains 10% by weight of kaolinite powder
- GP standard + Plastorit: the sand contains 5% by weight of Plastorit (mixture of muscovite and chlorite)

Except for the mortar which contains kaolinite, all mortars have properties significantly better than the minimum expected in the Workprogramme. After 56 days, however, kaolinite mortars have reached the expected strength. These tests confirm the exceptional properties of geopolymeric cements in chemically corrosive environments.

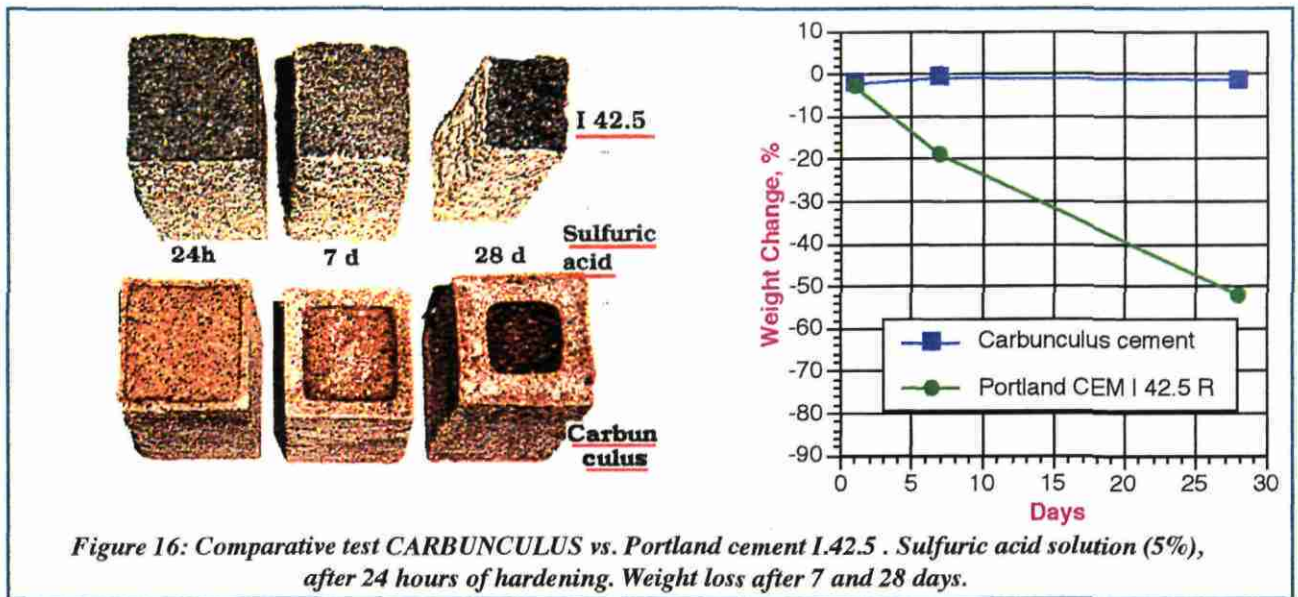


**2.3.5.2. Concrete with CARBUNCULUS cement: resistance to strong Sulfuric Acid medium**

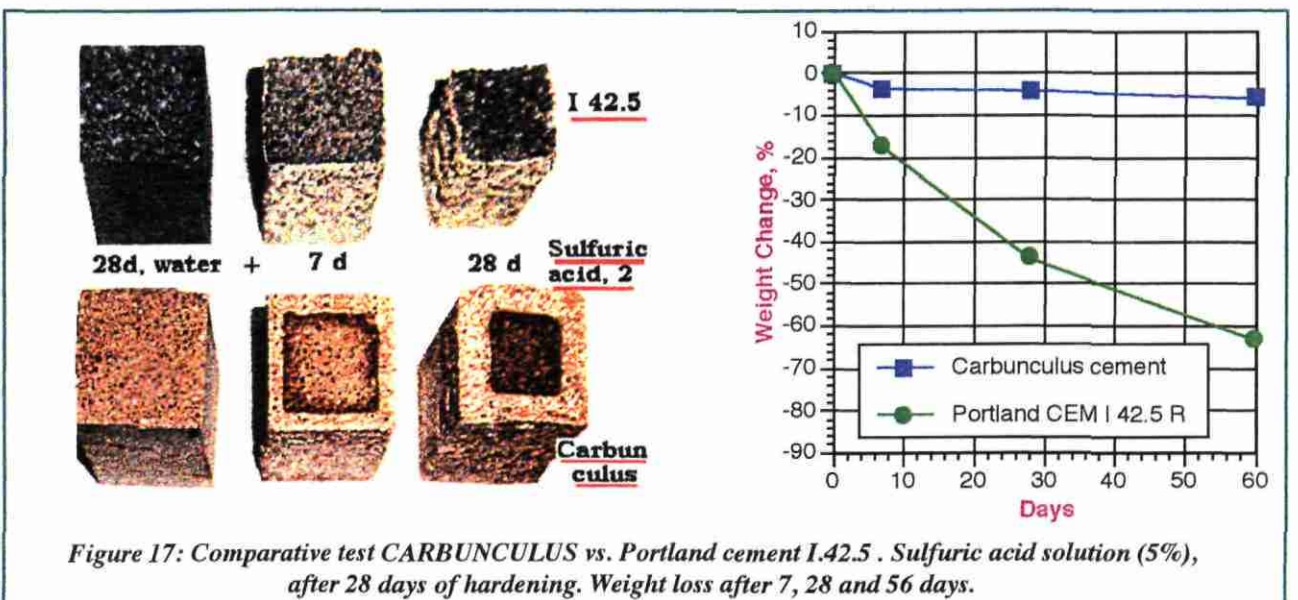
Metallic mine tailings are usually generating sulfuric acid that results from the oxidation of pyrite. The resistance to strong sulfuric acid solution (5% H<sub>2</sub>SO<sub>4</sub> solution) was investigated in two series of test:

- 1) after only 24 hours of hardening (Fig. 16)
- 2) after the standard 28 days of hardening (Fig. 17).

A comparison with regular Portland Cement from our Italian cement partner CEMENTI BUZZI, shows the excellent properties displayed by the CARBUNCULUS cement. After 28 days, in the first test, CARBUNCULUS cement remains intact (Fig. 16) whereas the acid corrosion has destroyed more than 50% of Cement I.42.5 (weight loss and change in shape and volume).



In the second test (Fig. 17), CARBUNCULUS cement loses less than 5% after 56 days, whereas Cement I.42.5 is strongly affected by the acidic medium (-63% of weight loss after 56 days).



### 2.3.6. Long-term simulation: geological analogues, archaeological analogues

This main-task required a multidisciplinary approach involving chemistry, NMR Spectroscopy, mineralogy, bio-degradability, linguistic study and archaeology.

#### 2.3.6.1. Structural make-up of the hardened geopolymeric Cement Base:

Both cements, Melilite glass and Carbunculus, result from the addition of heat treated geological materials to a geopolymeric base made of Kandoxi, K-silicate and slag. The know-

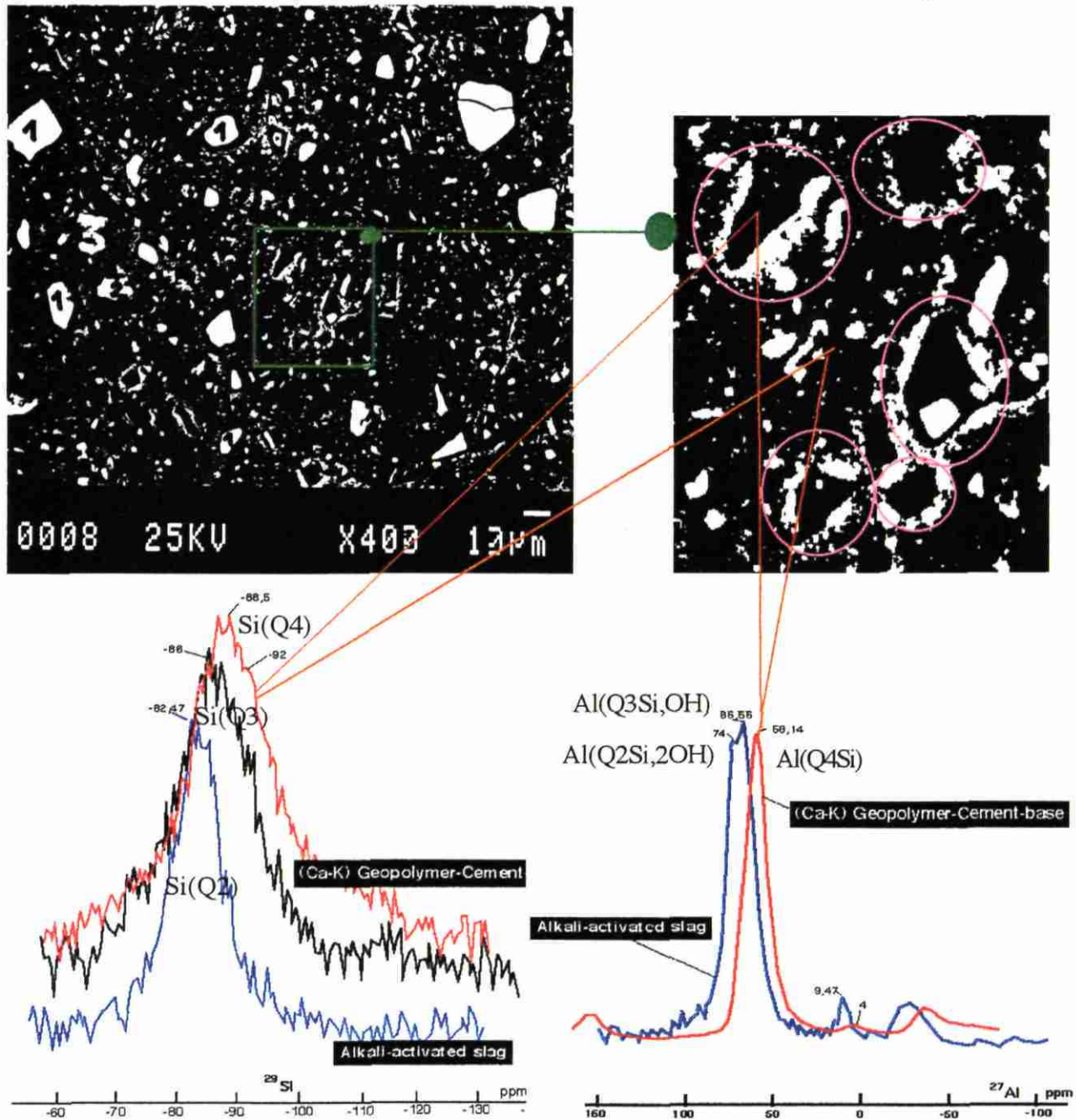


Figure 18: E. micrograph of hardened geopolymeric Cement Base and NMR spectra evolution from alkali-activated slag towards geopolymer cement.

ledge on the chemistry structural make-up of this hardened Cement Base is essential for the understanding to longterm behaviour.,

In Fig. 18, the electromicrography provided by BRGM shows that in the Cement Base, slag crystals are digested by the K-Silicate slurry, then react with Kandoxi, leaving the imprint of the grain surrounded with materials non participating into the reaction (Mg, Ca, Si).

The NMR spectra show the transformation from the simple alkali activated slag (SiQ2 disilicate) into a three dimensional tecto-alumino-silicate (Si(Q3-Q4) and Al(Q4Si), after re-

action with KANDOXI.

<sup>29</sup>Si NMR Spectra for Carbunculus cement (800°C) (Fig. 19)

All cements display broad resonances in the -80 to -110 ppm range.

As previously mentioned, CARBUNCULUS cements comprise two separate phases. The whole spectrum results from the addition of the cement Base (peak between -84 and -90 ppm) to the geological element 800°C (peak between -90 and -110 ppm).

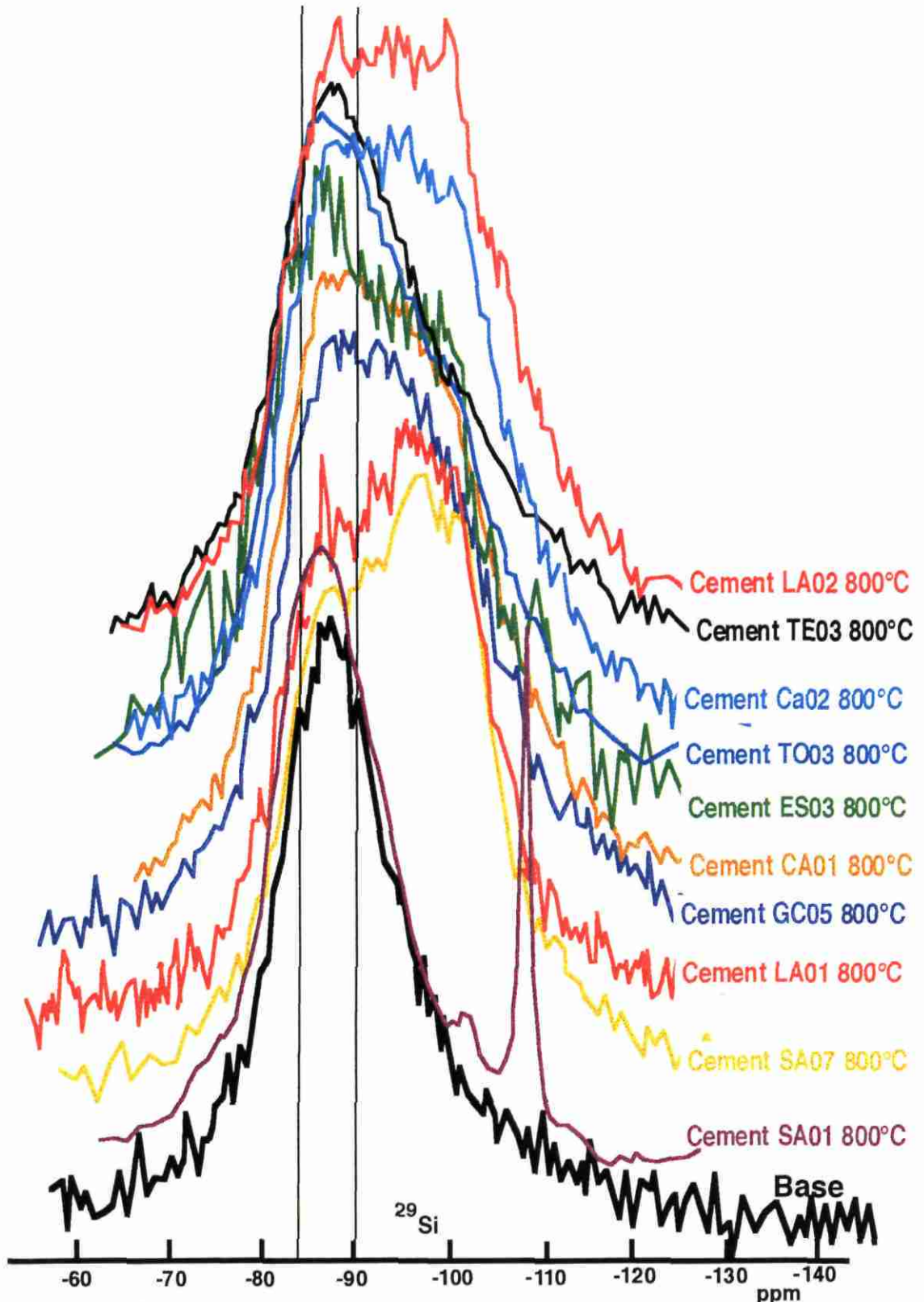
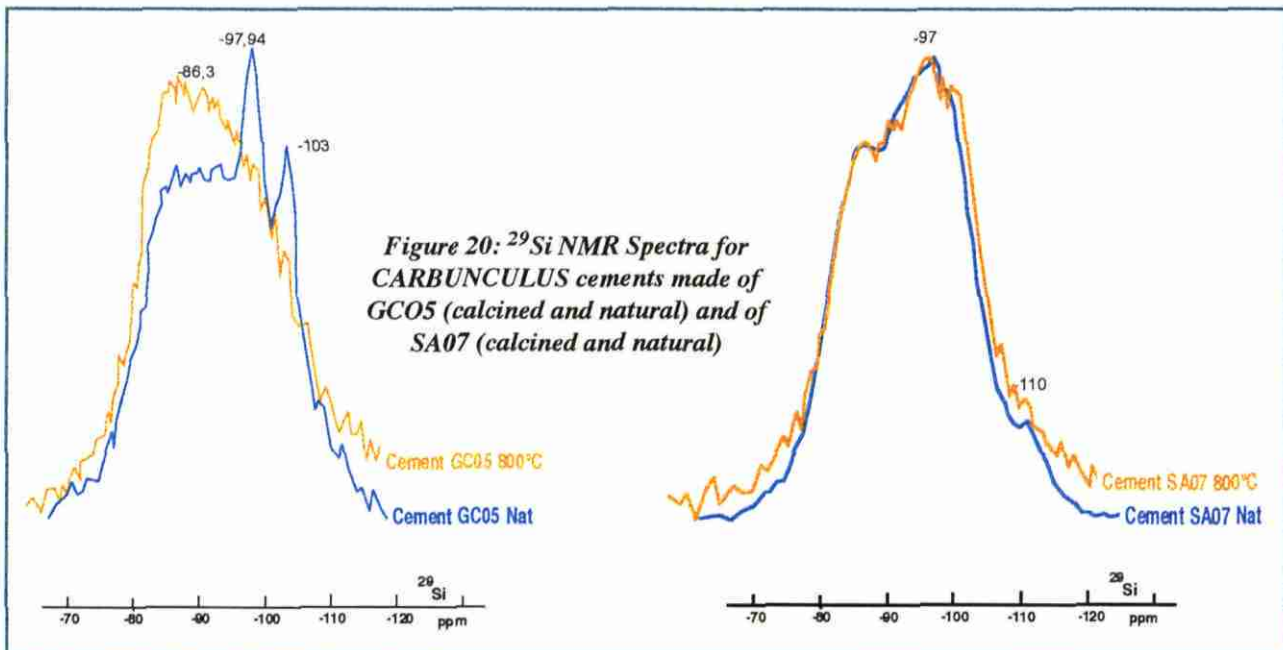


Figure 19: <sup>29</sup>Si NMR Spectra of the 10 CARBUNCULUS cements studied in GEOCISTEM and of the geopolymeric Cement Base (in black)

Cements with calcined 800°C and natural geological materials.

One has above outlined the differences between cements made with 800°C calcined and uncalcined (natural) material (see in Fig. 13 in Chapter 2.3.2.). For 7 samples out of 10, calcination increases significantly the 28 day compressive strength. For 3 samples, calcination does not increase the 28 day compressive strength.

$^{29}\text{Si}$  NMR data are providing first comparative results. In the first category (sharp increase through calcination), the natural materials display sharper resonances in the -98 to -105 ppm range. These resonances may be applied to  $\text{Si}(\text{Q}_4,3\text{Si},1\text{Al})$  groups, such as those found in clays, or to silica. Calcination may desegregate these groups, which become reactive, in a manner similar to what happens during the calcination of kaolinitic clays (the ingredient KANDOXI). See for example the Si NMR spectra for GC05 in Fig. 20. On the other hand, members from the second category (no increase with calcination) display Si NMR spectra that are practically identical for both materials, natural and calcined. See for example the Si NMR spectra for SA07 in Fig. 20.



The Annexe provides all NMR spectra studied so far.

2.3.5.2. Archaeological Analogues

This task was aimed at providing longevity prediction from archaeological materials studies. Two thousand years are generally accepted as a sufficient amount of time to permit decay of fission products that represent the most hazardous fraction in low-level radwaste material. Ancient Roman concrete structures (up to 2.000 years old and older) are still functioning today and thereby could provide historical documentation of the extended durability of zeolitic and geopolymeric cements.

Fundamental research carried out by GEOPOLYMERE scientist at Institute for Applied Archaeological Sciences, Barry University, USA, and studies performed by the University of Amiens, France, on Ancient Roman mortars, especially *Opus Signinum* masonry, in relation with the descriptions by the Roman author Vitruvius in *De Architectura*, provided Background knowledge for this task. *Opus Signinum* mortar involves a hardening mechanism based on the alkali-activation of KANDOXI materials with zeolites and lime. Recent studies performed by the same researcher at University of PARIS-Nanterre, Archaeology Department, on Vitruvius' text have clearly demonstrated the link between Roman Concrete and

Italian zeolitic tuffs [13]. According to the Roman author Vitruvius in *De Architectura*, another raw material for concretes and mortars is a very unique geological material called *carbunculus*. Carbunculus was processed at high temperature, i.e. in the range of 800°C. From the study of the Latin text, it has been deduced that *carbunculus* was a volcanic tuff of the ignimbritic type. It could be similar to the geological samples LA01 and CA02 tested in task GP-CEMENT («glass» and «carbunculus»).

The linguistic and archaeological approach of this task was carried out in Italy, by the same researcher now at CERLA (Caen University). A sampling of archaeological mortars and concretes dating back to the 3rd century BC and later was carried out in Rome and Ostia, Italy. Two series of artefacts: *Opus Signinum* (in Rome), *Opus Caementicum / Testacem*: mortars and concretes (*carbunculus?*), (in Ostia):

*Opus Signinum*: 7 samples (Rome). The *Opus Signinum* contains the element *testa*, which is a calcined kaolinitic clay equivalent to the Kandoxi used in the GEOCISTEM cements, and carbonated lime.

*Opus Caementicum / Testacem*: (Rome and Ostia): 15 samples of mortars and concretes. The mortar usually contains carbonated lime and volcanic tuff aggregates and sand called in Italian *cretoni*. Some of the *cretoni* could be the element *carbunculus*, which is equivalent to the calcined volcanic tuffs used in the GEOCISTEM cements.

The elementary chemical and mineralogical analysis carried out by the geologist team at Cagliari on these ancient mortars, does not provide detailed information on the make-up of the lime-cement (see the complete report in the Annex). Comparative NMR spectra made on the coarse aggregates (*testa* and *cretoni*) on one part, and on lime-cement on the other part are providing some very interesting clues. We found at least two specimens of Roman cement (*Opus Signinum* and *Opus Testacem*) whose  $^{29}\text{Si}$  NMR Spectrum show the same resonance at -86 ppm as those of GEOCISTEM CARBUNCULUS cements. Fig. 21. compares the  $^{29}\text{Si}$  Spectra for the *Opus Signinum* sample ROM 4, and the sample OST 7G, *Opus Testacem* mortar, with LA01 Carbunculus cement. The cement spectra are different from those of the aggregates (*testa*, *cretoni*, LA01). This suggests that, at least for these two specimens, the hardening mechanism is not a simple lime carbonation as generally claimed by archaeology (and by the Cagliari team). Rather, the hardening would result from a chemical reaction between the lime and the alumino-silicates, comprising calcined clay *testa* and the volcanic tuff *cretoni*. This chemical reaction yields an alumino-silicate structure with a major resonance at -86 ppm suggesting a

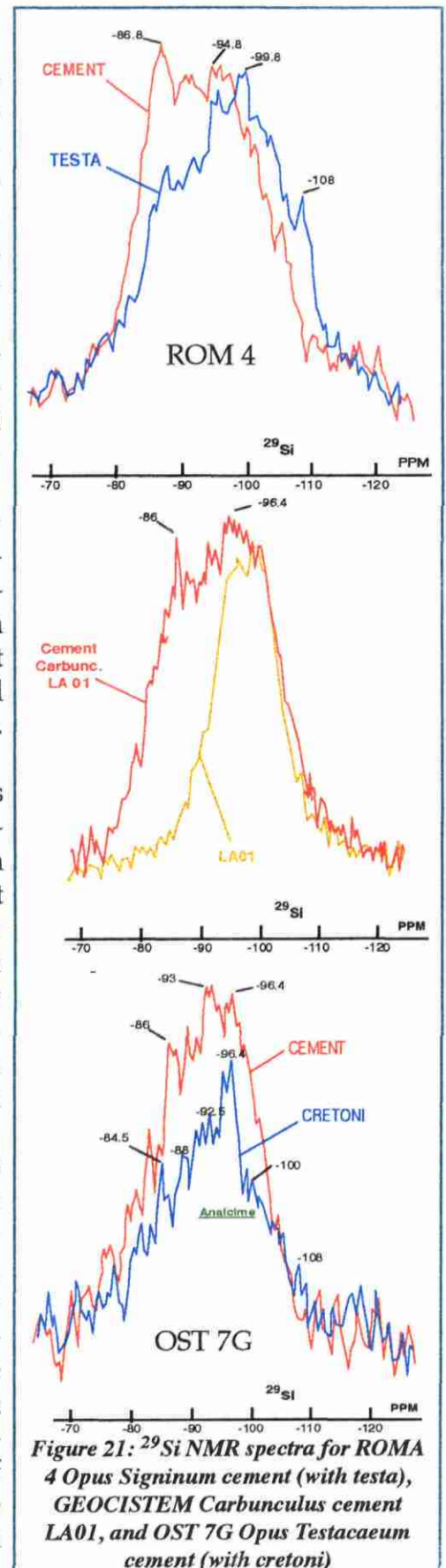
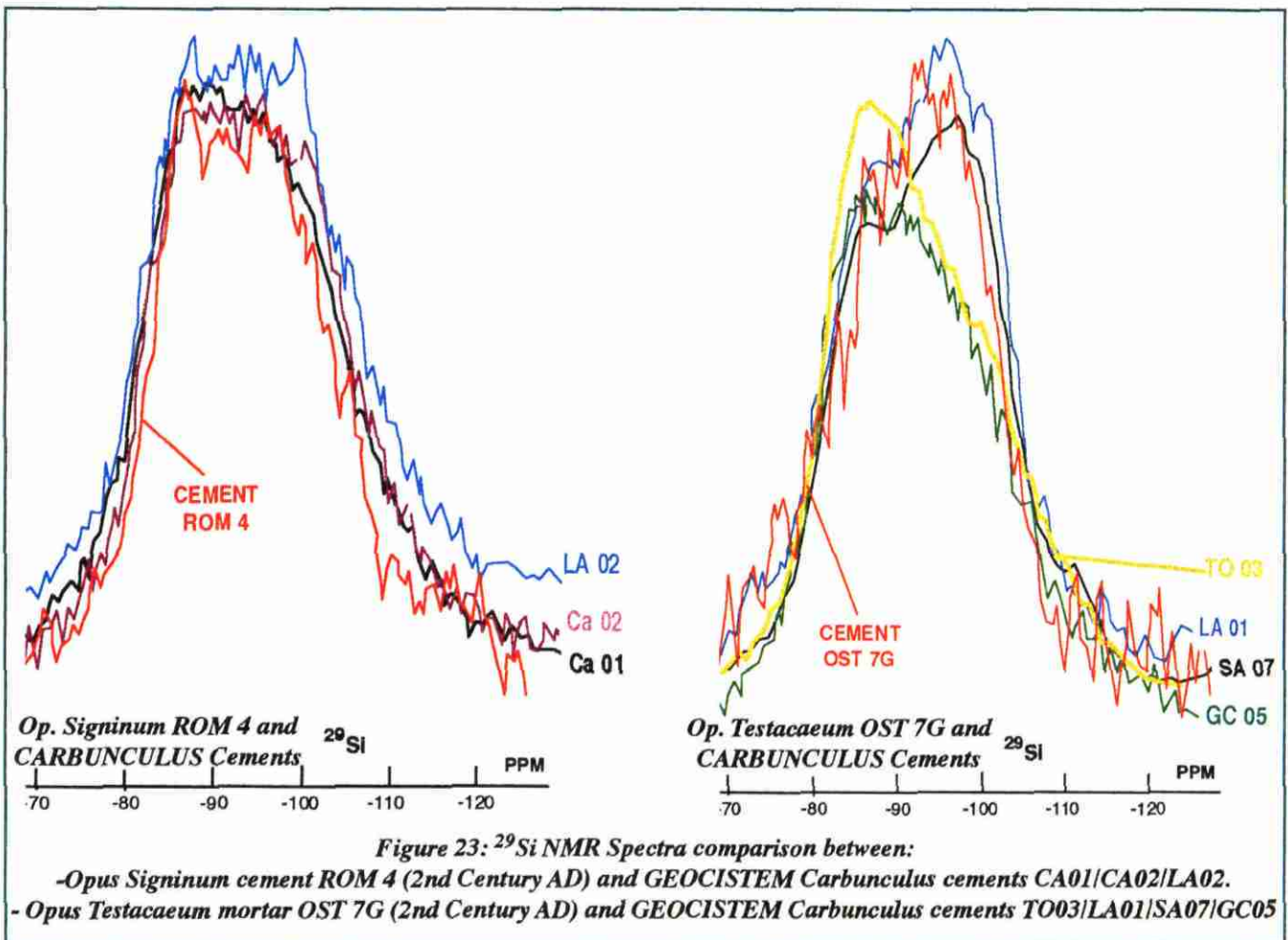


Figure 21:  $^{29}\text{Si}$  NMR spectra for ROMA 4 *Opus Signinum* cement (with *testa*), GEOCISTEM Carbunculus cement LA01, and OST 7G *Opus Testacem* cement (with *cretoni*)

structure of the Si(Q3Si,1OH) and Si(Q4) types. This chemical reaction could be of the geopolymeric type. The chemically un-reacted lime will then slowly recarbonate into calcite, with time. This explains why the cement matrix of the mortar contains calcium carbonate and aluminosilicates.

We have compared the spectra of these two Roman cements (from 2nd Century AD) with the spectra of the GEOCISTEM CARBUNCULUS cements. Fig. 23 shows that the spectrum for the cement ROM 4 (*Opus Signinum*) is similar to the spectra of CA01/CA02 cements and also to LA02. We know that these particular GEOCISTEM cements are made of KAN-DOXI and zeolitic tuffs LA02, CA01, CA02 (phillipsite type). We also know that the *Opus Signinum* consists of lime and calcined ceramic, *testa*. The chemical mechanism of the two cement types will be discussed in Chapter 3.5.2..

Concerning the cement OST 7G, the equivalent GEOCISTEM cement is the LA01 cement.



### 2.3.6.3. Geological Analogues

Any risk assessment must contain input from geological and geochemical analogues. The target was the determination of the best leachate test procedure connected with the best geologically predictable long-term durability.

Structural characterization of geopolymeric binders, cements, high-tech materials by means of  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS-NMR Spectroscopy, in the Background knowledge of GEOPOLY-MERE, demonstrated tecto-aluminosilicate type frameworks. The technical approach set forth in the WORKPROGRAMME for this PRENORM 1 task planned:

- Literature: selection of geological analogues (zeolites, melilite, alkali volcanic glass, leucite)

using available geological data.

- Field work: identification of samples in selected corrosive sites, acidic medium (geothermal fluids, fumarolic smoke), mineralogy and geochemistry.

Field work could not be performed as planned, because of a total lack of data on this topic. We (BRGM) did not find any geochemical and geological literature that could have helped us to start this part of the programme. We, therefore, modified the programme by focusing on:

- characterization of the GEOCISTEM Carbunculus cement, namely SA07 cement (texture, chemistry, mineralogy);
- identification of natural zeolitic analogues;
- testing natural analogues with respect to acid medium corrosion (test method identical to procedure in use for the cements), and also with respect to bio-lixivation.

#### Characterisation of SA07 Carbunculus cements and zeolitic analogues

The composition of the vitreous matrix (see Fig. 18) in undried sample is the following:

SiO<sub>2</sub> 37%; Al<sub>2</sub>O<sub>3</sub> 14%; K<sub>2</sub>O 7%; CaO 6%; H<sub>2</sub>O 34%.

Tab. 9 gives the overall chemical composition for SA07 cement and for the selected zeolitic analogues, which were:

- CHTCO: commercial zeolitic rock, origin Turkey
- CHIMM: commercial zeolitic tuff, origin Italy
- LA02: zeolitic tuff selected in GEOPROSPEC 1, origin Latium, Italy

*Table 9: overall chemical composition for SA07 cement and zeolitic analogues*

Sample .....	SA07 .....	CHTCO .....	CHIMM .....	LA02 .....
L.O.I. ....	23.63 .....	13.36 .....	13.86 .....	12.31 .....
P <sub>2</sub> O <sub>5</sub> .....	< 0,05 .....	<0.05 .....	0.14 .....	0.18 .....
SiO <sub>2</sub> .....	45.13 .....	66.93 .....	52.05 .....	50.65 .....
Al <sub>2</sub> O <sub>3</sub> .....	14.11 .....	11.22 .....	16.17 .....	16.28 .....
Fe <sub>2</sub> O <sub>3</sub> .....	0.82 .....	0.97 .....	3.48 .....	4.16 .....
CaO .....	6.89 .....	2.65 .....	5.05 .....	4.93 .....
MgO .....	1.77 .....	1.00 .....	1.45 .....	1.35 .....
Na <sub>2</sub> O .....	1.30 .....	0.46 .....	0.66 .....	1.48 .....
K <sub>2</sub> O .....	6.34 .....	3.44 .....	6.17 .....	7.49 .....
TiO <sub>2</sub> .....	0.13 .....	<0.05 .....	0.47 .....	0.48 .....
MnO .....	0.09 .....	<0.02 .....	0.09 .....	0.10 .....

#### Acid corrosion of zeolitic analogues

The experimental method was based on the acid resistance testing of cements performed on GEOCISTEM cements, see Chapt. 2.3.4.2., namely:

- grain size of the sample: 3.15-5 mm
- HCl and H<sub>2</sub>SO<sub>4</sub> solutions at 5% (pH=0)
- 10g sample in 100 g solution, at 20°C ,
- measurement after 7, 14, 21, 28 days: pH, conductivity, mass loss, cations leachate.
- mineralogical make-up, after 28 days.

H<sub>2</sub>SO<sub>4</sub> corrosion is most common in mine tailings and therefore very important for the

potential application of GEOCISTEM Car-bunculus cement. The results on the zeolitic analogues are summarized in the following Fig. 24, 25. For all natural analogues, the most soluble cation is Mg. We have seen in Chap. 2.3.5.1., Fig. 18, that in GEOCISTEM cement base, Mg does not react within the vitreous matrix and is left over in the remains of the digested slag grains. Mg content in Cement Base and in volcanic tuffs, is therefore determinant in the H<sub>2</sub>SO<sub>4</sub> resistance of GEOCISTEM cements.

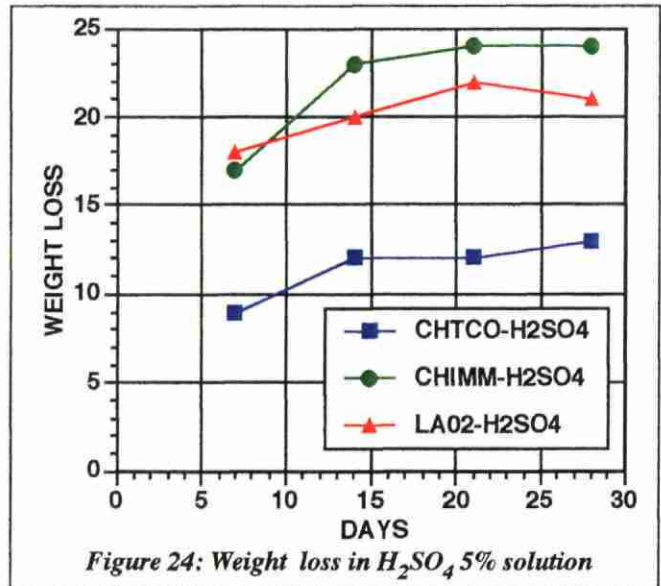


Figure 24: Weight loss in H<sub>2</sub>SO<sub>4</sub> 5% solution

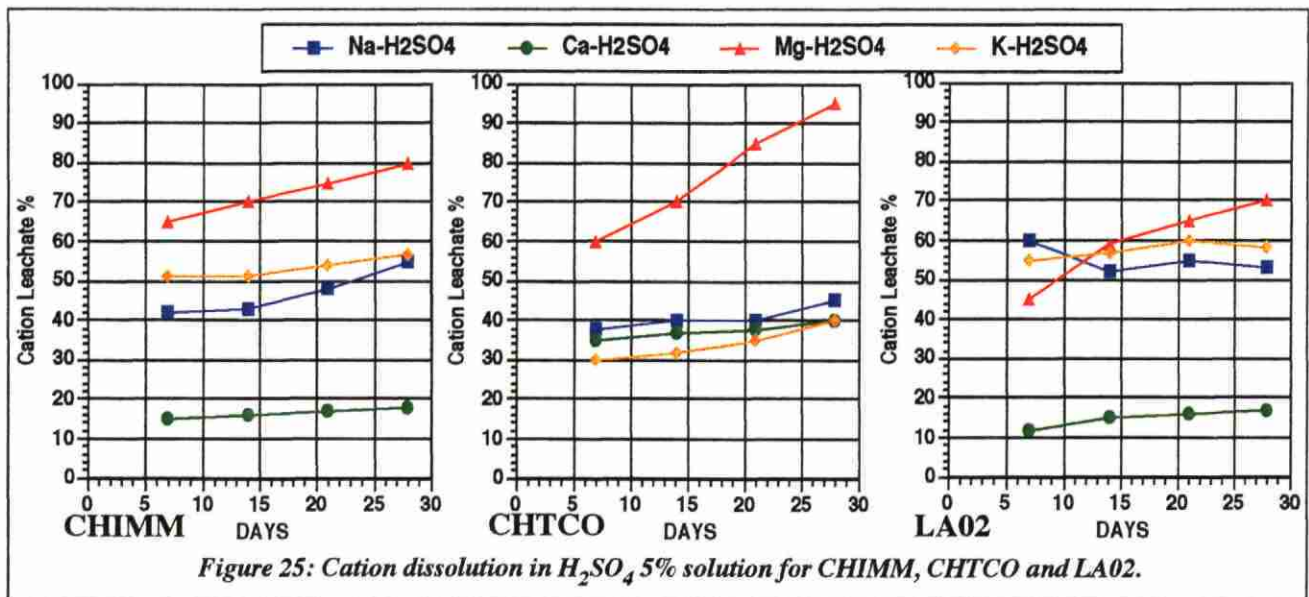


Figure 25: Cation dissolution in H<sub>2</sub>SO<sub>4</sub> 5% solution for CHIMM, CHTCO and LA02.

Bio-Lixivation.

Bacteria found in base metal mining sites are of the *Thiobacillus ferroxydans* and the *Thiobacillus thiooxydans* types. (see the report in the Annex)

Because this type of long-term evaluation was not planned in the Workprogramme, it is not possible to compare the bio-lixivation of GEOCISTEM cements with the results obtained in this task. However, these bacteria are essentially pH sensitive, i.e. they require a pH close to 1.7 for a maximum growth rate. It can therefore be stated that, as long as the pH of any material encapsulated with GEOCISTEM cement or of any storage medium, remains higher than 1.7, say higher than 3, there should be no risk of any Bio-Lixivation of this type.



### **3. Scientific and Technical Description**

### 3.1 PROCESSING GEOPOLYMERIC CEMENT

Task Leader: CORDI-GEOPOLYMERE, Joseph Davidovits

Geopolymeric cement results from blending following ingredients (Tab. 10):

- Alumino-silicate oxide (calcined kaolin KANDOXI), ( $\text{Si}_2\text{O}_5, \text{Al}_2\text{O}_2$ )
- Potassium disilicate  $\text{K}_2(\text{H}_3\text{SiO}_4)_2$
- Calcium disilicate  $\text{Ca}(\text{H}_3\text{SiO}_4)_2$  (blast-furnace iron slag)
- and high alkali-geological material (MELILITE glass or CARBUNCULUS)

Table 10: Chemical composition of the commercial geopolymeric cement ingredients

	SiO2	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O	others	water	total
KANDOXI	54.23	42.38	0.52	0.32	0.04	0.14	1.46	0.52	0.88	100.49
	54.44	42.55	0.52	0.32	0.04	0.14	1.47	0.52		100.00
iron slag	38.71	8.29	1.53	10.49	39.64	0.19	0.30	3.07	-1.98	100.24
	37.87	8.11	1.50	10.26	38.78	0.19	0.29	3.00		100.00
K-silicate sol.	20.95						25.98		53.03	99.96
	44.64	0.00	0.00	0.00	0.00	0.00	55.36	0.00		100.00

The research has focused on the ingredients:

KANDOXI, MELILITE Glass and CARBUNCULUS

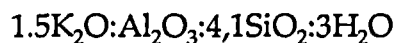
#### 3.1.1. Sub-Task 2.1 KANDOXI (KANDOXI 1 and 2, NMR 1)

planned start: March 94    actual start: March 94  
 planned end: April 95    actual end: December 96

##### 3.1.1.1 Chemical Reactivity Test for Kandoxi Materials.

This test provides information equivalent to the  $^{27}\text{Al}$ -MAS-NMR data and was used to select geological samples (see in Chapter 2.3.2.2., Kaolinitic Clay resource in Sardinia).

Pure calcined kaolin =  $\{9[\text{Si}_2\text{O}_5, \text{Al}_2\text{O}_2], [\text{Si}_2\text{O}_5, \text{Al}_2(\text{OH})_4]\}$  is reacting with potassium silicate solution with the molar ratio  $\text{SiO}_2/\text{K}_2\text{O}=1.85$ , yielding a hard silico-aluminate product with the following molar composition:



##### Thermography:

The chemical hardening, performed in an oven at  $85^\circ\text{C}$ , is strongly exothermic. The exothermicity characterises calcined kaolin with Al (IV-V). Several thermal analytical methods have been used and are providing useful data. D.T.A. (Differential Thermal Analysis) determines the quantity of heat generated during the chemical hardening,  $+\Delta\text{H}$ , which is proportional to the quantity of Al (IV-V) groups involved in the calcined kaolin.

Thermography plots the temperature of the hardening sample. This simple method, which may be carried out with regular laboratory equipment, is illustrated by Fig. 26. The exothermicity generated by the  $750^\circ\text{C}$  calcined kaolinitic clay is clearly displayed on the curve. The  $600^\circ\text{C}$  curve is identical to the heating curve of a blank sample.

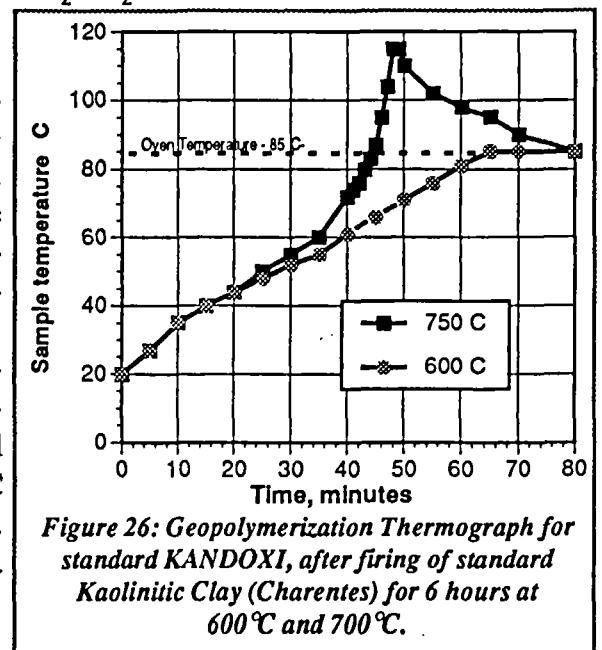


Figure 26: Geopolymerization Thermograph for standard KANDOXI, after firing of standard Kaolinitic Clay (Charentes) for 6 hours at  $600^\circ\text{C}$  and  $700^\circ\text{C}$ .

##### Preparation of the samples:

*Mineralogy of the clays:* quantitative determination of the kaolinite content; determination of reactive  $\text{Al}^{3+}$ .

**Calcination:** 6 hours at 750°C. Each sample should weight at least 500g.; median diameter: 3.7microns.

**Preparation of the potassium silicate solution:** addition of KOH flakes to the commercial solution in order to reach the molar ratio  $\text{SiO}_2/\text{K}_2\text{O}=1.85$ .

**Preparation of the reactive mixture:** 200 g of potassium silicate are added to the amount of calcined clay corresponding to the molar ratio  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3=1.5$ . After fast speed mixing, the mixture rests 1 hour long at room temperature, for example 23°C.

**Geopolymerization Thermography:** hardening occurs in a plastic container (coffee cup type) placed in an oven, or an oil bath at 85°C. The temperature is measured with electronic devices (thermoelements) or simple thermometers. Hardening samples must be covered with a plastic film in order to avoid water evaporation during the setting.

### 3.1.1.2. Sub-Task 2.13 NMR Spectroscopy

The objectives are to set up calcination parameters for industrial manufacture. We have compared the NMR spectras of 3 samples (Fig. 27).

sample # 1 = Kandoxi, material currently supplied (from ECC)

sample # 2 = Kandoxi A: laboratory calcination at 750°C, 3 hours, in a closed container

sample # 3 = Kandoxi B: lab. calcination at 750°C, 3 hours, on a flat ceramic plate.

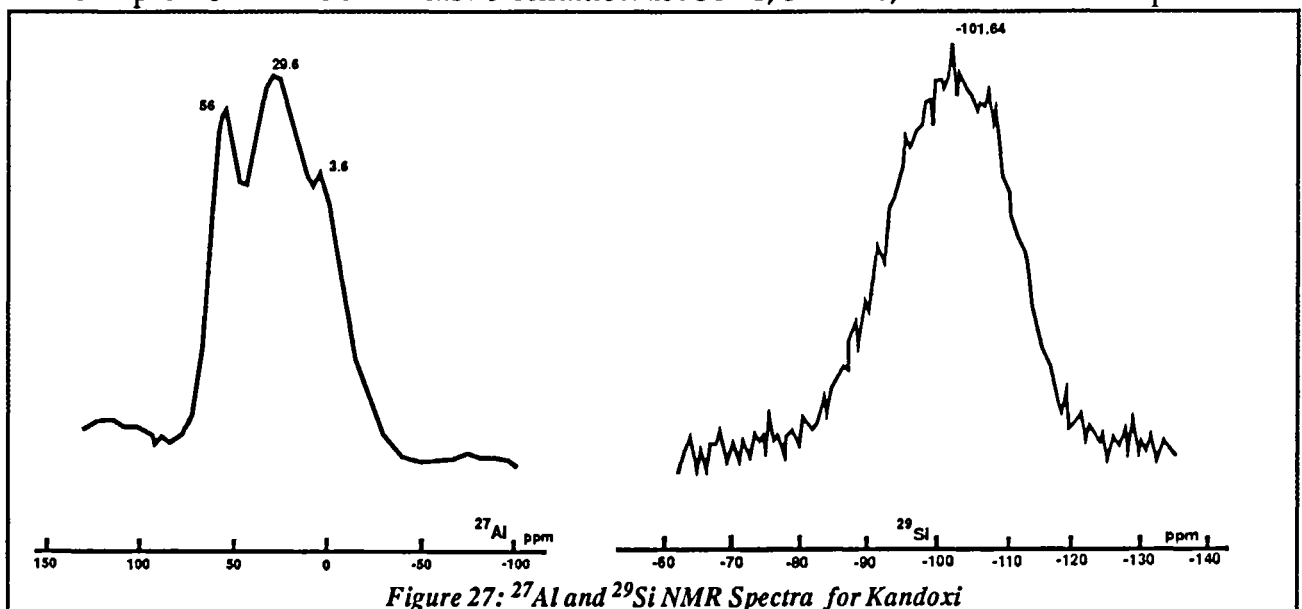


Figure 27:  $^{27}\text{Al}$  and  $^{29}\text{Si}$  NMR Spectra for Kandoxi

$^{29}\text{Si}$  spectra are identical. A small difference between the  $^{27}\text{Al}$  spectra has been detected (see in Annexe). The intensities of the 3 resonances Al(VI), Al(V), Al(IV) are:

	Al(IV)	Al(V)	Al(VI)
Kandoxi	27%	49%	24%
Kandoxi A	24%	47%	29%
Kandoxi B	24.7%	50%	25.3%

### 3.1.2. Processing of MELILITE glass, Sub-task 2.2

planned start:	March 01	actual start:	July 4
planned end:	January 95	actual end:	May 95

#### Technical approach:

The method involves the steps of:

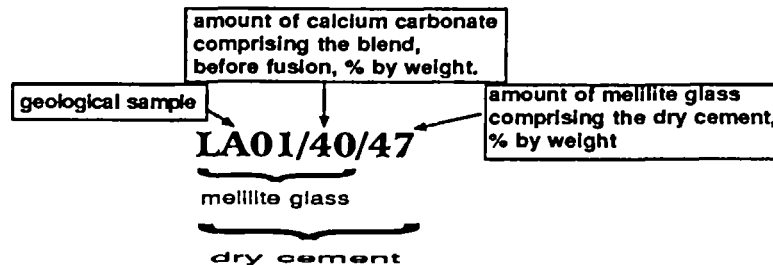
- preliminary grinding of the geological samples, grain size range 50-200  $\mu\text{m}$
- blending with calcium carbonate, or blending with CaO
- melting at temperatures in the range of 1250°C-1350°C

- subsequent rapid cooling in water
- drying
- fine grinding, final grain size: <30µm with 50% <10 µm

The work involved the fabrication of 20 samples changing following parameters:

- a) quantity of calcium carbonate added to the geological sample, before melting;
- b) fusion temperature

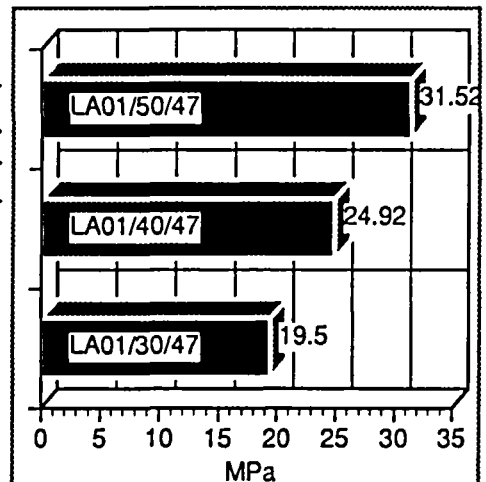
**Sample label:** each sample is designated by its provenance, the quantity in weight % of calcium carbonate comprising the blend, before fusion, and the quantity of melilite glass comprising the final dry cement. For example: LA01/40/47 means that the blend contains 60% by weight of geological sample LA01 and 40% by weight of calcium carbonate. The dry cement LA01/40/47 contains 47% by weight of melilite glass..



**a) Calcium carbonate addition:**

The blend contains 30%, 40%, 50% of calcium carbonate, i.e. 70%, 60%, 50% of geological material, respectively. As displayed in Fig. 28, the compressive strength of the resulting cements increases with the addition of calcium carbonate.

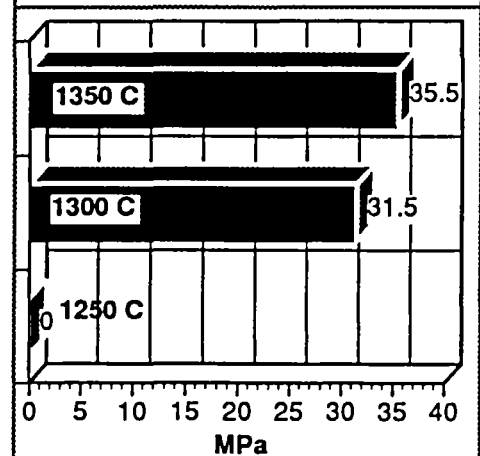
*Figure 28: 8 day compressive strength of cement obtained with 30, 40, 50 % calcium carbonate blend, LA01 series*



**b) Fusion temperature:**

The optimum fusion temperature depends on the calcium carbonate content. The higher the calcium carbonate content in the blend, the higher the fusion temperature. The compressive strength of the resulting cement is also a function of the fusion temperature (see Fig. 29).

*Figure 29: Relation between fusion temperature and compressive strength (after 8 days) for the LA01/50/47 series*



**Degree of crystallinity, vitrification and reactivity control:**

X-rays powder diagram performed by BRGM have confirmed the amorphous structure of the melilite glass (see in Annex for series SA07/30). Yet, this X-rays tests are not convenient for a rapid determination of the optimum vitrification conditions, i.e. optimum reacti-

vity of the glass and optimum properties of the cement. The bottom line is to determine the degree of transformation of added CaO, into any calcium silicate. We have discovered that free CaO induces an erroneous value for the grain size distribution measured with the BLAINE method (surface evaluation of grains, used in the cement industry). Standard routine measurements are providing values which are 2 times or 3 times higher than expected, when free CaO is still present in any melilite glass sample. This effect is due to the rapid rehydration of CaO into Ca(OH)<sub>2</sub>. Free CaO generates an instantaneous flash set (hardening in the mixer) of the cement, which is therefore not workable. Generally, a flow time greater than 3min indicates the presence of free CaO, i.e. inadequate vitrification conditions (inappropriate fusion temperature in relation with the calcium carbonate content). The following Tab.11 provides some values for melilite glasses, with and without free CaO.

Along with the determination of the best relationship between calcium carbonate content and fusion temperature, we have implemented this simple laboratory BLAINE method for an easy control of the vitrification conditions.

*Table 11: Blaine method (time for the air to flow through the sample) for various melilite glasses, in relation with fusion temperature and calcium carbonate content of the blend.*

Sample	Fusion T°C	Blaine flow time	Workability of the cement
LA02/35	1250	4min30sec	none (free CaO)
LA02/35	1300	2min25sec	excellent
LA01/40	1250	>5min	none (free CaO)
LA01/40	1300	2min18sec	excellent
LA01/50	1300	2min20sec	excellent
LA01/60	1300	>5min	none (free CaO)

### GP CEMENT: processing of geopolymeric cements

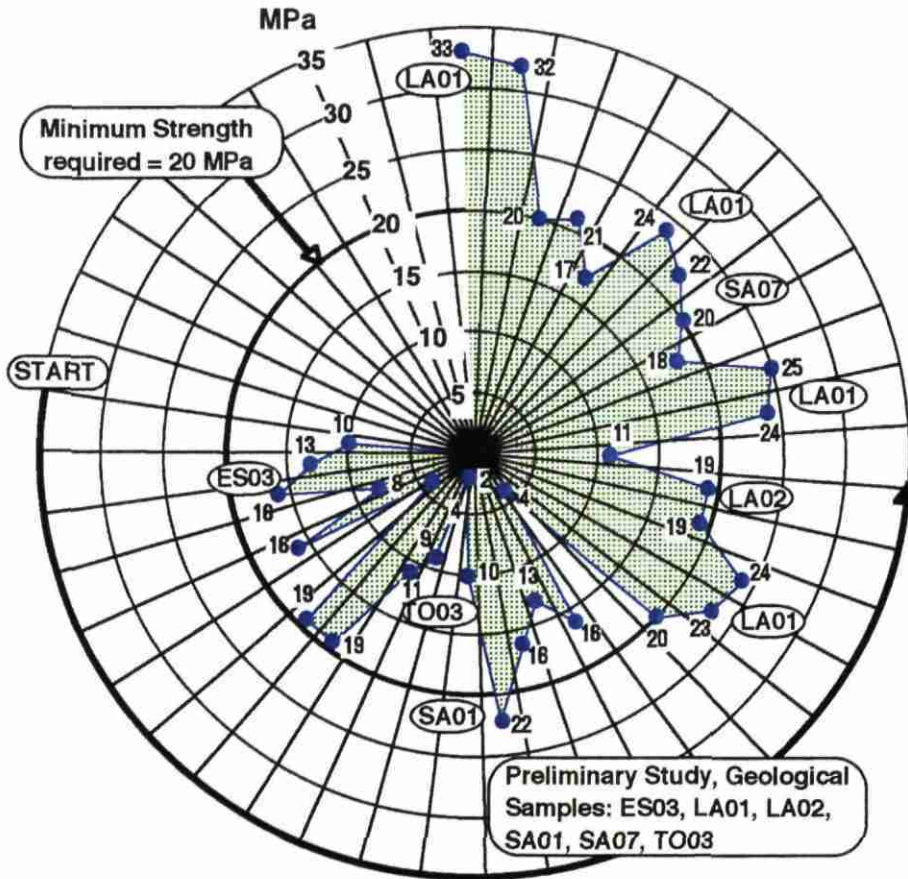
55 cement blends were tested according to the GEOPOLYCEM reactivity test (not described in the Workprogramme) and 15 cement blends according to the PZ-GEOPOLY reactivity test (described in the Workprogramme, Table 3, page 16) (total: 70). The new GEOPOLYCEM test is more appropriate for the comparative study of geological samples, and does not necessitate as many trials as planned. The planned PZ-GEOPOLY test provides a better input in terms of the economics and exploitation possibilities. The latter test has been carried out only on 1 geological sample, namely on LA01, and the resulting LA01/40 melilite glass.

### GEOPOLYCEM test series

The cement formulations are displayed in Tab. 12 and the overall results in Fig. 30. In addition to the parameters discussed above, the compressive strength is a function of the melilite concentration. See in Annex for the detailed results of these series.

*Table 12: Standard cement formulation and GEOPOLYCEM formulations*

ingredient	standard	GEOPOLYCEM series		
Kandoxi	42	41	36	31
K.Silicate	25	12	10	9
Iron slag	33	17	15	13
melilite	0	30	39	47
	100	100	100	100



**GEPOLYCEM progression chart  
8 Day Compressive strength, MPa**

Figure 30: non workable samples (with free CaO) are not plotted in this progression chart. Weak values for ES03 and TO03 are due to bad workability and inadequate fusion temperature (too low) for the melilite.

PZ-GEOPOLY reactivity test series

In these series K-silicate is replaced with the corresponding amount of melilite glass, namely LA01/40 glass. The cement formulation is the standard formulation given in Table 12.

Fig. 31 displays the 8 day compressive strength in relation with K-silicate replacement. It is interesting to note that the strength increases and then decreases when the replacement amount is greater than 50%. A cement without K-silicate does not set after 8 days. A 80% replacement of K-silicate provides significant strength (in the 30 MPa range).

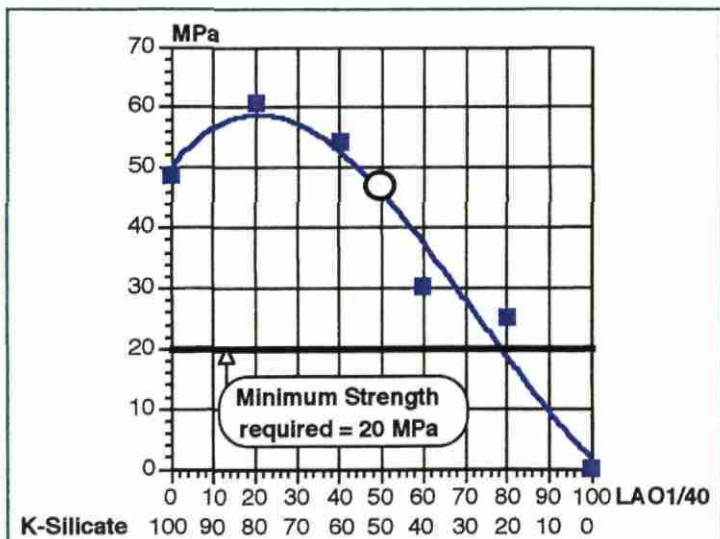


Figure 31: replacement of K-silicate with LA01/40 glass. 8 day compressive strength. A 50% replacement provides high strength equivalent to the standard formulation.

The best results of both test series, in terms of 8 day compressive strength >30 MPa, for the lowest K-silicate content, are plotted in the ternary diagram of Fig. 8 of Chapter 2.3.1. above, and their composition displayed in Tab. 13. These results were obtained with the

LA01 geological samples.

Table 13: Cement composition for the samples of Figure 8 (Chapt. 2.3.1.)

ingredient	1)=standard	2)=Geopolycem	3)=PZ-Geopoly
Kandoxi	42	31	38
K-silicate	25	9	4
iron slag	33	13	32
melilite glass	0	47	24

### 3.1.3. Processing CARBUNCULUS cements (Task 4-6 CEMENTMANUFA/CONCRETE)

Task Leader: CORDI-GEOPOLYMER, E

part subcontracted to CEMENTI Buzzi (L. Buzzi), Italy.

planned start: July 4, 1995

actual start: Sept. 1, 1995

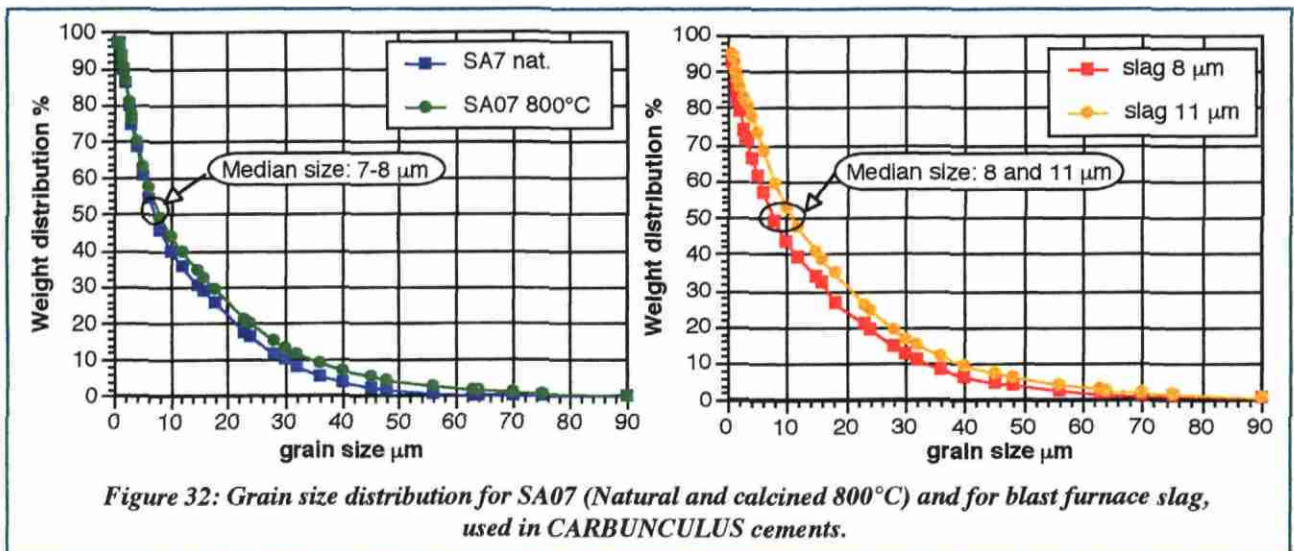
planned end: January 2, 1996

actual end: September, 1996

The geologists at Cagliari University have supplied 100 kgs of SA07; 50 kgs were calcined at 800°C, 3 hours, by Geopolymere in the small laboratory oven. The calcination process took 7 days at a ratio of 7 kgs/day (two batches of 3,5 kgs); 50 kgs are kept natural. The materials (calcined and uncalcined) were grounded at the cement plant (Cementi Buzzi, Italy) and blended with commercial Kandoxi and Slag. The material was used in Task 6 CONCRETE. Samples (2x3kgs) were sent to LAVIOSA for Task 7 TOXIC ENCAPS.

The commercial Kandoxi is the calcined kaolin brand 501 from ECC International.

The slag supplied by Cementi Buzzi was grounded at two different granulometries. According to the work performed previously the reactivity of the materials depends strongly on their grain size. The optimum grain size lies in the range of 7 µm to 10 µm. A finer grain size yields higher strength but induces very fast setting or very short feasibility time. The grain size distribution for SA07 samples (natural and calcined 800°C) and for two grounded slags are plotted in Fig. 32 (Granulometer CILAS).



Standardized mortar mixes were prepared, cast and tested for their physico chemical properties, using accelerated testing procedures and normal codified tests in conformity with standard Portland cement laboratory mortar testing.

Correlation: Lab. test on Paste and Cement test on Mortars

The tests performed in Géopolymère's Lab. comprised plain cement phase, i.e. without any fillers or sand. Standardized cement tests carried out in Cementi Buzzi's Lab. on mortar bars with tailored equipment, do involve standardized sand. The values obtained at Cementi Buzzi's Lab. for the same CARBUNCULUS cement formulation (Stampo n. 1 in Tab.14), are significantly higher (twice the value of Géopolymère Lab.), essentially at 1 day and 7 days (Fig. 33). Because the 28 day values are close to one another (45 Nmm<sup>2</sup> and 55 Nmm<sup>2</sup>) it can be postulated that the blending and mixing procedure with sand according to the standard testing method at Cementi Buzzi's Lab. is effectively accelerating the hardening of the mortar. This is due to the heat of mixing with sand.

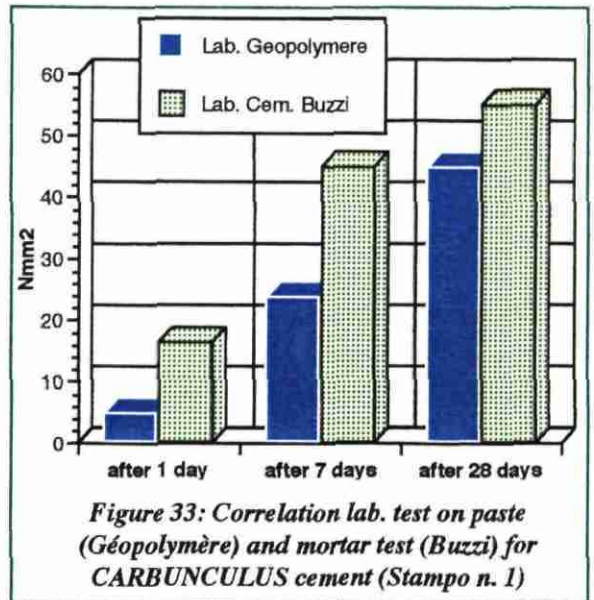


Figure 33: Correlation lab. test on paste (Géopolymère) and mortar test (Buzzi) for CARBUNCULUS cement (Stampo n. 1)

Consequently, the standard mix recommended by Géopolymère (Stampo n.1) happens to work too fast. When cast into the mold it hardens at a rapid rate, it is not workable from a regular concrete point of view. **It is however very good if the application requires very high early strength (equivalent to rapid setting Portland cements).**

However, from a practical point of view, the workability of the mix must be suitable with the standard methods. This testing involved 19 different mixes. Twelve formulations are listed in Tab. 14 and the graph of Fig. 34 displays the corresponding compressive strengths obtained for each mortar tested.

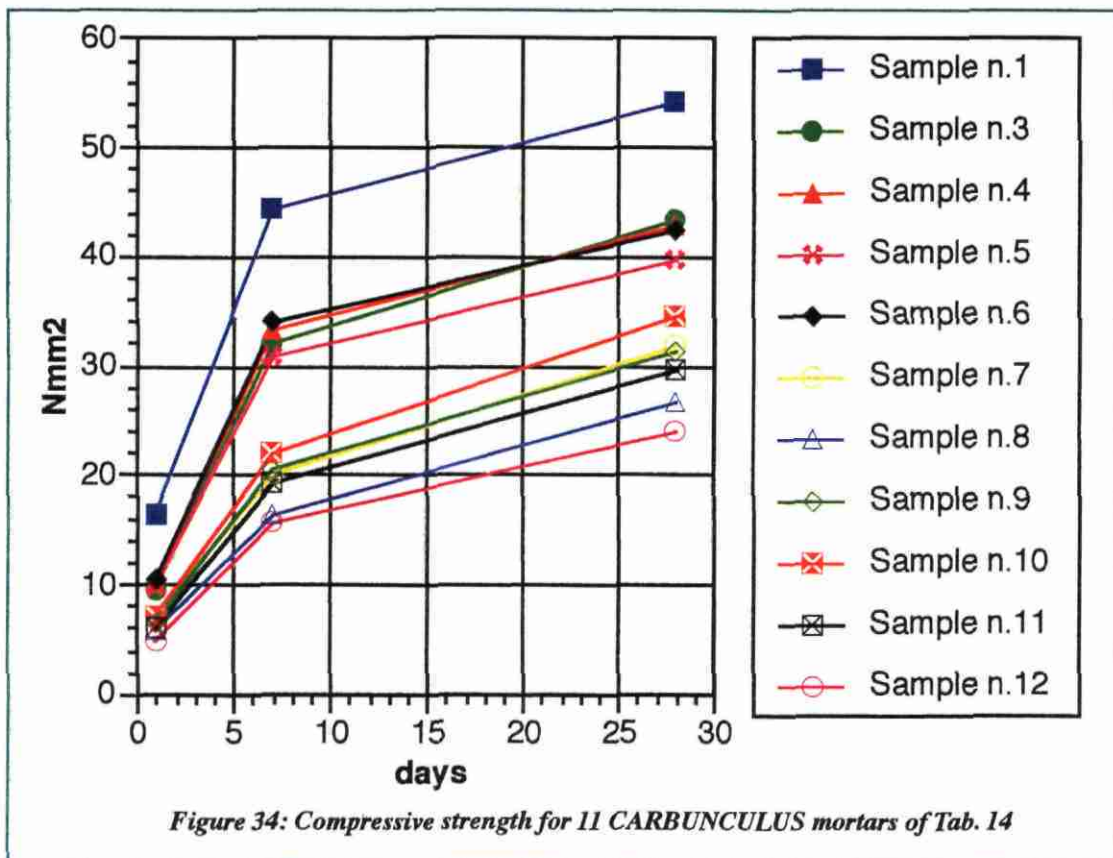


Figure 34: Compressive strength for 11 CARBUNCULUS mortars of Tab. 14

Table 14: Twelve formulations tested

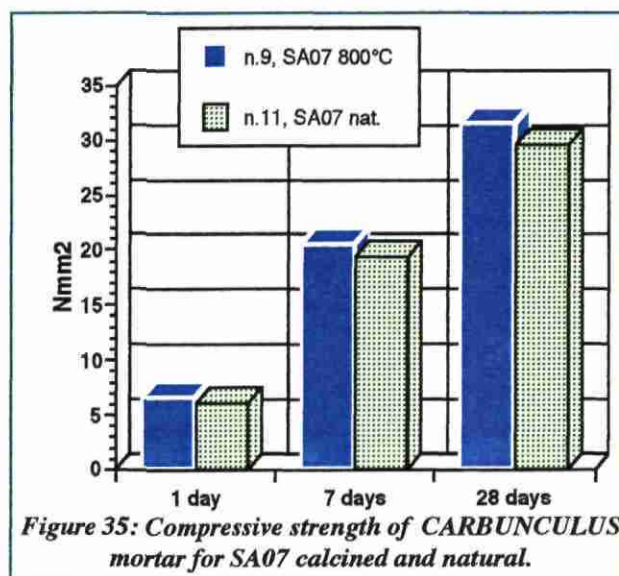
Sample nr.	1	2	3	4	5	6	7	8	9	10	11	12
SA07 calcined	46.7	51.7	51.7	51.7	51.7	56.7	51.7	51.7	56.7	56.7		
SA07 natural	-	-	-	-	-	-	-	-	-	-	56.7	56.7
slag d50 = 8µm	25.3	20.3	20.3	20.3	20.3	20.3						
slag d50 = 11µm	-	-	-	-	-	-	20.3	20.3	20.3	20.3	20.3	20.3
Kandoxi	28.0	28.0	28.0	28.0	28.0	23.0	28.0	28.0	23.0	23.0	23.0	23.0
total powder	100	100	100	100	100	100	100	100	100	100	100	100
K-silicate, 47%sol.	23.4	23.4	23.4	23.4	23.4	23.4	23.4	23.4	23.4	23.4	23.4	23.4
water	29.0	29.0	29.0	29.0	29.0	29.0	29.0	31.9	29.0	29.0	29.0	31.9
Plasticizer	-	-	1%	1%	2%	1%	1%	1%	1%	-	1%	1%

Each ingredient, taken separately, can alter or enhance the workability:

- slag:** increasing the grain size; 10-11 mm instead of 8 mm, slows down the hardening.
- Kandoxi:** reducing the quantity of this fine filler enhances the flowability of the mix.
- K-silicate:** reducing the quantity slows down the hardening, however changes the rheology of the mix.
- SA07:** increasing the grain size; 10-11 mm instead of 7 mm, enhances the flowability of the mix.
- Plasticizer:** the cement industry uses organic plasticizers; 0,5%-2% by weight of cement paste enhance the flow and workability.

#### SA07 calcined 800°C versus SA07 natural:

Four batches (Stampo n. 8, 9, 11, 12) compare SA07 800°C with SA07 uncalcined. From a compressive strength point of view, the results confirm the data obtained in the Géopolymère' lab. (see Fig. 13 in Chapter 2.3.2.), namely that calcination of SA07 does not increase the strength very significantly (Fig. 35). Yet, in terms of workability, calcination does provide better flow and rheological behaviour for the mortar, and, therefore, should be recommended.



### 3.2 SELECTION OF GEOLOGICAL SAMPLES

Partners: BRGM (Philippe Rocher), Barcelona U.(Domingo Gimeno), Cagliari U. (Carlo Marini, Sandro Tocco).

#### 3.2.1. Task 1 GEOPROSPEC 1: 10 SAMPLES for cement testing (see also in 2.3.2. Large scale geological resources)

planned start:	March 01	actual start:	March 15
planned end:	October 94	actual end:	May 95

#### Technical Programme

- Literature: selection of targets (proven or potential deposits) using available geological data (maps, petrography, mineralogy, geochemistry) and industrial specifications (chemical composition, etc.)
- Field work: assessment of deposit homogeneity, identification of criteria controlling the quality of the resource, collection of representative samples.
- Rough characterization of the raw material: petrography, mineralogical and chemical compositions of the rocks and their main constituents (qualitative and quantitative analyses, major elements).

The representative samples were selected not only for their chemical/mineralogical make up, but also for their economical accessibility. These samples involve geological formations which comply with following economical requirements:

- large deposits, several meters to several decametres thickness and several kilometres/decakilometres area continuity, broadly homogeneous composition;
- no legislative or environmental constraints;
- easy to reach (logistic) and to exploit.

Literature search performed, key words "volcanic rocks with high K<sub>2</sub>O content, in Europe" has selected 3 magmatic types: alkaline, calco-alkaline and shoshonitic. Explorations in Phases 1 and 2 were carried out in 6 regions and 10 representative samples sent to GEOPOLYMER (see Tab. 15 and Fig. 10).

*Table 15: Chemical composition of the selected samples, % by weight*

Sample	SA01	SA07	LA01	LA02	TO03	ES03	CA01	CA02	GC05	TE03
SiO <sub>2</sub>	71.48	74.16	58.06	52.52	55.35	88.42	57.94	57.61	56.50	56.76
Al <sub>2</sub> O <sub>3</sub>	14.55	13.80	19.26	16.41	19.20	10.80	17.66	18.59	15.86	18.45
Fe <sub>2</sub> O <sub>3</sub>	1.60	1.13	4.17	3.67	4.00	5.80	3.72	4.74	3.74	3.39
MgO	0.04	0.17	1.20	1.73	1.15	8.68	0.70	1.16	0.63	0.47
CaO	0.07	0.43	3.14	7.54	2.95	2.56	2.61	3.52	0.44	0.99
Na <sub>2</sub> O	0.69	4.33	2.22	0.58	2.35	1.50	3.50	3.25	6.21	7.28
K <sub>2</sub> O	10.41	4.89	8.80	6.34	8.25	8.35	7.99	7.60	5.63	5.77
TiO <sub>2</sub>	0.16	0.13	0.61	0.51	0.54	1.40	0.41	0.47	0.74	0.45
P <sub>2</sub> O <sub>5</sub>	0.04	0.02	0.15	0.17	0.17	0.76	0.13	0.19	<0.05	<0.05
MnO	0.01	0.02	0.16	0.10	0.13	0.09	0.12	0.16	0.27	0.25
L.O.I.	0.96	0.92	2.23	10.43	6.00	1.15	5.76	2.56	9.34	6.67

In addition to the locations studied so far, **Sardinia, Central Italy (Latium, Toscana), South-East Spain, Canary Islands**, phase 3 of GEOPROSPEC 1 has determined the potentiality of the resources in Greece. Literature studies suggest interesting potential resources in other European regions, such as:

- Germany, Eifel, - France
- Central Europe (Slovakia, Romania, Hungary, Bulgaria).

3.2.2. Task 5 GEOPROSPEC 2

planned start: June 6, 1995      actual start: Sept. 1, 1995  
 planned end: January 16, 1996      actual end: July 31, 1996

- Detailed geological synthesis (geology, mapping, etc.) of the deposits SA07 Paringianu, near Sulcis, Sardinia, Italy, selected for the first industrial tests and used in task n°4 CEMENTMANUFA, see in Fig. 36.

- Additional sampling of SA10 to SA19 outcrops including materials displaying structural and textural alterations on the basis of about 20-30 samples, fine characterization of the material:

- mineralogical and chemical analyses of selected volcanic tuffs, see in Tab. 16.

- mineralogical and chemical analysis of separated phases (e.g. clay minerals, volcanic glasses),
- micro-analysis of all the minor components and trace elements.

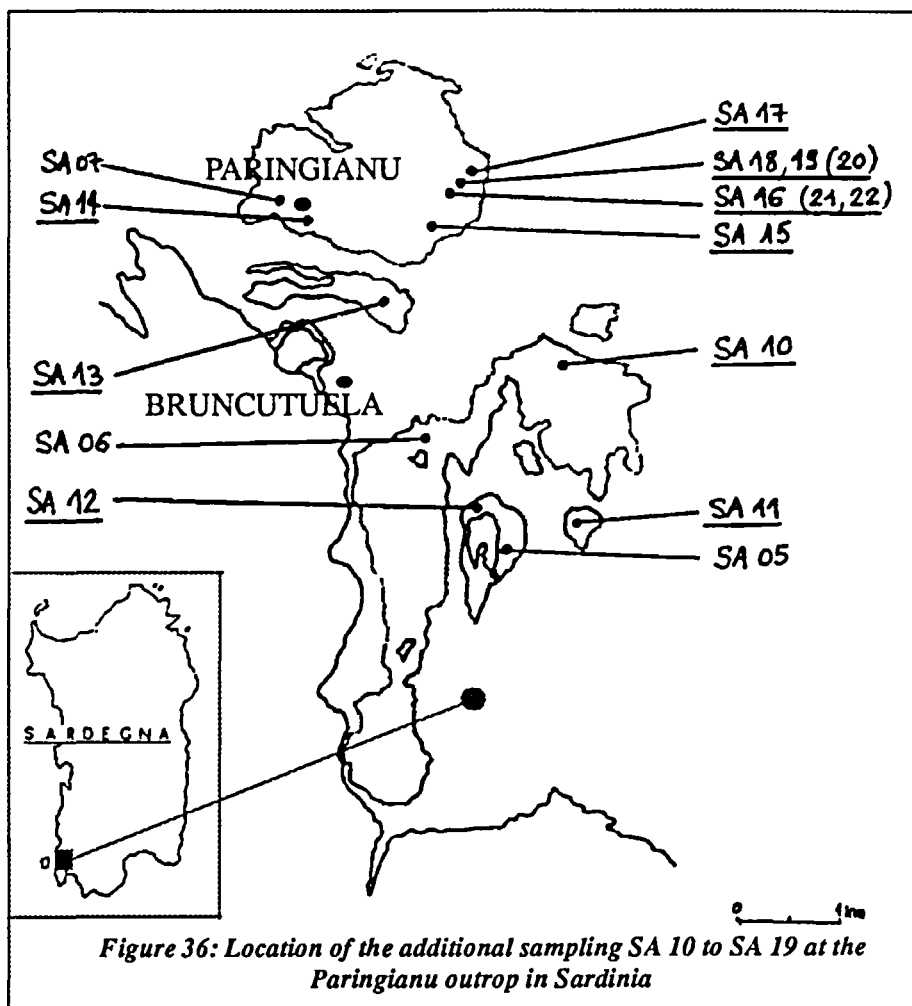


Figure 36: Location of the additional sampling SA 10 to SA 19 at the Paringianu outcrop in Sardinia

Table 16: Chemical composition of samples SA 10 to SA 19, Paringianu Unit, Sardinia

Sample	SA10	SA11	SA13a	SA13b	SA14	SA15	SA16	SA17	SA18	SA19
SiO <sub>2</sub>	74.16	75.26	71.00	72.38	75.36	74.56	74.49	74.64	73.65	73.68
Al <sub>2</sub> O <sub>3</sub>	13.89	13.37	12.61	12.84	13.40	13.54	13.49	13.14	13.37	12.98
Fe <sub>2</sub> O <sub>3</sub>	1.58	1.57	1.44	1.66	1.65	0.57	1.60	1.21	1.48	1.51
MgO	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
CaO	0.32	0.32	0.29	0.26	0.32	0.34	0.23	0.26	0.28	0.26
Na <sub>2</sub> O	3.66	4.16	4.66	4.39	4.13	4.06	4.08	3.77	4.09	4.34
K <sub>2</sub> O	5.15	5.09	4.79	4.84	5.12	5.19	5.06	5.14	5.07	5.02
TiO <sub>2</sub>	0.13	0.12	0.11	0.11	0.12	0.12	0.11	0.11	0.12	0.11
P <sub>2</sub> O <sub>5</sub>	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
MnO	<0.02	0.03	<0.02	<0.02	0.04	<0.02	0.03	<0.02	<0.02	<0.02
L.O.I.	1.50	0.76	4.41	2.84	0.82	1.08	1.02	1.13	1.36	1.78

The overall outcrop possess a high chemical homogeneity, which corresponds to an alkaline Rhyolite.

### 3.3. Application of geopolymeric cements for waste management and Ecology

#### 3.3.1. Cement for Uranium mine tailings Task 3.1 BARRIER

Task Leader: CORDI-GEOPOLYMERE,

part subcontracted to Heidelberger Zement (Germany)

planned start: January, 1994

actual start: January, 1994

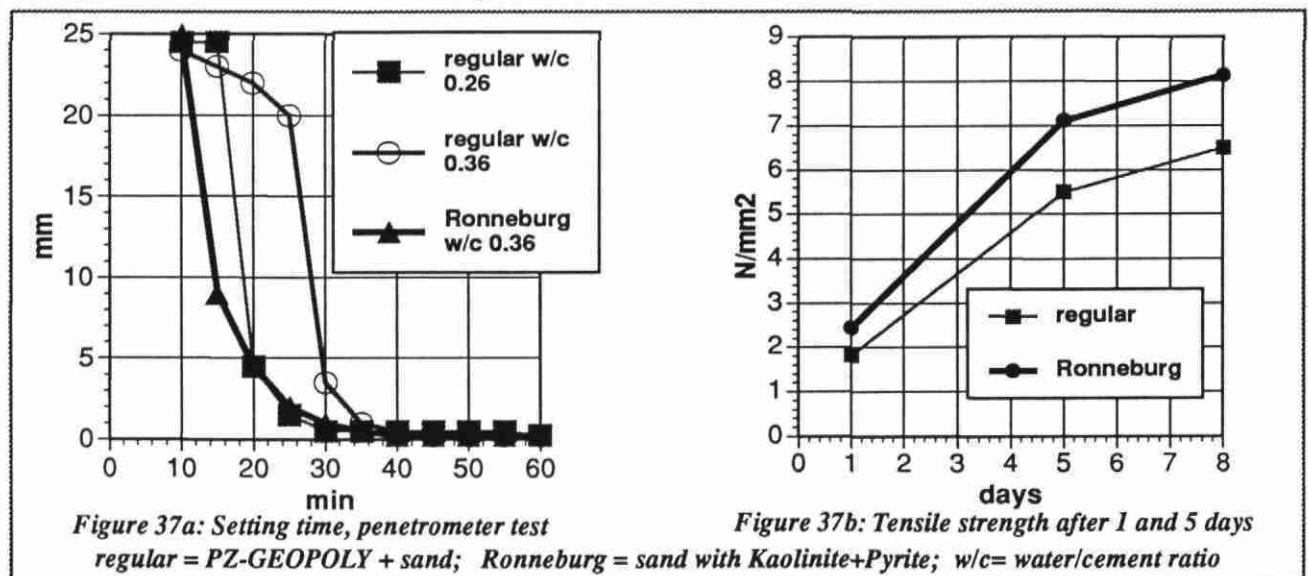
planned end: December, 1995

actual end: February, 1996

The research has tested the basic properties of concretes elaborated with local polluted aggregates on a WISMUT's uranium mining site, in Ronneburg, Thüringen.

The technical approach consisted in a series of tests on mortar bars in order to determine mechanical and physico-chemical properties (chemical corrosion). Designed materials and technology could be applied later to borehole plugging, shaft sealing, geological barriers, cappings, dams and walls, for cleanup uranium mine tailings.

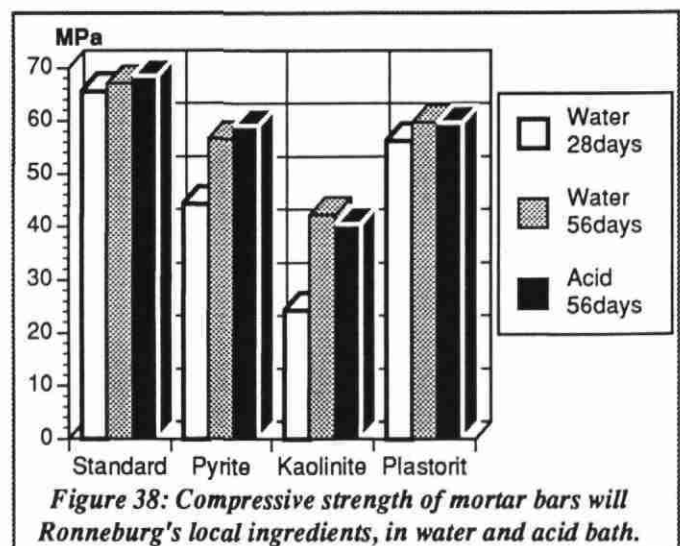
All the tests have been carried out with laboratory geopolymeric binders from type PZ-GEOPOLY. The tests series were split into 2 phases. Phase 1, performed in GEOPOLYMERE laboratory, has determined the basic properties of sand mortars containing these ingredients (Fig. 37a,b). These tests were run with a mortar composition comprising 15% Kaolinite and 7% Pyrite. It is called «Ronneburg».



Phase 2 performed in Geopolymere Cement associate (Heidelberger Zement) consisted on a series of tests on mortar bars (synthetic «Ronneburg aggregates) in order to determine mechanical, physico-chemical properties and durability (chemical corrosion) in acidic medium,  $\text{pH}=2.8$ , after 28 days and 56 days in water bath and/or acid bath. Following mortars were tested

Mortar with sand (see Fig.38):

- 1) Standard;
- 2) with 7% Pyrite;
- 3) with 10% Kaolinite;
- 4) with 5% Plastorit :



Except for the mortar which contains kaolinite, all mortars have properties significantly better than the minimum expected in the Workprogramme. After 56 days, however, kaolinite mortars have reached the expected strength. These tests confirm the exceptional properties of geopolymeric cements in chemically corrosive environments.

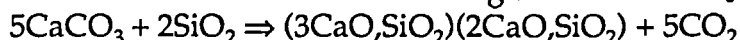
### 3.3.2. CARBUNCULUS Cement with low-CO<sub>2</sub> emission to mitigate «Global-Warming», Task 6, CONCRETE

Task Leader: CORDI-GEOPOLYMERE,  
part subcontracted to Cementi Buzzi (Italy)

planned start:	July, 1995	actual start:	January, 1996
planned end:	November, 1995	actual end:	December, 1996

The production of CARBUNCULUS geopolymeric cements does not require any calcination of calcium carbonate, like it is the case in the manufacture of ordinary Portland Cement which involves the calcination of limestone. Successful accomplishment of the GEOCISTEM project will demonstrate that it is possible to manufacture new cements with low-CO<sub>2</sub> emission during their fabrication, to minimize the «Green House» Global-Warming.

Cement (ordinary Portland cement O.P.C.) results from the calcination of limestone (calcium carbonate) and silico-aluminous material according to the reaction [14]:



The production of 1 tonne of O.P.C. directly generates 0.55 tonnes of CO<sub>2</sub> and requires the combustion of carbon-fuel to yield an additional 0.40 tonnes of CO<sub>2</sub>.

*To simplify: 1 T of Portland cement = 1 T of CO<sub>2</sub>.*

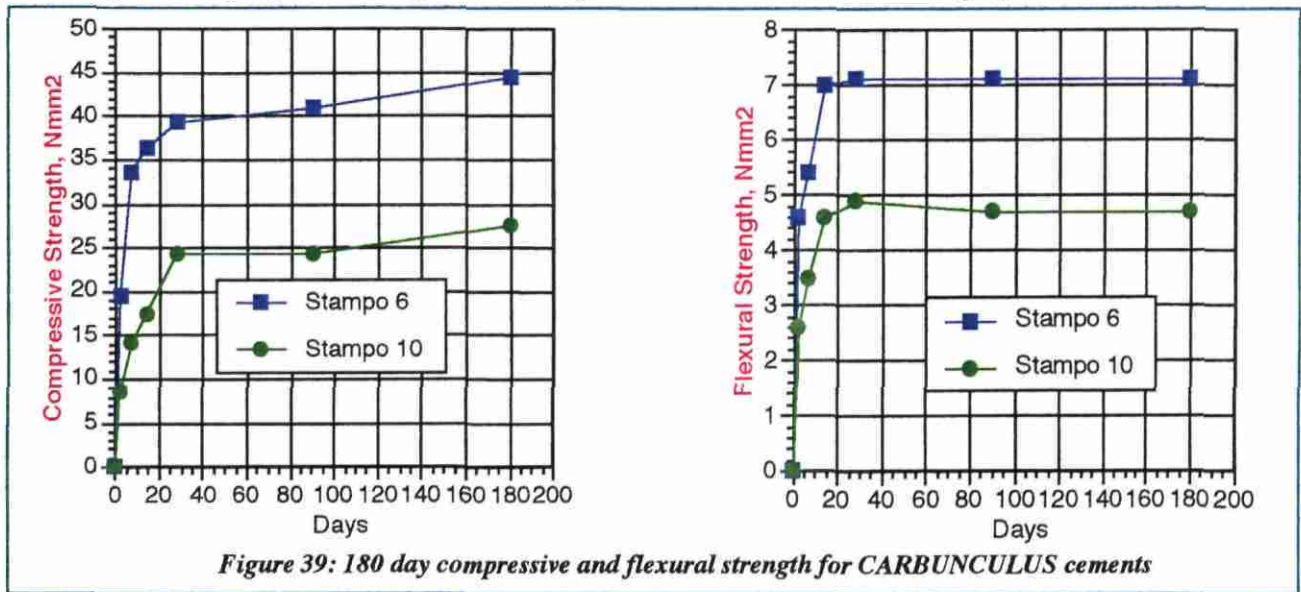
CARBUNCULUS cement, for example batch Stampo n. 6 in Tab. 14, requires the calcination at 800°C for two ingredients, SA07 and Kandoxi. High furnace slag is a by-product that no longer needs any subsequent treatment. The production of 1 tonne of CARBUNCULUS cement generates 0.184 tonnes of CO<sub>2</sub>, from combustion carbon-fuel (see in Tab.18 for calculation). In Tab. 18, the value for K-silicate includes carbon-fuel and chemical-CO<sub>2</sub> produced by the decomposition of K-carbonate. K-silicate produced by reacting KOH and amorphous silica yields lower CO<sub>2</sub> emission .

*Table 18: CO<sub>2</sub> emission during the manufacture of 1 tonne of CARBUNCULUS cement*

Ingredient	heat treatment	CO <sub>2</sub> /tonne of ingredient	CO <sub>2</sub> ratio in 1 tonne of cement
SA07	800°C	0.17 t	0.095 t
Kandoxi	750°C	0.15 t	0.035 t
Slag	-	-	-
K-silicate	1200°C	0.30 t	0.034 t
Energy for grinding	-	-	0.020 t
<b>Total, for 1 tonne of CARBUNCULUS cement:</b>			<b>0.184 t</b>

This low value (0.184 T/tonne of cement) confirms the results of the Background knowledge, based on laboratory formulations [14] and set forth in the GEOCISTEM WORKPROGRAMME on pages 4-5.

Fig. 39 displays the long-term compressive and flexural strength, at 180 days for two



cements, a rapid setting (Stampo 6) and a slow setting (Stampo 10).

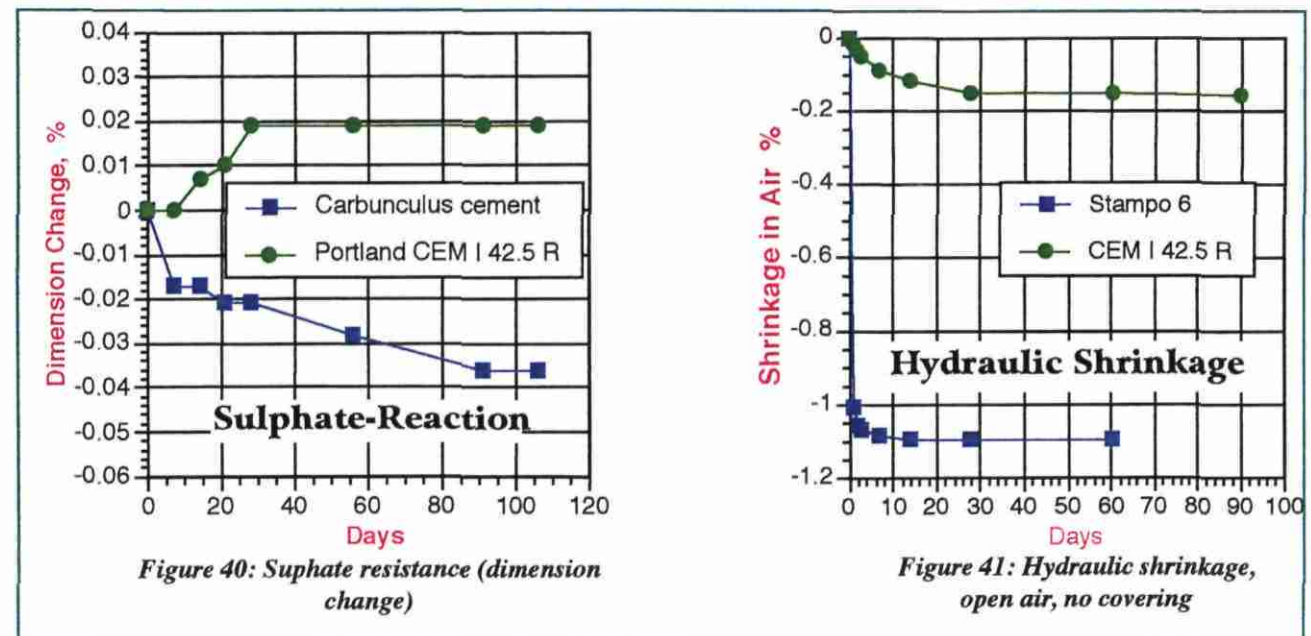
CARBUNCULUS cement of the type Stampo n.6 and a comparative Portland cement from Cement Buzzi (CEM I 42.5 R) were tested together with standardized Portland cement methods.

Sulphate resistance (ASTM C 1012) (Fig. 40)

CARBUNCULUS cement shows no expansion, on the contrary it shrinks slightly. This ASTM Standard prescribes to put the mold, immediately after molding, in a curing tank in water at 35°C / 100% moisture for 24h and to check the compr. strength after 24h, which should be at least 20 MPa to start the Sulphate resistance test. It is interesting to note that CARBUNCULUS cement (Stampo n.6) reaches in this conditions a pretty high compressive strength value (27 N/mm²), even better than the value for Portland CEM I 42.5 R (26 N/mm²).

Length Change (hydraulic shrinkage) (Fig. 41).

Hydraulic shrinkage test mortar bars in standard condition, the same one usually carried out with OPC (hum. 50%, demolding after 1 day of setting, no covering). Carbunculus ce-

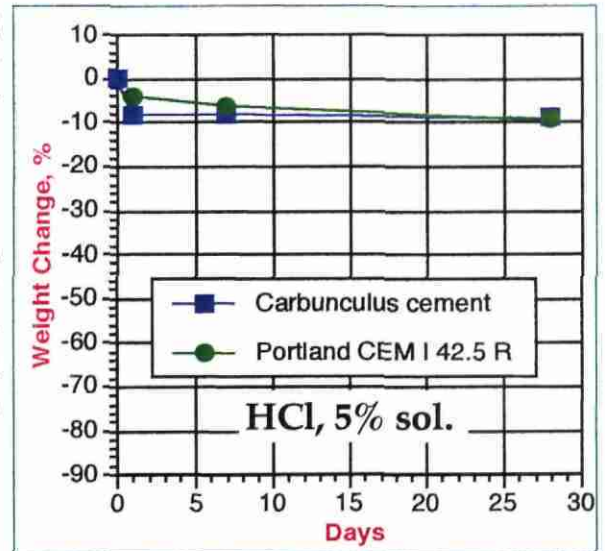


ment is very sensitive to drying conditions during the first day of setting. The cement should be always covered during the first setting days, in order to avoid this type of shrinkage.

#### Chemical corrosion, HCl (Fig. 42)

In addition to the results previously described in chapter 2.3.4.2. (Fig. 16, 17) concerning the very good resistance to Sulphuric acid, comparative testing with HCl 5% solution was carried out on sand mortar. CARBUNCULUS cement is equivalent to the Buzzi cement CEM I 42.5 R .

*Figure 42: Chemical corrosion: HCl, 5% solution after 24 hours hardening*

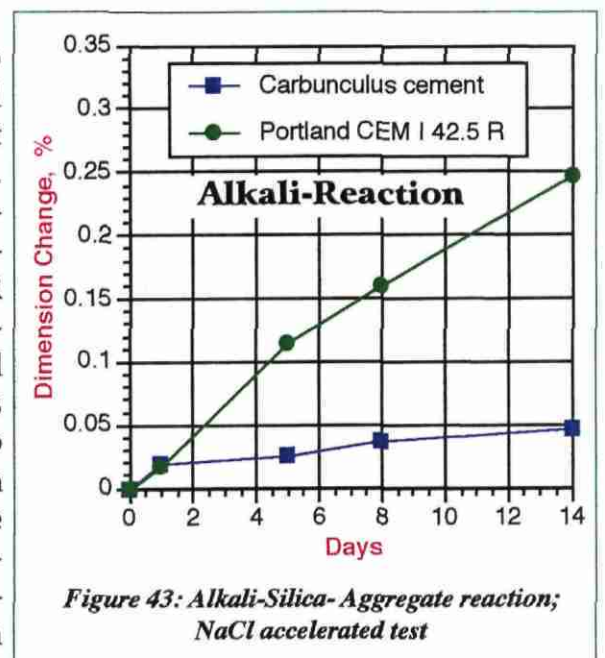


#### Alkali—Silica-Aggregate reaction (Fig. 43) (Task PRENORM 2)

CARBUNCULUS cement contains ca. 10% by weight of alkali  $K_2O/Na_2O$ . This high alkali content poses problem to the concrete industry. It is well known that with Portland cement, any excess in alkali above 1% by weight generates the deleterious Alkali reaction with Silica.

As a consequence, the tendency has been to avoid any addition of alkali in ordinary Portland cement and commonly to require from the cement manufacturers the supply of low-alkali cements. Preliminary studies carried out by CORDI-GEOPOLYMER and associated cement manufacturers, involving  $^{27}Al$  MASNMR and  $^{29}Si$  MASNMR spectroscopy [15], revealed that geopolymeric cements are the synthetic analogues of natural pozzolans which are known to effectively suppress the alkali-aggregate reaction. The chemical make up of geopolymeric cement is close to that of Italian pozzolan and Rhineland trass. Fig.43 displays the results of the tests carried out according to an accelerated expansion test in saturated NaCl bath, developed in Denmark and tested in various Italian cement laboratories, including CEMENTI BUZZI.

The results obtained confirm the good properties of CARBUNCULUS cement, which does not show any expansion in comparison to Portland cement. These results are equivalent to the good results obtained previously in the Background Knowledge on laboratory PZ-GEOPOLY binder (see WORKPROGRAMME, pages 5-6). Geopolymer cements, even with alkali contents as high as 10%, do not generate any dangerous alkali-aggregate reaction.



*Figure 43: Alkali-Silica-Aggregate reaction; NaCl accelerated test*

The fostering of alkali-based CARBUNCULUS cements will mean a dramatic change in the normative development presently carried out on Portland cement related concretes.

### 3.4 Waste Encapsulation on Bentonite:

#### Task 3.2 TOXIC ABSORB and Task 7. TOXIC ENCAP

Task Leader: Laviosa Chimica Mineraria Spa, Athos Rinaldi

planned start:	March 01	actual start:	March 01
planned end:	June 95	actual end:	December 96

This type of applied research was particularly in line with LAVIOSA CHIMICA MINERARIA SPA expertise on high absorbent bentonites treated in different manners (with basis, acids, organic substances) and the knowledge of all clay materials such as kaolinites, sepiolites, attapulgites, expanded materials utilized in different applications such as the building, ceramic and refractories industries.

The GEOCISTEM research began with a preliminary bibliographical study on the different types of liquid wastes that should be taken care of. Following equipment necessary and specific to the research, which were not in LAVIOSA CHIMICA MINERARIA SPA possession, were purchased:

- one homogenising-mixing-extruder by Vicentini-Vicenza
- one Perkin-Elmer atomic absorption spectrometer
- one edometer and triaxial permeameter with accessories afterwards potentiated (1995) by Tecnotest - Modena

A Brookfield viscosimeter was bought later to verify the influence of heavy metals on the colloidal properties of absorbent materials utilized in the Toxic Absorb Task. The Vicentini homogenizer is utilized for a complete mixing of the hazardous liquid with absorbent materials, before granulation; the Perkin Elmer-spectrometer is utilized for the determination of heavy-metals contained in the leachates, while the edometer and the triaxial permeameter are utilized to measure the water permeability in normal conditions, and under pressure, respectively. The water permeability and the heavy metals content are providing data on the treatment efficiency.

The experimental studies to be performed consisted of three separate phases, as summarised below:

- Phase I- Compare absorption capacities with capacities of other absorbents
- Phase II- Pelletization of sorbents with laboratory geopolymeric binders and CAR-BUNCULUS cement.
- Phase III- Toxicity Characteristics Leaching Procedure (TCLP) Characterization

#### Absorption capacity

A percolate solution leaching out of a Land Fill of type B located near Livorno has been used for these preliminary tests. The percolate solution contains following heavy metals:

Ca	25.5	mg/kg
Fe	5.5	"
Mn	10.0	"
Ni	2.3	"
Pb	3.6	"
Cr	24.8	"
Zn	10.0	"
Al	4.8	"

During this Task, a great quantity of absorbent materials were tested, such as:

- smectic clays absorbent materials ( in particular natural, calcic, sodic and activated bentonites), attapulgites, sepiolites,
- volcanic tuffs, expanded clays and other expanded materials such as perlite and vermiculite,
- organophil clays such as smectites exchanged with organic salts capable of better absorption of oily substances and coordinate the heavy metals,
- active coals having high absorbent properties included bad smells one,
- colloidal silica having absorbent and waterproofing properties,
- diatomites and pumices in general, natural and synthetic zeolites.

It is very important to utilize, if it is possible, amorphous substances instead of the crystalline ones, because if they contain free silica they could cause toxicity problems during the process application.

***Experimental:***

Solid material was crushed to a granulometry in the range of 0,5-4,75 mm and soaked in percolate. Powdered material was granulated with a laboratory Eirich RTV/O granulator with rotating tank and reverse current internal mixer. The granulating liquid is the percolate liquid and the granules are in the range of 0,5-4,5 mm.

**The best mixture is the one constituted by**

- 83% of dry activated Bentonite BP 100,
- 15% of pozzolanic cement
- 2% carboxymethylcellulose (CMC).

1 kg of this Bentonite mixture absorbed 750 g of percolate solution, yielding granules of a good consistency, in particular if they are stored during at least 24 hours, because in such a manner, the sodic bentonite starts developing its binding property.

If we evaluate all the 114 tests reported in Annex and the summary in Tab. 7 in Chap. 2.3.3., we note that this mixture is not the one of the best absorbent properties as there are some better ones. For example expanded perlite and vermiculite absorb 2.000 g of liquid per kg of solid, but, because they are very light, they are very difficult to encapsulate with cement. However, a mixture based on sodium bentonite is comparatively cheaper (about 170 Lire/kg.) than expanded materials.

***Encapsulation technique and results***

The encasing operation consists in coating the granules with a resistant waterproof geopolymeric binder or cement. First we had to invent a suitable technology, which mainly consisted in blending the granules at a low velocity (40/70 RPM) with a round grazing propeller, able to move the granules without breaking them, then adding the cement slurry at higher velocity. The granules, once so encased, are submitted to an hot air insufflation, for a quicker hardening of the coating. As already mentioned it was not possible to coat satisfactorily the granules deriving from expanded minerals. On the contrary, all the granules based on smectites, in particular sodium bentonite, combine well with the cement slurry and provide good coated granules with specific weight convenient to be mixed with natural materials such as coarser sand and river gravel, all suitable for the utilization as building blocks or as loose material for road foundations.

The encapsulation parameters were the following:

- 1) Bentonite mix consisting of: 83 % sodium Bentonite BP, 15% pozzolanic cement, 2% CMC);
- 2) granulation with 800g of percolate solution for 1000 g of Bentonite mix, cured for

at least 24 hours or more;

3) coating with GEOPOLYMITE GPZ: 40g of binder for 100g of granule.

The properties of these granules are listed in Tab. 19.

Blocks were made of cylindrical dimension with height 5 cm, diameter 5 cm in the formulation 100/100 GEOPOLYMITE GPZ and granules 35.1. One obtains very high compression strength, superior to 250 kg/cm<sup>2</sup> (41.1) (see Tab. 19).

The same procedure was repeated with CARBUNCULUS cement of the type Stampo n6. This cement hardens too fast and was not usable. We got a slower setting cement of the type Stampo n.10. The granules obtained have very good attrition (7%) quite similar to GEOPOLYMITE GPZ. However, we had problems during the confection of blocks. The material required too much water to work with. Water does slow down the hardening of CARBUNCULUS cement. The 5 day Compressive value are consequently too low. (Tab. 19).

We also compared these two geopolymeric cements with commercialized Portland cements, namely: "Buzzi Pronto", a pozzolanic one manufactured by Sacci Company, and a speedy hardening one manufactured by Italcementi; we noted that their quality are between the CARBUNCULUS sample and the GEOPOLYMITE GPZ, in terms of compressive strength and waterproof properties, but not in terms of the Attrition test, which was always very bad for Portland cement.

*Table 19: Encapsulation test with Geopolymeric cements and Portland cements*

CEMENT TYPE	Attrition % (granules)	Leaching heavy metals (gran)	5day compressive strength, kg/cm <sup>2</sup>	Waterproofing granules
GEOPOLYMITE GPZ	3	0.15 ppm	> 250	++++
CARBUNCULUS (n.10)	7	0.30 ppm	30	--
BUZZI type B	16.5	0.50 ppm	130	+
SACCI (pozzolanic)	24	0.40 ppm	70	--
ITALCEMENTI	18	0.30 ppm	> 250	+

It seems obvious that the process with CARBUNCULUS cement must be optimised and adapted, in order to avoid the high addition of water, which «kills» the short term compressive strength at 5 days.

#### Raw Material Costs

The Bentonite absorbing mixture contains :

83% sodic bentonite - cost in bulk L. 70/kg.

15% pozzolanic cement - cost in bulk L. 100/kg.

2% CMC - cost in bulk L. 1.000/kg.

total cost: L. 196/kg.

1 kg of this mixture absorbs 0,75 kg. of percolate solution; this means that to absorb 1 kg. of liquid one needs 1,330 kg of bentonite mix, i.e. a total cost of L. 260/kg.

100 g of granules are encapsulated with 50 g of GEOPOLYMITE GPZ or 80 g of CARBUNCULUS cement. With the expected cost of 513 FF/tonne for the cement (see Tab. 3 in Chapt. 2.3.1.), i.e. L. 200/kg, this yields a total material cost for inertising 1 kg of percolate solution to L. 460/kg.

To the above cost must be added the industrial costs for thermic and electric power and labour (2 persons manufacturing 5 tons/hour).

### 3.5. Long-term durability diagnosis

#### Tasks PRENORM 1 and 2, LONGTERM 1 and 2

This part of the project involved chemical, archaeological and geological investigations.

- The chemical study dealt with the in depth knowledge of the chemistry mechanism, based on NMR Spectroscopy.
- The archaeological research investigated ancient Roman cements and mortars dating back between the 3rd Century B.C. to the 3rd Century A.D., and compared their make up with CARBUNCULUS cements. Investigation method was essentially NMR Spectroscopy, associated with conventional mineralogical methods.
- The geological part of this long term study was devoted to the chemical behaviour of natural zeolitic elements with chemical composition close to CARBUNCULUS cements, in acid mediums identical to those used for the testing of CARBUNCULUS mortar (see Chapters 2.3.4.2. and 3.3.2.)

#### 3.5.1. Chemistry mechanism. NMR Spectroscopy (Task PRENORM 2)

Task Leader: CORDI-GEOPOLYMERE,  
part subcontracted to NAMUR University (Belgium)

planned start:	June, 1995	actual start:	November, 1995
planned end:	April, 1996	actual end:	December, 1996

The purpose of the study, in terms of long-term stability, is to demonstrate that the end product of the geopolymeric reaction are always high-molecular silicates or alumino-silicates. Low molecular weight silicates would lead to poor stability and weakness, essentially towards acid medium and biodegradability. It is therefore important to follow the reaction steps between each reactive ingredient of the Cement Base, with the geological elements: glass or calcined 800°C.

##### 3.5.1.1. Reaction of K-Silicate ( $K_2O \cdot 1,85SiO_2 \cdot nH_2O$ )

Fig. 44 displays  $^{29}Si$  NMR spectra for the reaction of K-Silicate with SA01 800°C and ES03 800°C., and the correspondent Carbunculus cements. There is no low molecular K-silicate from type SiQ0, SiQ1 or SiQ2 (-70 to -80 ppm range).

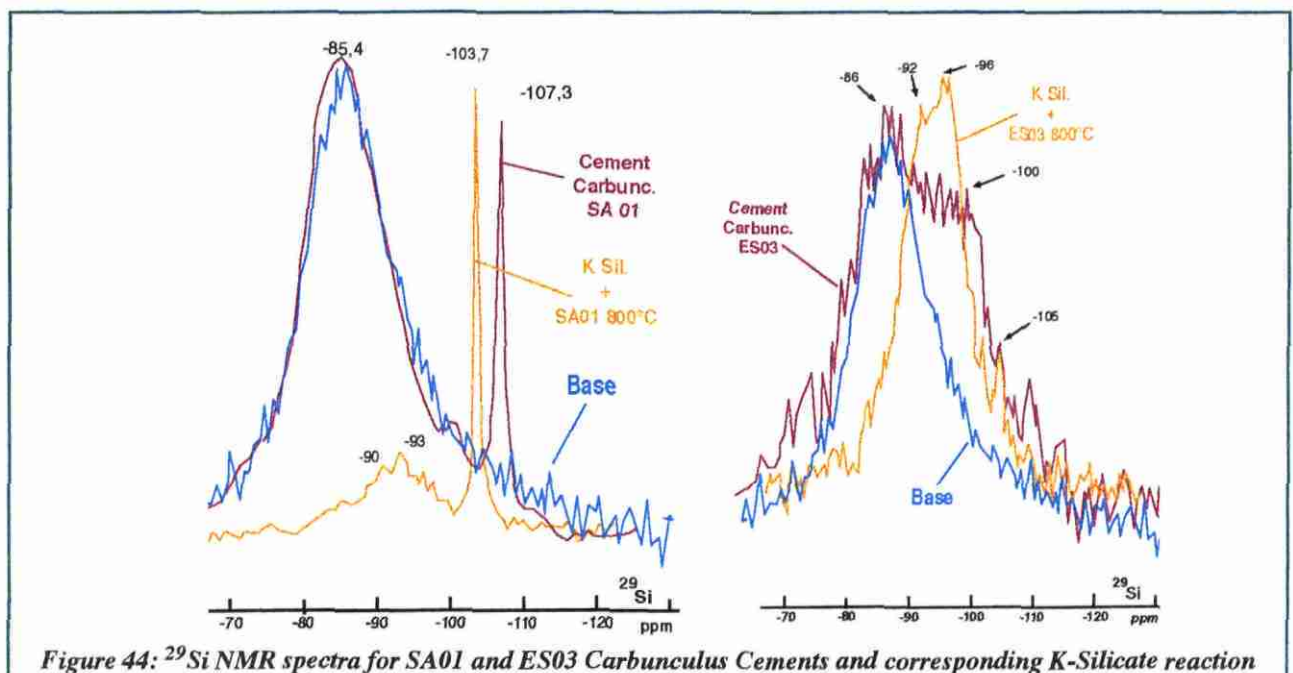


Figure 44:  $^{29}Si$  NMR spectra for SA01 and ES03 Carbunculus Cements and corresponding K-Silicate reaction

Fig. 45 displays  $^{29}\text{Si}$  NMR spectra for the reaction of K-Silicate with glasses LA01 1350°C and GC05 1350°C., and the correspondent Glass cements. There is no low molecular K-silicate from type SiQ0, SiQ1 or SiQ2 (-70 to -80 ppm range).

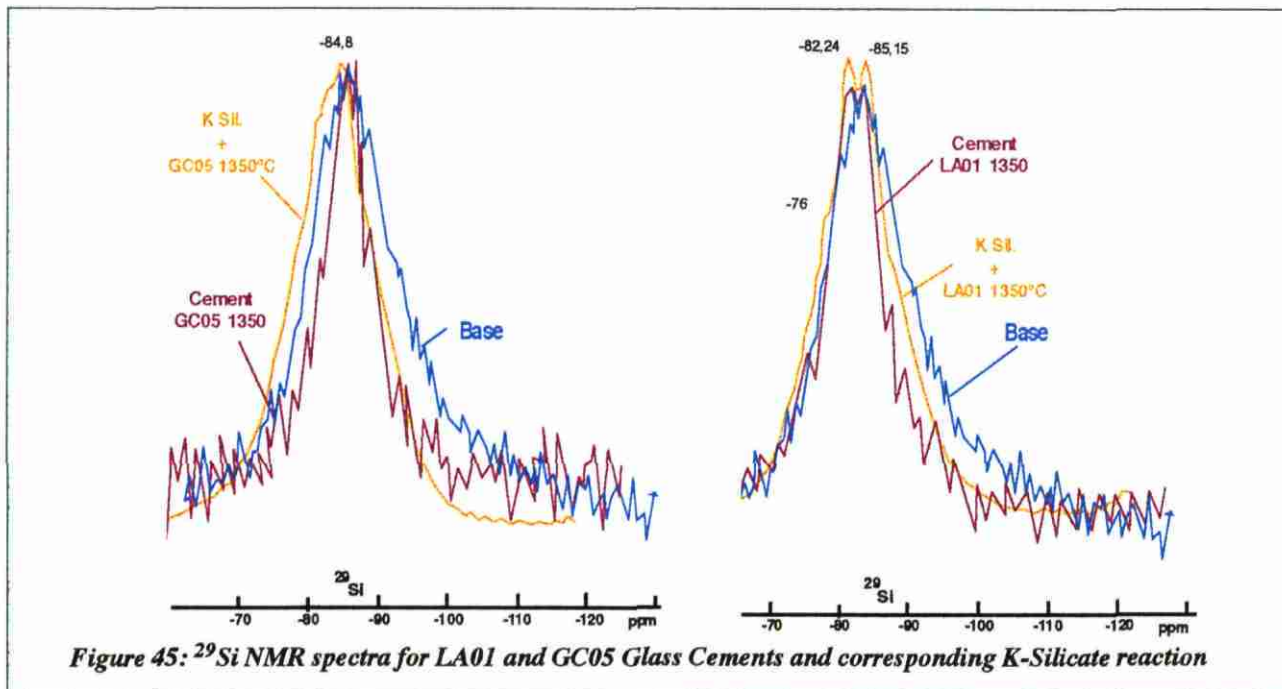


Figure 45:  $^{29}\text{Si}$  NMR spectra for LA01 and GC05 Glass Cements and corresponding K-Silicate reaction

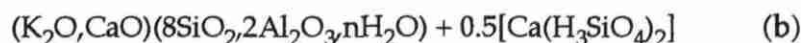
#### 5.3.1.2. Reaction of Kandoxi on Slag+K-Silicate.

Fig. 46 displays the evolution of the alkali activated slag (with K-Silicate) in function of Kandoxi added, namely: 0%, 22%, 36% by weight of the mix slag+K-silicate. The alkali-activated slag shows a main resonance at -82 ppm for a Si(Q2,2OH) low molecular, linear, silicate structure. The addition of Kandoxi generates a shift of the main resonance towards -86, -88 and -92 ppm, for framework silicate structures of the type Si(Q3,1OH) and Si(Q4).

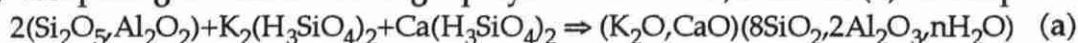
Chemical stability implies a silicate structure from type Si(Q4) found in laboratory GEOPOLYMITE binders of the Background knowledge [3]. In the present Cement Base, even with the addition of 33% Kandoxi, a substantial quantity of Si(Q3,1OH) sites are still present in the structure. The chemical analysis of the hardened Cement Base performed in Task PRENORM 1 by BRGM, provides an explanation. The chemical composition of the vitreous matrix (Chapt. 2.3.5.2.):

$\text{SiO}_2$ : 37%     $\text{Al}_2\text{O}_3$ : 14%     $\text{K}_2\text{O}$ : 7%     $\text{CaO}$ : 6%     $\text{H}_2\text{O}$ : 34%

corresponds to a general formula:  $(\text{K}_2\text{O}, 1.5\text{CaO})(9\text{SiO}_2, 2\text{Al}_2\text{O}_3, 27\text{H}_2\text{O})$  that can also be written:



By comparing it with the basic geopolymeric reaction, formula (a) of Chap. 1



one understands that it is the excess in calcium disilicate  $\text{Ca}(\text{H}_3\text{SiO}_4)_2$  produced by the alkali reaction on the melilitic slag, that might induce the Si(Q3, 1OH) structure.

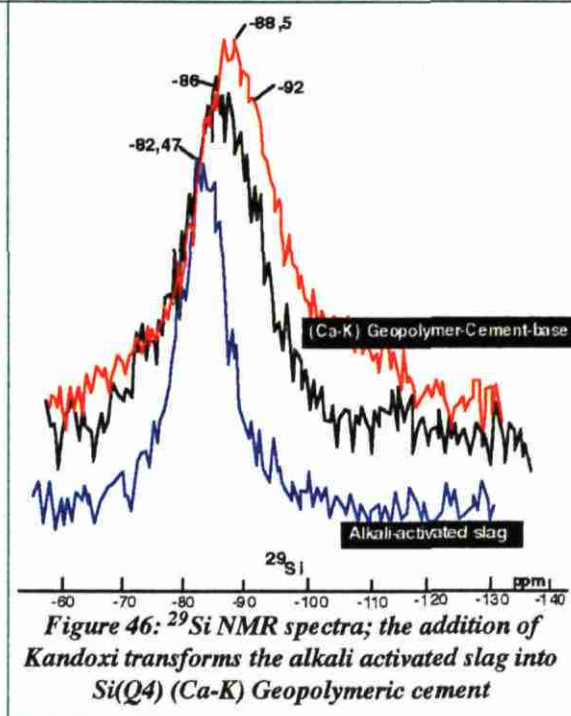


Figure 46:  $^{29}\text{Si}$  NMR spectra; the addition of Kandoxi transforms the alkali activated slag into Si(Q4) (Ca-K) Geopolymeric cement

### 5.3.2. The make-up of ROMAN CEMENTS and their modern counterpart GEOCISTEM Carbunculus cements: NMR Spectroscopy (Task LONGTERM 1 and 2).

Task Leader: CORDI-GEOPOLYMERE ; NMR Spectroscopy performed at NAMUR University (Belgium); Archaeological/Linguistic part subcontracted to CAEN University (France)

planned start:	January, 1995	actual start:	January, 1995
planned end:	April, 1996	actual end:	December, 1996

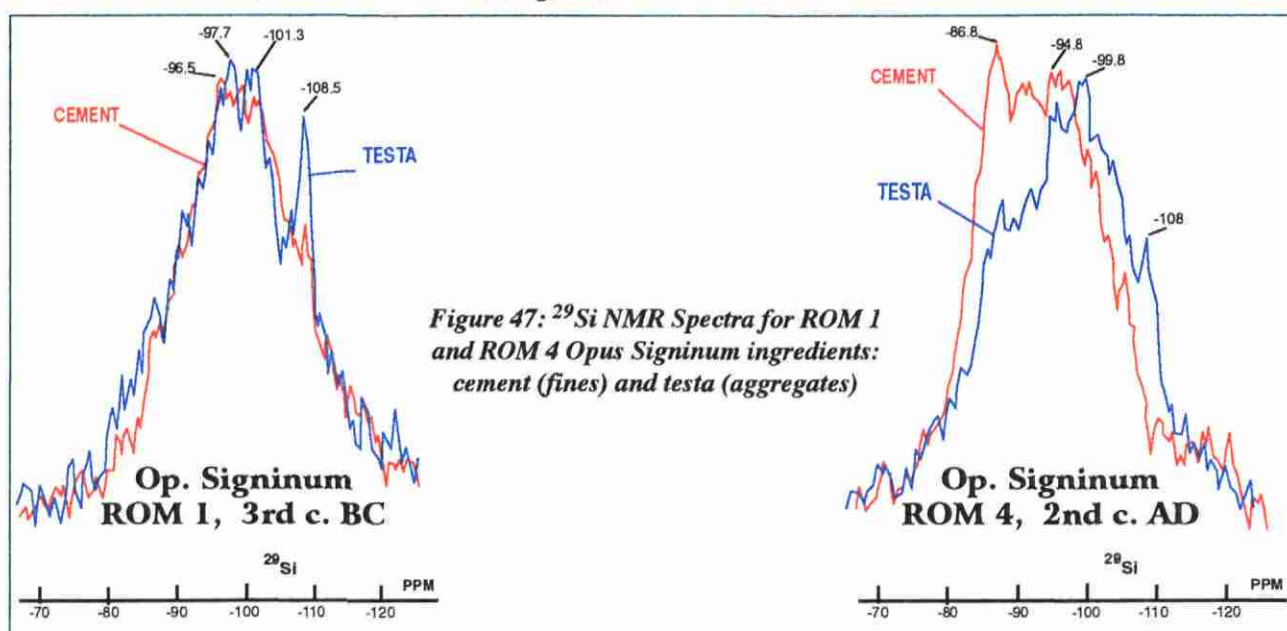
From the digging of ancient Roman ruins, one knows that approximately 95% of the concretes and mortars constituting the Roman buildings consist of a very simple lime cement, which hardened slowly through the precipitating action of carbon dioxide  $\text{CO}_2$ , from the atmosphere. This is a very weak material that was used essentially in the making of foundations and in buildings for the populace. But for the building of their "ouvrages d'art", the Roman architects did not refrain from employing more sophisticated and expensive ingredients. These technologies are described by several ancient authors such as Vitruvius (1. Century BC) and Plinius (1. Century AD). Technical keywords related to these high-performance cements have not been properly understood before recent linguistic studies shed new light and new interpretation on these texts.

#### 5.3.2.1. The first high-performance Roman cement. *Opus Signinum*.

Civil infrastructures, especially works related to water storage (cisterns, aqueducts) required a high-performance material and a special technology. This technology was known under the generic technical term of *Opus Signinum*.

*Opus Signinum* (cf. [Vitruvius](#), Book II, 5,1 and Book VII, 1,3) is obtained by blending crushed and sieved potsherds (in Latin *testa*) with lime, in the proportion of three to one. It yields a high quality plaster that is waterproof and is used to coat the interior of cisterns and aqueducts. According to the Roman author [Plinius](#) (Natural History, Book 35, 165), this technology was recognized as: "..one of the most spectacular invention of mankind.." The ingredient *testa* is a ceramic powder from calcined kaolinitic clay and therefore very close to the KAN-DOXI ingredient.

We selected two *Opus Signinum* samples dating to different epoch: ROM 1 (pavement of Santo Omobono, Rome, 3rd c. BC) and ROM 4 (interior coating of Cistern, Trajan Baths, 2nd. c. AD), and performed  $^{29}\text{Si}$  and  $^{27}\text{Al}$  NMR Spectroscopy on the aggregates (the crushed *testa*) and on the fines (the lime cement) (Fig. 47).





The presence of hydrated gehlinitite in ROM 4 cement is deduced from  $^{27}\text{Al}$  Spectroscopy (Fig. 48). The content in Al(6) in the ROM 4 cement (13%) is three times the content of Al(6) in *testa* (4.5%). The final make-up of ROM 4 cement would be:

- hydrated gehlinitite
- recarbonated lime
- hydrated feldspathoid
- fine grained zeolitic volcanic tuff

Hydrated gehlinitite and hydrated feldspathoid are X-rays amorph. This explains why they are not detected with conventional techniques (see CAGLIARI report in Annex)

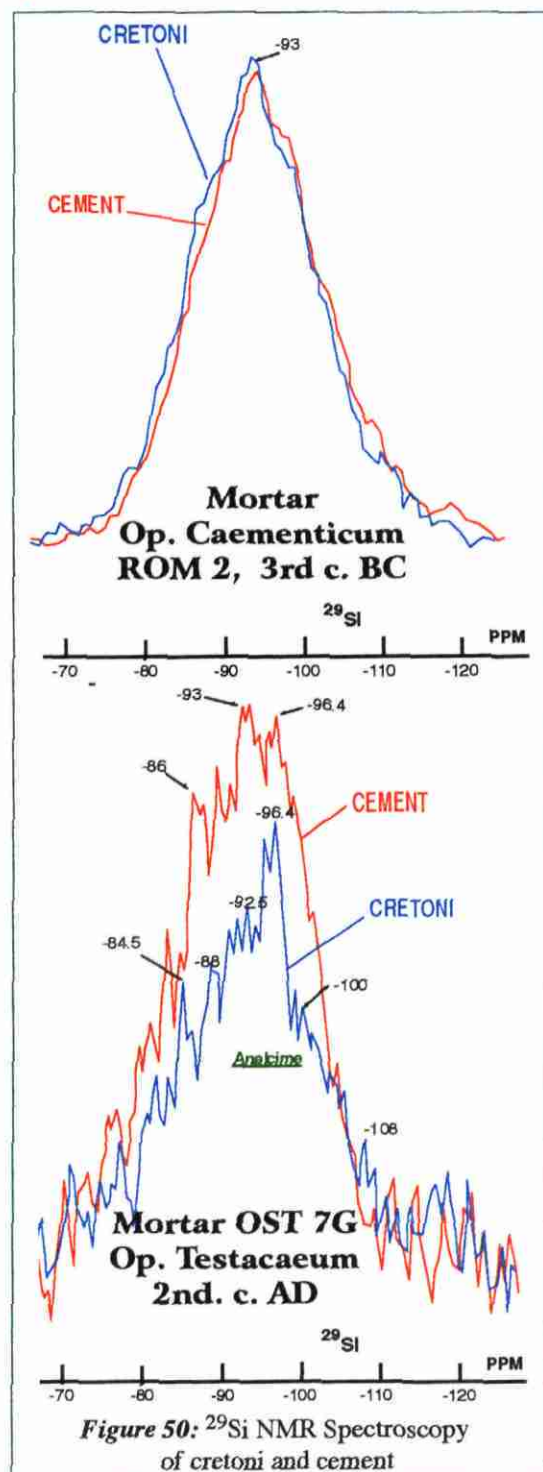
### 5.3.2.2. The second high-performance Roman cement, with *Carbunculus*.

Vitruvius outlines that natural pozzolanic tuffs *harena fossicia* may only be used if they are fresh from the pit (*quae sunt de harenariis recentes*). When lying too long, they cannot bind together the aggregates and the walls and vaults collapse. In modern Italian, *harena fossicia* is designated by archaeologist sometimes by *cretoni*. The mortar of ROM 2, Fig. 50, dating back to the Republican Era, illustrates Vitruvius teaching. The NMR Spectra for *cretoni* and cement are absolutely identical. This means that the silicates in the *cretoni* fines are acting as inert materials, having not participated into any hardening reaction with lime. Hardening of this mortar would have occurred through regular slow recarbonation. There is a general consensus in the literature [18] that the products of the lime-pozzolan reaction are:

- a) hydrated calcium silicate  $\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$
- b) hydrated calcium aluminate  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$
- c) ettringite, calcium sulphate.

ROM 2 cement does not exhibit any low molecular silicate Si(Q1-Q2). However, the difference in Al(6) content (Fig. 48) suggests a remain of hydrated calcium aluminate, i.e. a small chemical reaction.

Another solution for getting high quality hydraulic mortars is provided by *carbunculus*. In Book II, Chapter VI, Vitruvius compares the properties of the true natural pozzolan from the Bay of Naples around Mount Vesuvius (Pozzuoli), with those of *carbunculus*, a calcined stone from Etruria (North of Rome) (*sic in Etruria excocta materia efficitur carbunculus*). Both are excellent for concrete structures, yet *carbunculus* has advantages in buildings on land, whereas true pozzolan is best for piers built into the sea. We have seen, above that the reaction of lime with alkaline pozzolan yields a soluble alkaline silicate. We have previously shown that the  $^{29}\text{Si}$  NMR spectrum OST 7G cement is equivalent to the one of the LA01 GEOCIS-TEM Carbunculus cement (Fig. 21 in Chap. 2.3.5.2.). OST 7G mortar (Fig. 50) results from the reaction between lime and analcime type *cretoni*. The product of



this reaction is an alumino-silicate of type Si(Q3Si, 1OH) and Si(Q4Si) (-86 ppm to -94 ppm range) different from those expected with regular pozzolan. There is no hydrated gehlinites in OST 7G cement deduced from  $^{27}\text{Al}$  Spectroscopy (Fig. 45). The content in Al(6) in the OST 7G cement (3%) is equal to the content of Al(6) in *cretoni* (3%). The final make-up of OST 7G cement would be:

- recarbonated lime
- hydrated feldspathoid
- fine grained zeolitic volcanic tuff

Hydrated feldspathoid is X-rays amorph. This explains why it was not detected with conventional techniques (see CAGLIARI report in Annex)

### Conclusion:

The two archaeological analogues ROM 4 and OST 7G display NMR spectra similar to those of GEOCISTEM Carbunculus cements. They also have Si(Q3Si, 1OH) (-86 ppm) and Si(Q4Si) (-90 ppm) sites. This would suggest archaeological long-term durability for all GEOCISTEM Carbunculus cements. From an ingredient make-up point of view, we can also state that the archaeological equivalent for the GEOCISTEM Carbunculus cement is the *Opus Signinum* lime-mortar, provided its *testa* does contain a zeolitic temper (analcime-phillipsite type). However, GEOCISTEM cements are acid-resistant because they do not contain any calcium carbonate.

### 5.3.3. Zeolitic GEOLOGICAL Analogues (Task PRENORM 1).

Task Leader: B.R.G.M., Philippe Rocher

planned start:	June, 1995	actual start:	November, 1995
planned end:	April, 1996	actual end:	March, 1997

#### - Laboratory work:

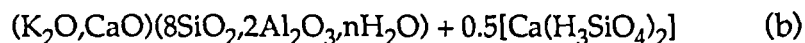
- mineralogical and texturological investigations of SA07 Carbunculus cement and zeolitic analogues described in Chapter 2.3.5.3.
- simulating alteration tests aimed at determining the most physico-chemical corrosive conditions: acid medium and bio-lixivation

#### 5.3.3.1. Mineralogical characterization:

Tab. 30 lists the mineralogical make-up of Cement Base; SA07 cements (calcined SA07 and Natural SA07) and the zeolitic analogues CHTCO, CHIMM and LA02. The chemical analysis of the hardened Cement Base was discussed previously in Chap. 5.3.1.2. in connection with the geopolymeric chemistry of the Cement Base. The chemical composition of the vitreous matrix

$\text{SiO}_2$ : 37%     $\text{Al}_2\text{O}_3$ : 14%     $\text{K}_2\text{O}$ : 7%     $\text{CaO}$ : 6%     $\text{H}_2\text{O}$ : 34%

corresponds to a general formula:  $(\text{K}_2\text{O}, 1.5\text{CaO})(9\text{SiO}_2, 2\text{Al}_2\text{O}_3, 27\text{H}_2\text{O})$  that can also be written:



In the Cement Base this tecto-aluminosilicate composition corresponds to the Chabazite/Phillipsite zeolites of the natural analogues CHIMM and LA02 and is not very far from the Heulandite in the sample CHTCO.

#### 5.3.3.2. Alteration tests of Geological analogues in acid medium.

The experimental method involved the acid resistance in HCl and  $\text{H}_2\text{SO}_4$  solution at 5% (see in Chapt. 2.3.5.3.), namely weight loss, pH, conductivity and cation leachate, at 7, 14, 21 and 28 days.

N° ECHANTILLON (ROCHE)	FRACTION VITREUSE AMORPHE AUX RAYONS X	ZEOLITES	FELDSPATHS	SILICE	CARBONATES	AUTRES
230996 A (BASE)	TA (matrice hydratée et mélilites)		orthose : Tr	quartz : Tr	calcite : Tr	hydroxydes de fer : Tr sillimanite : Pr
230996 B (SA07 cal.)	P (≥50%) : matrice hydratée et mélilites		sanidine + microcline et plagioclase / albite-oligoclase : P	crystalbite : P tridymite + quartz : It	calcite : It	hydroxydes de fer : Tr
230996 C (SA07 nat.)	P (≥50%) : matrice hydratée et mélilites		sanidine + orthose et plagioclase / albite-oligoclase : P	crystalbite : P tridymite : Tr	calcite : It	hydroxydes de fer : Tr
CHTCO	P	clinoptilolite : A heulandite : F	sanidine : Tr plagioclase : F	quartz : It		illite : Tr / F
CHIMM	P	chabazite : A phillipsite : It	sanidine : P / A plagioclase : F / Tr			mica ou illite : Tr
LA 02	P	chabazite : A phillipsite : Tr	sanidine : P plagioclase : P			clinopyroxène : F leucite : F mica ou illite : Tr serpentine : P

Echelle d'abondance relative :

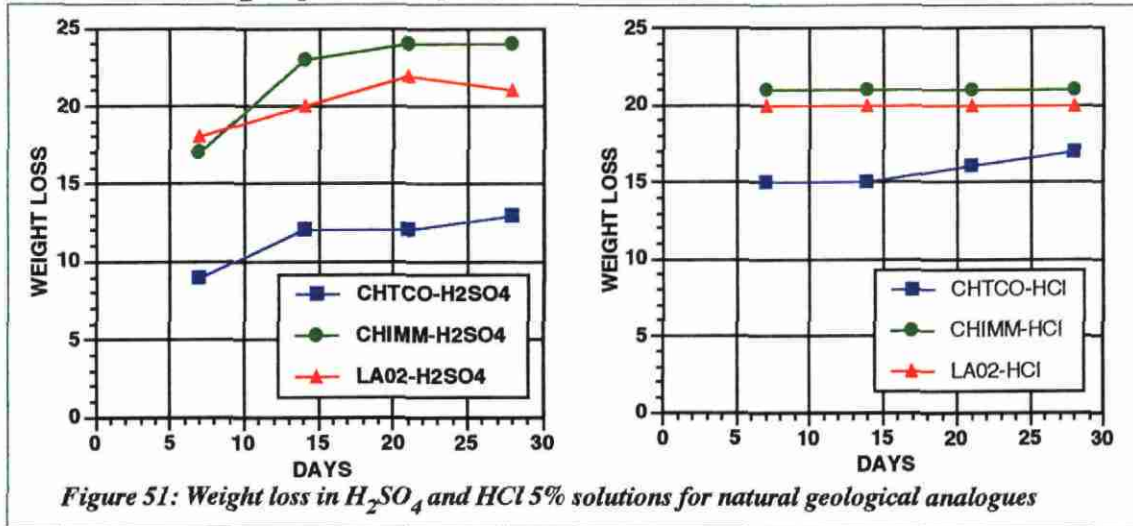
TA - Très Abondant  
A - Abondant  
P - Présent

F - Faible  
Tr - Traces  
Pr - Probable

It - Infra-traces

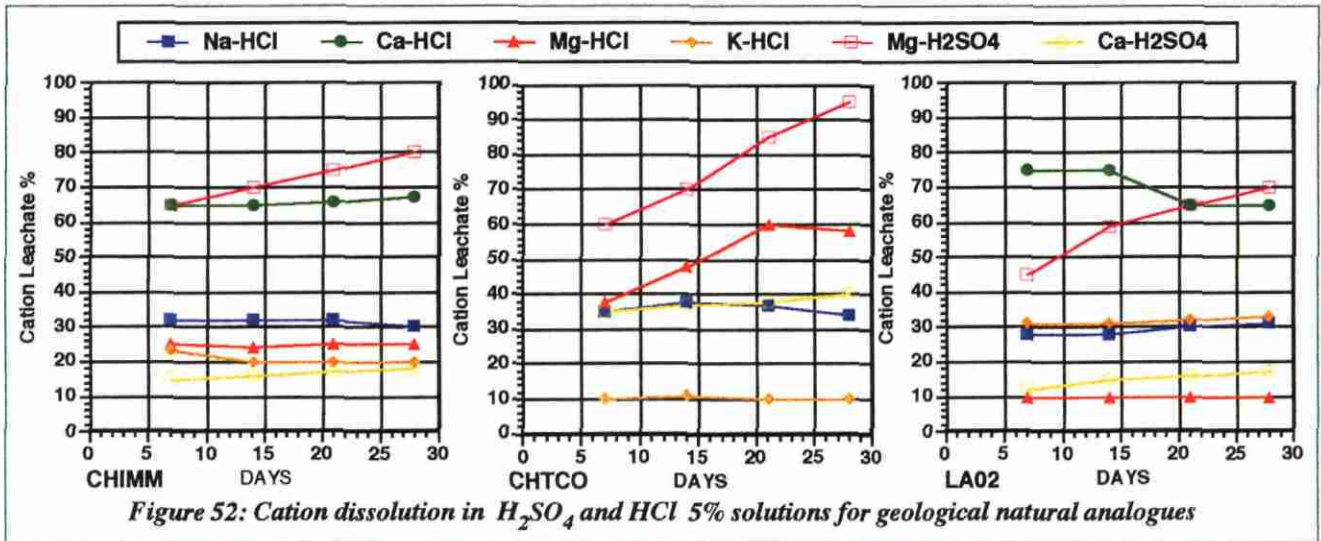
Table 30: Mineralogical composition of SA07 GEOCISTEM Cabunculus Cements and Cement Base, and selected natural geological analogues.

Weight losses in HCl and H<sub>2</sub>SO<sub>4</sub> solutions are plotted in Fig. 51. The attack in HCl is happening straight at the beginning and then stops. It seems that the chlorides are building a protective coating around the zeolites, preventing the material from a complete degradation. On the contrary, H<sub>2</sub>SO<sub>4</sub> attack is progressive. These results are similar to those claimed



in the Background knowledge and related with the acid resistance of pure geopolymer (zeolitic framework). See for example in the WORKPROGRAMME, Fig. 9, page 6. []

A comparison between the cation leachates (Fig. 52) emphasizes the deleterious role of the cation Mg in sulphuric medium and of the Ca cation in chlorhydric medium.



These findings confirm the Background knowledge pertaining to the safe trapping of heavy metals into the zeolitic framework, with the exception of the cation Mg (see Fig. 2, in Chapt. 1) [1, 2].



## **4. Achievements**

### **Comparison of Initially Planned Activities and Work Actually Accomplished**

#### **4.1 Achievements**

The expected achievements were (see WORKPROGRAMME, page 3):

- a) industrial applications for an unused mineral resource, volcanic tuffs.
- b) cheaper acid resistant zeolitic cements (geopolymeric cements).
- c) methods for encapsulation and containment of hazardous wastes involving absorption of the hazards in sorbents (bentonites, zeolites, vermiculites) and coating with geopolymeric cement.
- d) concretes for safe cleanup of contaminated mining sites and chemical processing sites.

Points a, b, c, have been achieved. The concrete of point (d) was developed but not tested on the mining site. Additional achievements were successfully performed namely:

- e) cements with very low CO<sub>2</sub> emission
- f) archaeological analogues detected in two ancient Roman cements (2nd.c. AD)
- g) geological analogues tested with natural zeolitic materials.





Accomplished work:

The Consortium selected the SA07 outcrop in Sardinia, Paringianu, near Sulcis.

**Task n° 6 : CONCRETE, geopolymeric concretes, barriers, cappings, walls.**  
**CORDI-GEOPOLYMERE and WISMUT**

Developing geopolymeric concretes to be used in the construction of acid-resistant geological barriers, cappings, walls and also borehole-plugging and shaft-sealing systems. Emphasis is to made on the use of local aggregates and of contaminated soils.

Task	Name	2, 1995		Qtr 3, 1995			Qtr 4, 1995			Qtr 1, 1996			Qtr 2, 1996			Qtr 3, 1996			Qtr 4, 1996			Qtr 1, 1997	
		May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb
6.0	CONCRETE																						80%

Accomplished work:

This task was reorganized because of WISMUT's default. Major target: comparison with regular Portland Cements; Low-CO<sub>2</sub> cements for regular concrete use.

**Task n° 7: TOXIC ENCAPS processing of geological materials to increase toxic absorption.**  
**LAVIOSA**

The purpose of the study is to provide pilot-scale quantities of sorbents, and to saturate them with various toxic elements, for subsequent pilot encapsulation, pelletisation or solidification of saturated sorbents.

Task	Name	2, 1995		Qtr 3, 1995			Qtr 4, 1995			Qtr 1, 1996			Qtr 2, 1996			Qtr 3, 1996			Qtr 4, 1996			Qtr 1, 1997	
		May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb
7	TOXIC ENCAPS																						100%

Accomplished work:

Pelletisation with new CARBUNCULUS cement, comparison with GEOPOLYMERIC binders and Portland cement.

**Task n° 8 : ONSITE**  
**CORDI-GEOPOLYMERE, WISMUT, LAVIOSA**

The purpose is to follow the evolution of the physical, mechanical and physico-chemical properties of:

- encapsulated or solidified radioactive waste and other hazards/sorbent materials,
  - concrete materials in form of barriers, caps, walls or dams,
- disposed of and built on the contaminated uranium site of WISMUT, over a period of approx. 1 year.

Task	Name	Qtr 4, 1995			Qtr 1, 1996			Qtr 2, 1996			Qtr 3, 1996			Qtr 4, 1996			Qtr 1, 1997			Qtr 2, 1997		Qtr	
		Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul
8.0	ONSITE WISMUT																						100%

Accomplished work:

Task involving LAVIOSA on WISMUT's site was cancelled. Task with CORDI-GEOPOLYMERE was rediscussed at the end of the project, in preparation of the application sets forth in Exploitation Report.

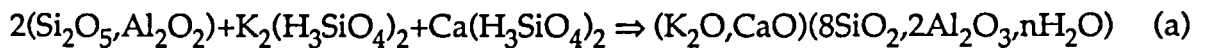






## 5. Conclusion

Regular geopolymeric advanced binders produced at laboratory scale (costs approx. 3-4 FF/kg) are too expensive for mass application. They comprise three ingredients namely: expensive potassium silicate, calcined kaolinite clay (KANDOXI), and cheap blast furnace slag. The chemical reaction



yields a rapid-setting inorganic geopolymeric binder.

### 5.1 Replacement of K-Silicate

The GEOCISTEM project was aimed at manufacturing cost-effectively these geopolymeric cements at a cost in the range of 0.5-0.7 FF/kg. The development of these new geopolymeric cements was based on the replacement of the very expensive K-silicate, with a selection of cheap high alkali volcanic tuffs. It has been demonstrated that a minimum amount of K-Silicate is always necessary in order to provide physico-chemical properties closed to the original experimental geopolymeric binders of the Background knowledge. For practical applications, the K-silicate content would range between 4-9%, down from 25%, with an optimum around 8% by weight of the dry compound. The geopolymeric cement of the type CARBUNCULUS SA07 tested at the Cement Laboratory at CEMENTI BUZZI, Italy, comprised:

geological elements (Kandoxi+SA07)	68-76%
Iron blast furnace slag	20-23%
K-Silicate	4-9 %

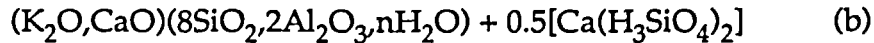
The unique properties of the expensive experimental Geopolymeric Binders of the Background knowledge are found in this new cheaper cements, namely: high early strength, sulphate resistance, corrosion resistance to sulphuric acid, no Alkali-Aggregate-Reaction, which make them ideal for long term containment. Testing involved comparative sand mortar standard methods with Portland cement (type I 42.5 R from Cementi Buzzi) and CARBUNCULUS cement from the SA07 sample in Sardinia. A study determined the best possible uses for geopolymeric cements in the cleanup of polluted mine tailings sites (uranium mine tailing at the German WISMUT site), and decantation ponds. Another study dealt with regular concrete applications.

## 5.2 Chemistry mechanism; MAS-NMR Spectroscopy

The chemistry mechanism was studied by the means of the very powerful Magic Angle Solid State Nuclear Magnetic Resonance Spectroscopy (MAS-NMR) of  $^{29}\text{Si}$  and  $^{27}\text{Al}$ . Both NMR spectra indicates that CARBUNCULUS cements comprise two separate phases: a vitreous matrix Base and a crystalline geological «carbunculus» phase. The chemical composition of the vitreous matrix :

$\text{SiO}_2$ : 37%    $\text{Al}_2\text{O}_3$ : 14%    $\text{K}_2\text{O}$ : 7%    $\text{CaO}$ : 6%    $\text{H}_2\text{O}$ : 34%

corresponds to a general formula:  $(\text{K}_2\text{O}, 1.5\text{CaO})(9\text{SiO}_2, 2\text{Al}_2\text{O}_3, 27\text{H}_2\text{O})$  that can also be written:



that is the basic geopolymeric reaction, formula (a) above with an excess in calcium disilicate  $\text{Ca}(\text{H}_3\text{SiO}_4)_2$  produced by the alkali reaction on the iron blast furnace slag. Both ingredients, matrix Base and geological «carbunculus», react only at the interfaces, yielding high strength. This confirms previous data pertaining to the Background knowledge. The resulting structure of the Matrix base belongs to the tecto-alumino-silicate  $\text{Si}(\text{Q}3, 1\text{OH})$ - $\text{Si}(\text{Q}4)$  types and the good properties of the CARBUNCULUS cements are essentially those provided by the geopolymeric Base reaction (a). Geological elements are reacting at the interface between Base and grain surface.

## 5.3 Long-term durability diagnosis

Two long-term durability studies of these new cements were performed.

a) the first research involved an archaeo-linguistic study based on Latin texts, for example *De Architectura* by Vitruvius, followed by a selection of Roman cements and mortars in Rome and Ostia dating from the 3rd c. BC to the 3rd c. AD. Archaeological analogues are based on the calcic activation of alkali rich volcanic tuffs, with lime. The excess of unreacted lime recarbonates slowly into Ca-Carbonate. Conventional mineralogical analysis does not provide satisfactory explanation. Yet, owing to the powerful MAS-NMR Spectroscopy investigation of these archaeological cements, one was able to distinguish two archaeological Roman cement analogues, dating to the 2nd. c. AD. The two archaeological analogues ROM 4 (*Opus Signinum* coating from the interior of a water cistern, Trajan Baths, Rome) and OST 7G (brick mortar, Capitulum, Ostia) display NMR spectra similar to those of GEOCISTEM Carbunculus cements. They also have  $\text{Si}(\text{Q}3\text{Si}, 1\text{OH})$  (-86 ppm) and  $\text{Si}(\text{Q}4\text{Si})$  (-90 ppm) sites. This would suggest archaeological long-term durability for all GEOCISTEM Carbunculus cements. From an ingredient make-up point of view, we can also state that the archaeological equivalent for the GEOCISTEM Carbunculus cement is the *Opus Signinum* lime-mortar, provided its *testa* does contain a zeolithic temper (analcime-phillipsite type). However, contrary to the Roman lime-based cements, GEOCISTEM cements are acid-resistant because they do not contain any calcium carbonate.

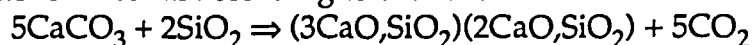
b) the second study focused on geological analogues. Structural characterization of geopolymeric binders, cements, high-tech materials by means of  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS-NMR Spectroscopy, in the Background knowledge of GEOPOLYMERE and in this present research, demonstrated tecto-aluminosilicate type frameworks, which are similar to those of natural zeolithic geological materials. Zeolithic analogues provide acid resistance and bio-lixivation behaviour.; for example, the most soluble cation in  $\text{H}_2\text{SO}_4$  medium is Mg. Therefore, Mg content in Cement Base and in volcanic tuffs, is determinant in the  $\text{H}_2\text{SO}_4$  resistance of GEOCISTEM cements. Concerning bio-lixivation, bacteria found in base metal mining sites are of the *Thiobacillus ferrooxydans* and the *Thiobacillus thiooxydans* types. These bacteria are essentially pH sensitive, i.e. they require a pH close to 1.7. It can therefore be stated that, as long as the pH of any material encapsulated with GEOCISTEM cement, remains higher than 1.7, say higher than 3, there should be no risk of any Bio-Lixivation of this type.

#### 5.4 Applications in Waste Management

The experimental geopolymeric binders and CARBUNCULUS cements were tested for their use in Waste management applications and Ecology. One study provides a valuable inertization method of toxic liquid (heavy metals) by absorption and subsequent encapsulation. Best results, with respect to absorption and encapsulation are obtained with Na-modified bentonites that absorb up to 850 g of liquid per 1 kg of bentonite. Pelletisation, coating and inertization was achieved with experimental GEOPOLYMERIC binders and the selected CARBUNCULUS cement. The results are compared with Portland cement coating. The best results are provided by laboratory GEOPOLYMERIC binders, followed by CARBUNCULUS cement, with respect to attrition behaviour.

#### 5.5 Applications to Global Ecology (Global Warming)

The production of CARBUNCULUS geopolymeric cements does not require any calcination of calcium carbonate, like it is the case in the manufacture of ordinary Portland Cement which involves the calcination of limestone. Successful accomplishment of the GEOCISTEM exemplifies the theoretical studies of the Background knowledge and demonstrates that it is possible to manufacture new cements with low-CO<sub>2</sub> emission during their fabrication, to minimize the «Green House» Global-Warming. As a mean of comparison, cement (ordinary Portland cement O.P.C.) results from the calcination of limestone (calcium carbonate) and silico-aluminous material according to the reaction:



The production of 1 tonne of O.P.C. directly generates 0.55 tonnes of CO<sub>2</sub> and requires the combustion of carbon-fuel to yield an additional 0.40 tonnes of CO<sub>2</sub>.

To simplify: 1 T of Portland cement = 1 T of CO<sub>2</sub>.

On the opposite, CARBUNCULUS cement only requires the calcination at 800°C for two geological ingredients, Carbunculus and KANDOXI. High furnace slag is a by-product that no longer needs any subsequent treatment. The production of 1 tonne of CARBUNCULUS cement generates 0.184 tonnes of CO<sub>2</sub>, from combustion carbon-fuel, to be compared with 1.00 tonnes of CO<sub>2</sub> for Portland Cement. Carbunculus cement generates five (5) times less CO<sub>2</sub> during manufacture than Portland Cement. This simply means that, in newly industrializing countries, five (5) times more cement for infrastructure and building applications might be manufactured, for the same emission of Green House gas CO<sub>2</sub>.

The geological study and mineralogical research on volcanic tuffs selected resources with high economic potentiality. A series of 10 geological materials from continental Italy, Sardinia, continental Spain and the Canary Islands was selected providing a wide range in mineralogical make-up. Interesting potential resources are found in other E.U. Countries, suggesting that the Low-CO<sub>2</sub> geopolymeric cements of the CARBUNCULUS types can be manufactured on all continents, using a cheap mineral resource.

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### GEOCISTEM Documents and Confidential Reports

*Patent Application:* Méthodes de fabrication de ciments géopolymériques et ciments obtenus par ces procédés, assigned to CORDI-GEOPOLYMER SA, patent application FR 97-00332.

*Trademark:* CARBUNCULUS Cement™, assigned to CORDI-GEOPOLYMER SA

#### Geology reports:

*Notes Complémentaires relatives à la tâche GEOPROSPEC-1*, by P. Rocher, D. Domingo, C. Marini and S. Tocco, April 1997

*Final Report GEOPROSPEC-2*, by P. Rocher, D. Domingo, C. Marini and S. Tocco, April 1997

### Geological Analogues:

*Final Report PRENORM 1*, by P. Rocher, C. Crouzet and J.F. Brunet, BGRM, April 1997.

### Archaeological Analogues:

*Tâches LONGTERM 2, Caracterisation des mortiers de Rome et Ostia*, by C. Marini and S. Tocco, March 1997

*Annexes to Final Report, Tasks LONGTERM-1, LONGTERM-2*, by J. Davidovits and F. Davidovits, April 1997.

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## Acknowledgement

- MAS-NMR Spectroscopy was performed at NAMUR UNIVERSITY, Belgium, Department of Chemistry, by Zelimir Gabelica and his team.
- Mortar and Concrete testing was carried out at CEMENTI BUZZI Laboratory, Trino, Italy, by Luiggi Buzzi and his team.
- The selection of ancient Roman Mortars in Rome, Italy, was directed by Dot.saa Sartorio, Director MUSEO DELLA CIVITA ROMANA, Rome.
- Discussions on WISMUT's applications involved:
  - at WISMUT GmbH, Dr. Hagen, Dr. Kiessig
  - at HEIDELBERGER ZEMENT, Dr. Schmidt, Ing. Vogel and Ing. Boeing

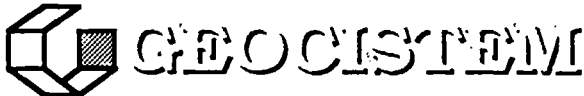
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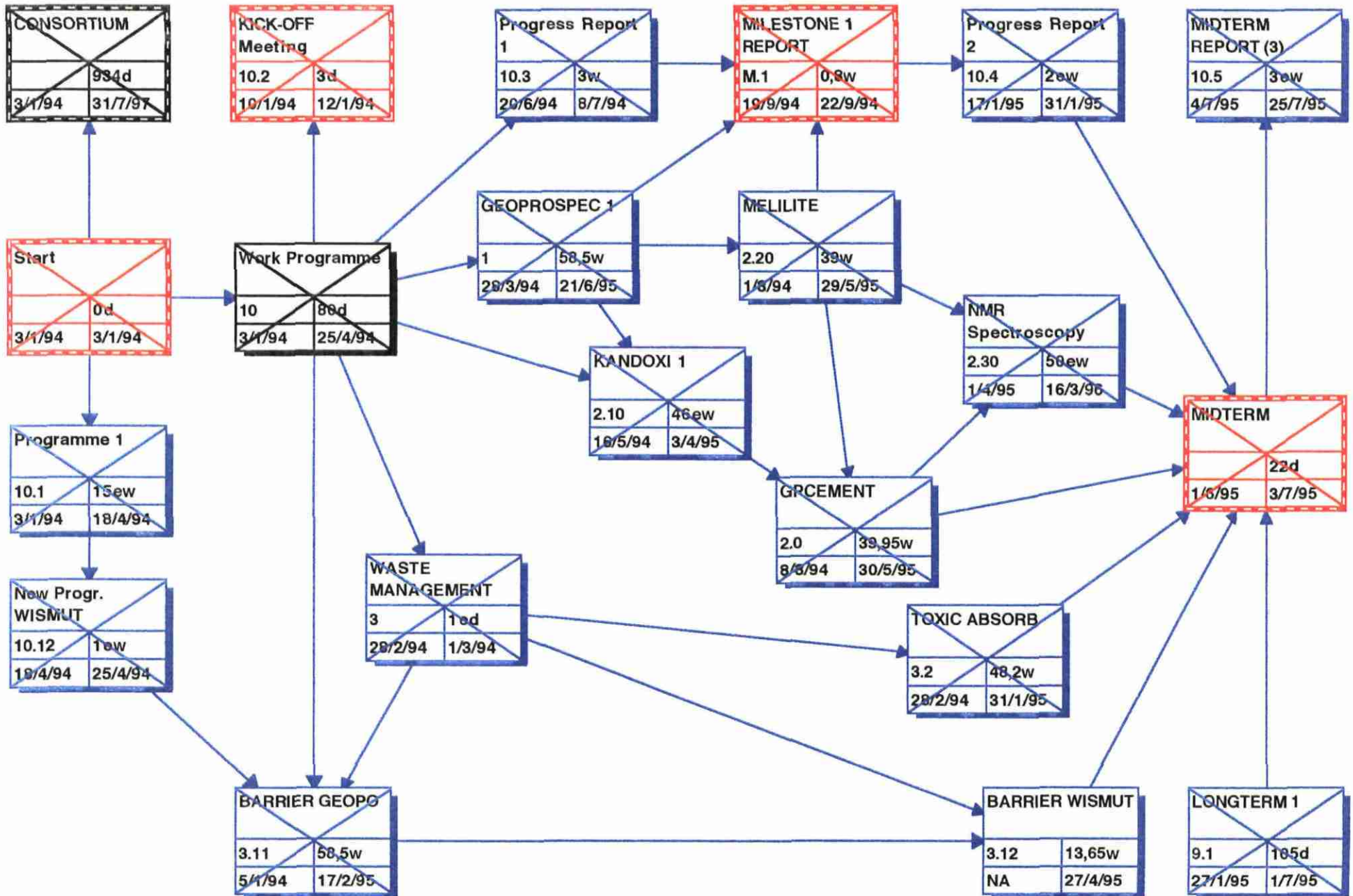
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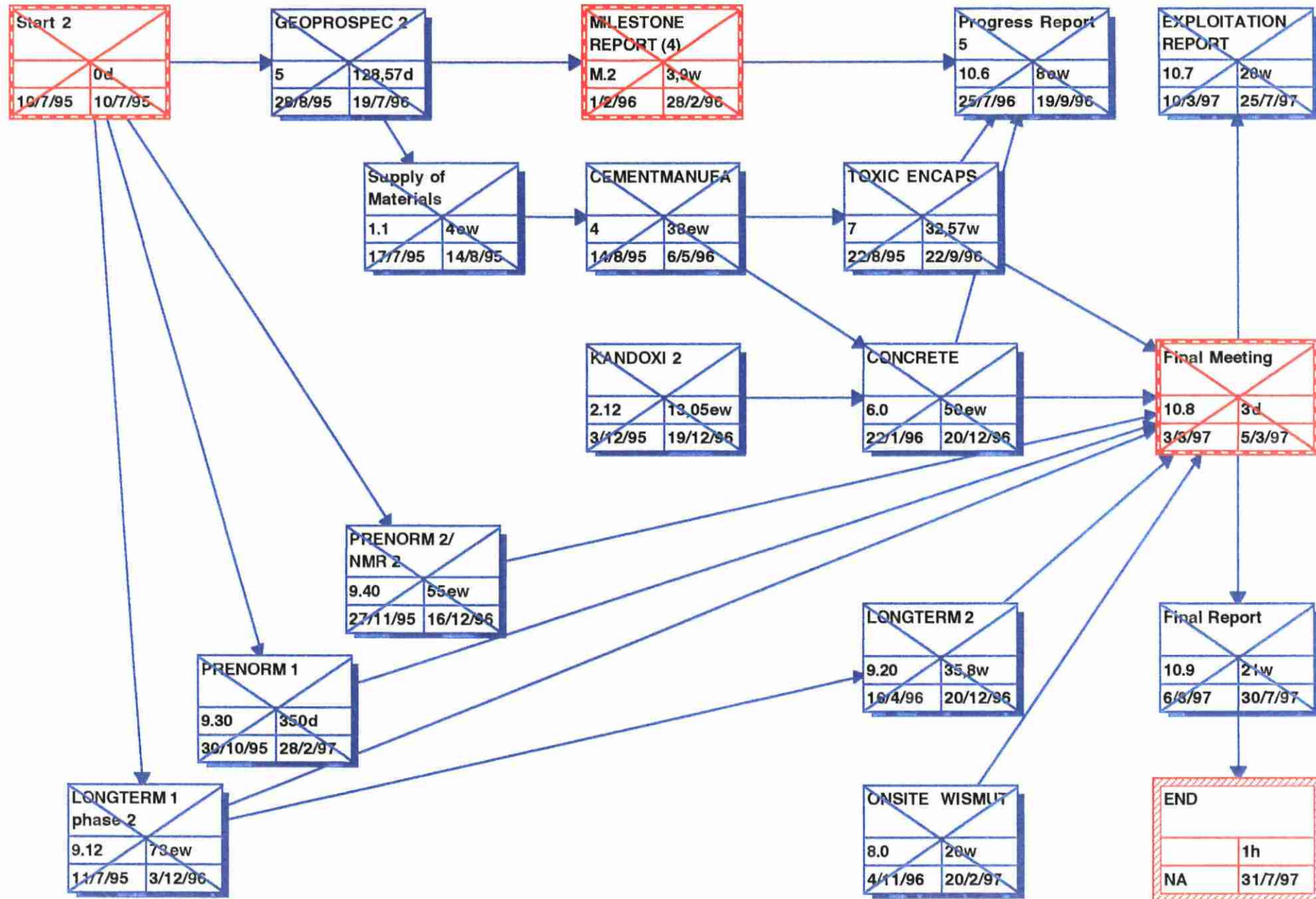
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  18. *ibid.* , References 1, 13, 15.
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PERT AND GANTT CHARTS









**BRITE-EURAM BE-7355-93**  
**Contract No. BRE2-CT93-0559**

**COST EFFECTIVE GEOPOLYMERIC CEMENTS  
FOR INNOCUOUS STABILISATION OF TOXIC ELEMENTS**



**ANNEXES TO FINAL REPORT**  
**TASK n° 6: CONCRETE**  
**TASK n° 9.1: LONGTERM 1**  
**TASK n° 9.2: LONGTERM 2**  
**TASK n° 9.4: PRENORM 2**

**CORDI-GEOPOLYMERE SA**



**Partners:**

B.R.G.M.

CORDI-GEOPOLYMERE SA

LAVIOSA CHIMICA MINERARIA SPA

CAGLIARI UNIVERSITY, Dpt Scienze della Terra

BARCELONA UNIVERSITY, Facultat de Geologia

**CONFIDENTIAL**

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**Project Leader: Joseph Davidovits**

**Saint-Quentin**  
**April 1997**

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## Task n° 6 : CONCRETE

### geopolymeric concretes, barriers, cappings, walls.

developing geopolymeric concretes to be used in the construction of acid-resistant geological barriers, cappings, walls and also borehole-plugging and shaft-sealing systems. Emphasis is to made on the use of local aggregates and of contaminated soils.

#### Accomplished work:

This task was reorganized because of WISMUT's default. Major target: comparison with regular Portland Cements; Low-CO2 cements for regular concrete use.

Task	Name	2, 1995		Qtr 3, 1995			Qtr 4, 1995			Qtr 1, 1996			Qtr 2, 1996			Qtr 3, 1996			Qtr 4, 1996			Qtr 1, 1997	
		May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb
6.0	CONCRETE																						100%

### Miscela CEMENTI GEOPOLIMERICI

% sec: % del singolo componente secco nella miscela secca (Sa07+Lait+Kandoxi)

% liq: % del singolo componente liquido rispetto alla somma del secco (Sa07+Lait+Kandoxi)

### Prove del 23/5/96

Nr. Mix	Den. misc.	SA07 calc. 800°C % sec	Laitier (d50=8µm) % sec	Kandoxi % sec	K-Silicat (soluz. 50%) % liq	H2O % liq	Additivo % del leg.	Stampo nr
1	base	46.7	25.3	28.0	23.4	29.0	/	n.1
2	base	46.7	25.3	28.0	23.4	29.0	/	/
3	base con <KSiO4	46.7	25.3	28.0	20.4	32.0	/	/
4	base con <<KSiO4	46.7	25.3	28.0	17.4	35.0	/	/
5	mod1: <Lait. >SA07	51.7	20.3	28.0	23.4	29.0	/	n.2
6	mod1 con <KSiO4	51.7	20.3	28.0	20.4	32.0	/	/
7	mod2: <<Lait. >>SA07	56.7	15.3	28.0	23.4	29.0	/	/
8	mod1 con Naftalen-S.	51.7	20.3	28.0	23.4	29.0	1 % FM 95	n.3
9	mod1 con Melamina	51.7	20.3	28.0	23.4	29.0	1 % FM 14	n.4
10	mod1 con Naftalen-S.	51.7	20.3	28.0	23.4	29.0	2 % FM 95	n.5
11	mod1 con latex-stirol- butadiene	51.7	20.3	28.0	23.4	29.0	1 % HB 3	
12	mod1 con Paver Plus	51.7	20.3	28.0	23.4	29.0	1.5 % Paver plus	
13	mod3: <Metak. <Lait. >>SA07	56.7	20.3	23.0	23.4	29.0	1 % FM 95	n.6

**Miscela CEMENTI GEOPOLIMERICI**

% sec: % del singolo componente secco nella miscela secca (Sa07+Lait.+Kandoxi)

% liq: % del singolo componente liquido rispetto alla somma del secco (Sa07+Lait.+Kandoxi)

**Prove del 24/5/96**

Campione macinato  
più grossolano

Nr. Mix	Den. misc.	SA07 calc. 800°C % sec	Laitier (d50=11µm) % sec	Kandoxi % sec	K-Silicat (soluz. 50%) % liq	H2O % liq	Additivo % del leg.	nr.
14	mod1: <Lait. >SA07	51.7	20.3	28.0	23.4	29.0	1 % FM 95	n.7
15	mod1 con aggiunta di H2O	51.7	20.3	28.0	23.4	29 + il 10 %	1 % FM 95	n.8
16	mod3	56.7	20.3	23.0	23.4	29.0	1 % FM 95	n.9
17	mod3 senza additivo	56.7	20.3	23.0	23.4	29.0	/	n.10
18	mod3 con SA07 <u>non</u> calcinato	56.7 NON CALC.	20.3	23.0	23.4	29.0	1 % FM 95	n.11
19	mod3 con SA07 n.c. e agg. H2O	56.7 NON CALC.	20.3	23.0	23.4	29 + il 10 %	1 % FM 95	n.12

**CARBUNCULUS Cement with low-CO<sub>2</sub> emission to mitigate «Global-Warming»,**

The production of CARBUNCULUS geopolymeric cements does not require any calcination of calcium carbonate, like it is the case in the manufacture of ordinary Portland Cement which involves the calcination of limestone.

Cement (ordinary Portland cement O.P.C.) results from the calcination of limestone (calcium carbonate) and silico-aluminous material according to the reaction:



The production of 1 tonne of O.P.C. directly generates 0.55 tonnes of CO<sub>2</sub> and requires the combustion of carbon-fuel to yield an additional 0.40 tonnes of CO<sub>2</sub>.

*To simplify: 1 T of Portland cement = 1 T of CO<sub>2</sub>.*

CARBUNCULUS cement, for example batch Stampo n. 6 in Tab. 14, requires the calcination at 800°C for two ingredients, SA07 and Kandoxi. High furnace slag is a by-product that no longer needs any subsequent treatment. The production of 1 tonne of CARBUNCULUS cement generates 0.184 tonnes of CO<sub>2</sub> from combustion carbon-fuel (see in Tab.18 for calculation). In the Table the value for K-silicate includes carbon-fuel and chemical-CO<sub>2</sub> produced by the decomposition of K-carbonate.

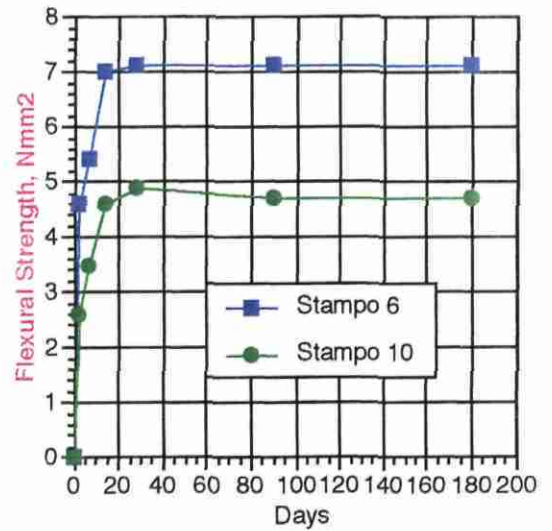
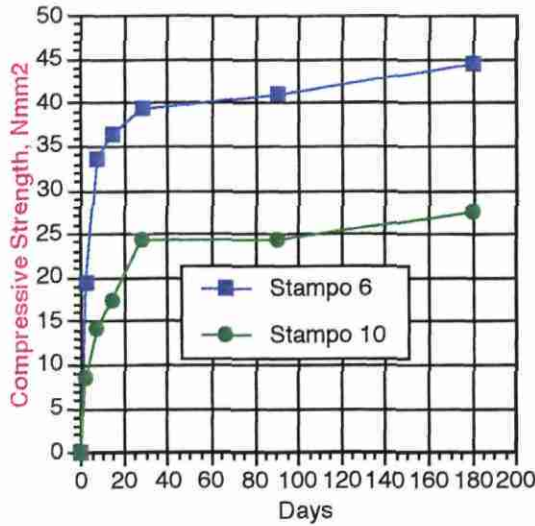
*CO<sub>2</sub> emission during the manufacture of 1 tonne of CARBUNCULUS cement*

Ingredient	heat treatment	CO <sub>2</sub> /tonne of ingredient	CO <sub>2</sub> ratio in 1 tonne of cement
SA07	800°C	0.17 T	0.095 T
Kandoxi	750°C	0.15 T	0.035 T
Slag	-	-	-
K-silicate	1200°C	0.30 T	0.034 T
energy for grinding	-	-	0.020 T

**Total, for 1 tonne of CARBUNCULUS cement: 0.184 T**

This low value (0.184 T/tonne of cement) confirms the results of the Background knowledge, based on laboratory formulations [ ] and set forth in the GEOCISTEM WORKPROGRAMME on pages 4-5.

The Figure displays the long-term compressive and flexural strength, at 180 days for twocements, a rapid setting (Stampo 6) and a slow setting (Stampo 10).



180 day compressive and flexural strength for CARBUNCULUS cements

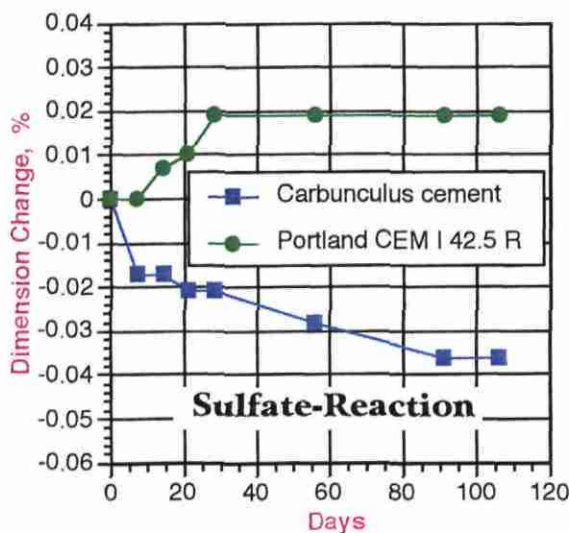
CARBUNCULUS cement of the type Stampo n.6 and a comparative Portland cement from Cement Buzzi (CEM I 42.5 R) were tested together with standardized Portland cement methods.

Sulphate resistance (ASTM C 1012)

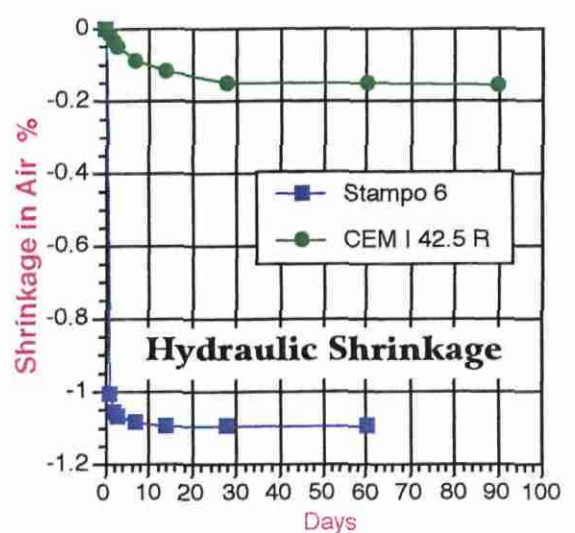
CARBUNCULUS cement shows no expansion, on the contrary it shrinks slightly. This ASTM Standard prescribes to put the mold, immediately after molding, in a curing tank in water at 35°C / 100% hum. for 24h and to check the compr. strength after 24h, which should be at least 20 MPa to start the Sulphate resistance test. It is interesting to note that CARBUNCULUS cement (Stampo n.6) reaches in this conditions a pretty high compressive strength value (27 N/mm²), even better than the value for Portland CEM I 42.5 R (26 N/mm²).

Length Change (hydraulic shrinkage)

Hydraulic shrinkage test mortar bars in standard condition, the same one usually carried out with OPC (hum. 50%, demolding after 1 day of setting, no covering). Carbunculus cement is very sensitive to drying conditions during the first day of setting. The cement should be always covered during the first setting days, in order to avoid this type of shrinkage.



Sulfate resistance (dimension change)



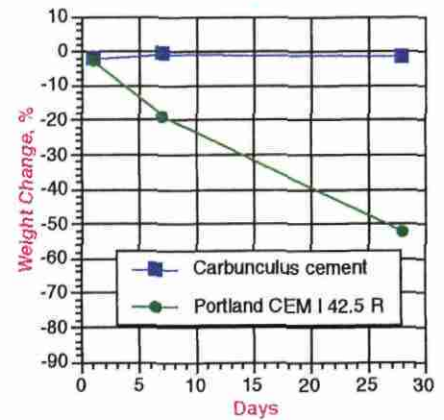
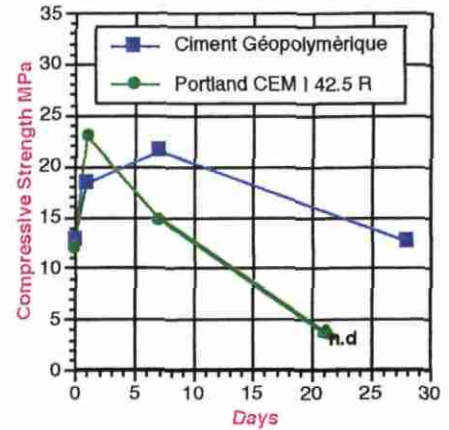
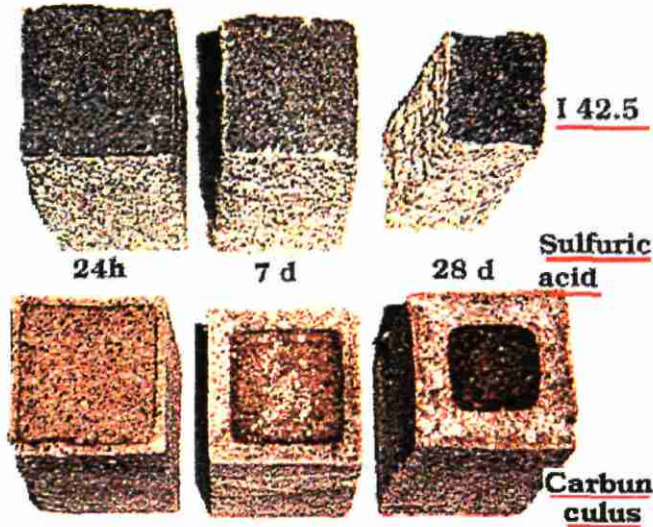
Hydraulic shrinkage, open air, no covering

### Resistance to strong Acid medium

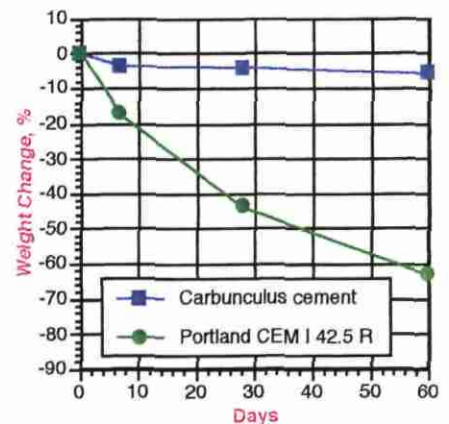
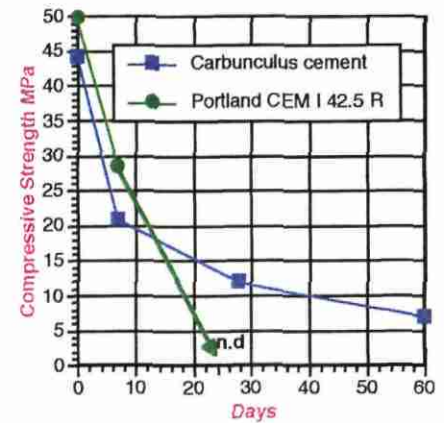
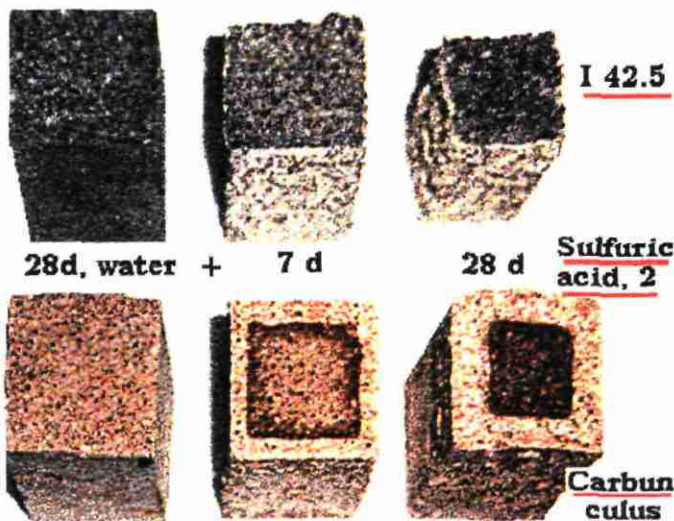
Metallic mine tailings are usually generating sulfuric acid that results from the oxidation of pyrite. The resistance to strong sulfuric acid solution (5% H<sub>2</sub>SO<sub>4</sub> solution) and strong HCl solution (5% HCl solution) was investigated in two series of test:

- 1) after only 24 hours of hardening
- 2) after the standard 28 days of hardening

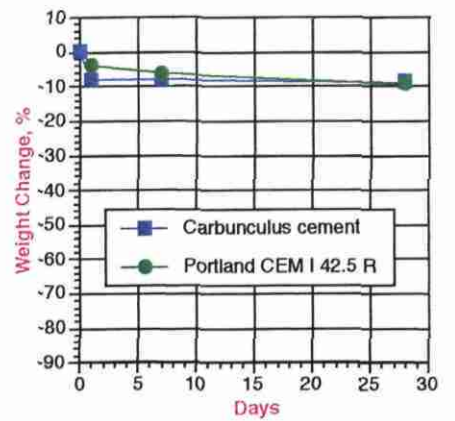
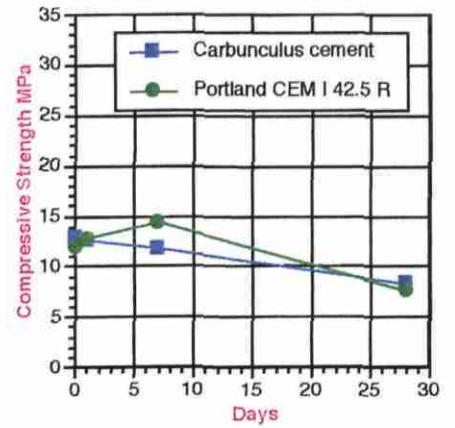
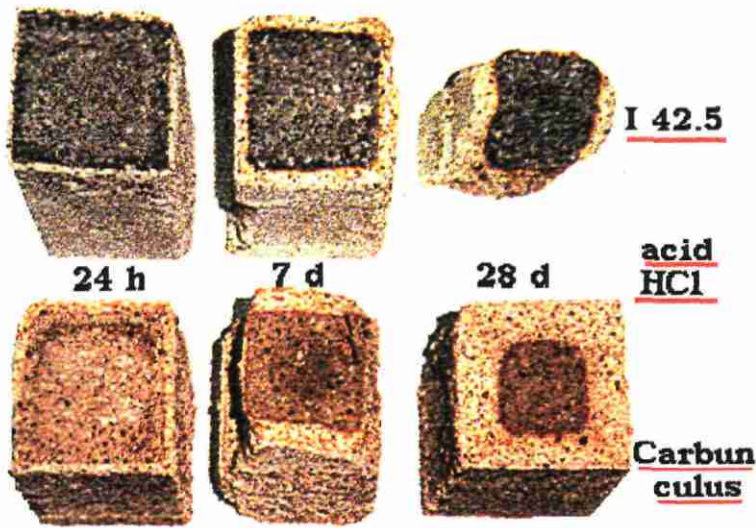
*Comparative test CARBUNCULUS vs. Portland cement I.42.5 . Sulfuric acid solution (5%), after 24 hours of hardening. Compressible Strength and Weight loss after 7 and 28 days.*



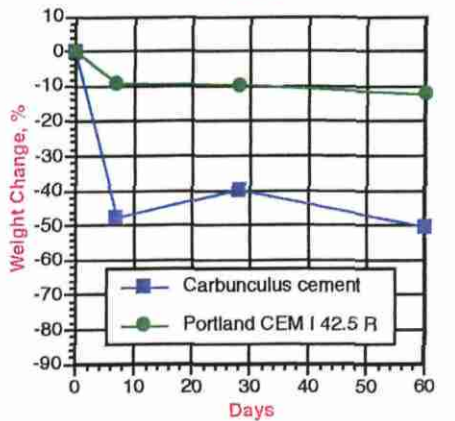
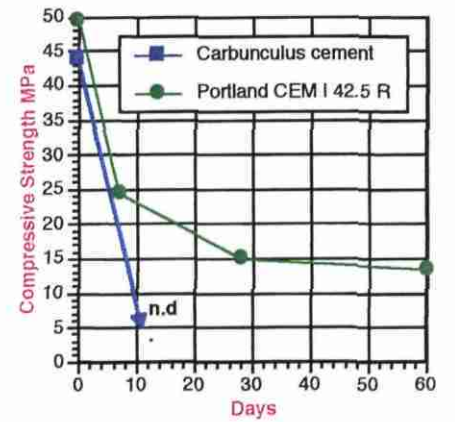
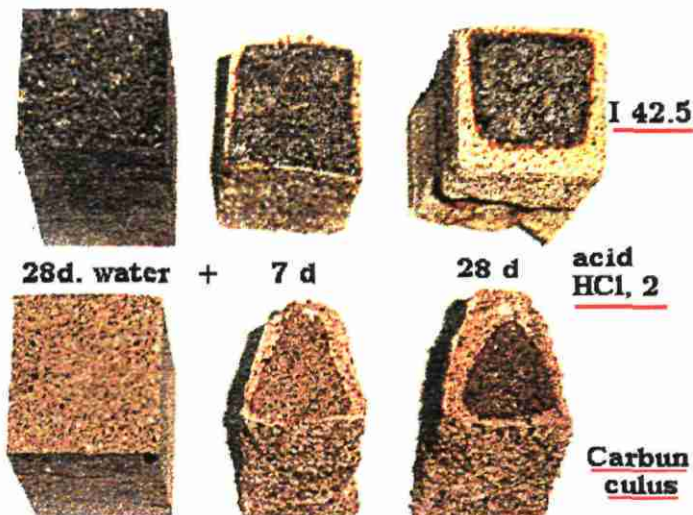
*Comparative test CARBUNCULUS vs. Portland cement I.42.5 . Sulfuric acid solution (5%), after 28 days of hardening. Compressible Strength and Weight loss after 7, 28 and 56 days.*



Comparative test CARBUNCULUS vs. Portland cement I.42.5 . HCl acid solution (5%), after 24 hours of hardening. Compressibve Strength and Weight loss after 7 and 28 days.



Comparative test CARBUNCULUS vs. Portland cement I.42.5 . HCl acid solution (5%), after 28 days of hardening. Compressibve Strength and Weight loss after 7 , 28, 56 days.







**Rapport Annuel  
du consortium GEOCISTEM  
Janv.-Décembre 1995**

**Tâche LONGTERM 1**



**Rapport semestriel  
Janv.-Juin 1995**

Durant ces six mois À L'UNIVERSITÉ DE BOLOGNA, Italie, mon activité s'est partagée en trois occupations:

- 1) L'étude bibliographique sur les mortiers romains
- 2) La recherche de sites archéologiques dans les régions d'Italie qui nous intéressent.
- 3) Le suivi du cours de géo-archéologie du professeur Claudio d'Amico, ce cours étant donné à la Faculté pour la Conservation des Biens Culturels à Ravenne.

### Introduction

Les Romains sont connus pour avoir développé à l'échelle industrielle un ciment et donc un béton de type hydraulique. Jusqu'à présent toutes les études faites sur le texte de Vitruve (Livre 2, Chapitre 3, 4, 5, 6) n'indiquaient pas quelle était la nature minéralogique de la *testa*<sup>1</sup> et celle des *harenae fossiciae* dont fait partie le *carbunculus*. J'ai fait l'analyse du terme *testa* dans mes mémoires de maîtrise et de DEA<sup>2</sup> et en ai déterminé la nature.

Les études archéologiques les plus

<sup>1</sup> L'argile cuite employée avec la chaux pour en faire un ciment hydraulique; c'est ce mélange qui sert de base au fameux *opus signinum*.

<sup>2</sup> F. DAVIDOVITS, *Vitruve et le mortier romain, étude archéologique et linguistique*, mémoire de maîtrise, Faculté des lettres, Amiens, 1992.

F. DAVIDOVITS, *Les mortiers de pouzzolanes artificielles chez Vitruve, évolution et historique architecturale*, D. E. A. "Les cultures de l'Antiquité Classiques", Université Paris X-Nanterre, 1993.

intéressantes sur le sujet se trouvent dans les ouvrages de Marion Elisabeth BLAKE<sup>3</sup>, travaux qu'a repris et approfondis l'Italien Guisepe LUGLI<sup>4</sup>. Pour BLAKE, les *harenae fossiciae* sont des pouzzolanes: "Vitruvius (2, 4, 2) and Pliny (N. H. 36, 175) classify sand in accordance with the place where it has been deposited: sea sand (*harena marina*), river sand (*harena fluvatica* or *fluviatilis*), and pit sand (*harena fossicia*), which is pozzolana."<sup>5</sup>

C'est pourquoi dans ses traductions des textes vitruviens, concernant le terme *harena*, G. LUGLI<sup>6</sup>, reprenant les remarques de M. E. BLAKE, (à moins que LUGLI ne les connaisse déjà), parle de *sabbia*, *arena*, ou *rena* en se limitant au sable fluvial ou marin; pour *pulus* (*puteolanus*), il emploie le terme de *pozzolana*, traduction qui comprend l'*harena fossicia*, ce sable qu'on extrait du sol, par opposition aux autres sables qu'on peut ramasser tel quel. G. LUGLI<sup>7</sup> utilise le terme *pozzolana* (pour traduire *harena*) lorsque Vitruve (2, 8, 2) parle de la composition du mortier à utiliser comme liant pour les différents *opera* (à savoir, *opus incertum* ou *reticulatum* pour les parements extérieurs et *opus caementicium* pour le noyau central). Il est donc clair que c'est du sable pouzzolanique (*harena fossicia*) que l'on emploie pour les maçonneries.

Résumons donc les interprétations de G. LUGLI; Vitruve indique, dans le quatrième chapitre du livre deux, l'utilisation de chaque sable. Il y a trois sortes d'*harena*:

<sup>3</sup> M. E. BLAKE, *Ancient roman construction in Italy from the prehistoric period to Augustus*, Carnegie Institution of Washington, Washington, 1947.

<sup>4</sup> G. LUGLI, *La tecnica edilizia Romana con particolare riguardo a Roma e Lazio*, 2 tomes, Rome, 1957.

<sup>5</sup> M. E. BLAKE, p. 41.

<sup>6</sup> G. LUGLI, p. 398.

<sup>7</sup> G. Lugli, "L'*opus caementicium* in Vitruvio", *Classica et Mediaevalia*, Vol. 17, Copenhagen, 1956, p. 99.

1) Les sables fluviaux (quartzeux): *Latium se fit jour.*  
*harena fluuiatica.*

2) Les sables marins (calcaires):  
*harena marina.* Ces deux sables sont utilisés pour les enduits.

3) Les sables pouzzolaniques que l'on extrait du sol et que l'on distingue les uns des autres par la couleur: *harena fossicia.*

Vitruve (2, 4, 1) conseille l'emploi de l'*harena fossicia* pour l'*opus caementicium* et distingue 4 *harenae fossiciae* par la couleur: *nigra* (noire), *cana* (grise ou blanche tout dépend du gisement), *rubra* (rouge) et le *carbunculus*.

Par comparaison, les sables de rivière ou de mer ne peuvent pas servir à l'édification des murs et des voûtes concrètes (2, 4, 2), alors que les *fossiciae* fraîchement extraites ont cette capacité.

Pour Vitruve, il est donc clair que seules les *harenae fossiciae* ont cette propriété pouzzolanique recherchée pour l'édification des structures de béton et c'est cela qui nous intéresse. A l'époque où je faisais mon DEA, après avoir découvert ce qu'a écrit G. LUGLI, j'en conclus que l'*harena fossicia* en général faisait une excellente pouzzolane. En fait, l'archéologie enseigne qu'elle fournissait un mortier moyen, qui certes est bien supérieure au simple mortier de chaux, mais qu'elle n'est pas ce produit exceptionnel auquel l'on s'attendrait à trouver pour l'architecture romaine. Comme toujours, pour la préparation du mortier, quel que soit l'endroit, les ouvriers prennent toujours le sable local, et la géologie fait que, par hasard, l'on découvre que le sable extrait à un endroit révèle soudain des qualités intéressantes. C'est probablement ainsi qu'apparurent les vertus de la pouzzolane de Baïa aux populations indigènes, vertus supérieures au sable marin ou fluvial. De même, à Rome, le caractère pouzzolanique de l'*harena fossicia* du

## La soudaine apparition du mortier rouge.

La pouzzolane change d'un lieu à un autre, il est plus ou moins terreux, et Vitruve se rend bien compte que c'est la présence de terre dans l'*harena fossicia* qui altère sa propriété. Ce qui fait que le ciment de l'époque républicaine à Rome (III<sup>e</sup> et II<sup>e</sup> av. J C) n'est pas d'une qualité exceptionnelle.

Puis soudain: "*In the days of Julius Caesar, Rome discovered, probably by accident, that the local red pozzolana made a superior mortar, but she had associated hydraulic properties with pulvis Puteolanus for too long a time to think of testing her new discovery for possible water-resisting powers.*"<sup>8</sup>

Dans le Sud de l'Italie, le mortier de pouzzolane n'a jamais pu être utilisé pour les enduits, où l'on préférerait celui de chaux et de sable issu des Grecs; "*in Rome, the development of a durable mortar from the local volcanic "sand" led to the evolution of a concrete architecture which was one of the greatest of her contributions of Western civilization.*"<sup>9</sup>

On a pu déterminer la manière de transmission de la technique des mortiers à base de chaux en Italie:

1° L'introduction du mortier de chaux de Grèce.

2° La découverte des propriétés hydrauliques de la *pulvis Baianus* en Campanie (région du Vésuve).

3° L'invention du mortier rouge au I<sup>er</sup> siècle av. J C qui améliore la possibilité d'édification des *structura caementicia*.

D'après M. E. BLAKE, à Rome et dans ses environs, de -200 à -87, le mortier est gris cendre et très friable, l'*harena* est terreuse. La chaux, en

<sup>8</sup> M. E. BLAKE *Op. Cit.* p. 313.

<sup>9</sup> *Id.*

quantité insuffisante, fait que le mortier est friable. Sous le dictateur Sylla, sa qualité s'est améliorée, car l'*harena* est moins terreuse. Mais le changement se fait vraiment sous Jules César:

*"His later buildings reveal a grayish-red mortar. The lime is much cleaner and more abundant; the "arena" is a true pozzolana, consisting of a sharp-angled particles which vary greatly in size and are often very large. This pozzolana is predominantly reddish brown and dark gray with some admixture of red. Although there is still a slight earthiness, the friability, which was the curse of the earlier mortars, has largely been eradicated."*<sup>10</sup>

La qualité du mortier change donc sous César par l'adjonction d'un sable rouge aux vertus pouzzolaniques. Mais quelle est la nature de ce sable? M. E. BLAKE suppose qu'il s'agit d'une *harena fossicia* rouge normale. Si ce sable est si remarquable, Vitruve doit en parler. Vitruve parle d'une *harena fossicia* particulière: le *carbunculus*.

Je résumerai ici ce que j'ai trouvé concernant le *carbunculus*, puisque dans le détail je l'ai déjà exposé dans notre précédente réunion (Janv.95, Laviosa).

1° Vitruve (2, 6, 6) qualifie le *carbunculus* de *materia excocta*, "matériau cuit dans un four". En effet, *excoquo* appartient au vocabulaire de la technique et signifie "cuire dans un four". C'est donc un matériau artificiel que décrit Vitruve.

2° Le *carbunculus* est un tuf volcanique dur qui a la propriété d'absorber de l'eau et de la restituer. Cette particularité est exploitée par l'agriculture romaine. L'on mélange de la poudre de tuf à la terre pour éviter le dessèchement des racines, comme l'indique Columelle dans *De re rust.* 3, 7, 11.

3° Cette *harena fossicia* une fois cuite

devient rouge ou brune et conserve cette couleur: son nom de *carbunculus* signifie à la fois *braise* et *grenat*.

### *Carbunculus et Peperino*

Durant mon séjour à Bologne, j'ai pu suivre les cours du Professeur Claudio d'Amico que vous tous connaissez de réputation. Au cours de nos discussions, j'ai pu me rendre compte qu'il possédait une connaissance remarquable de toute la géologie italienne.

Dans la vitrine d'exposition proche de la salle de cours, j'ai vu dans ce qui se rapproche le plus du "LA 01", ce tuf du Latium moderne et de l'Etrurie antique. Ce tuf est, d'après les résultats, le meilleur de la région pour faire du *carbunculus*. Cette Ignimbrite latitique provient de la région de Cimina (Viterbo): elle possède une structure vulcanoclastique et porfirique avec des phénocristaux, des fragments lithiques et pâte de fond. Elle rentre dans la catégorie du tuf "peperino".

Le nom de *peperino* est un nom générique pour désigner des tufs volcaniques italiens ayant le même aspect mais pouvant avoir une composition différente. Ainsi, nous avons ce *peperino* de Viterbo, mais le plus grand gisement de *peperino* se trouve dans les monts Albains au sud de Rome. Il servait de pierre de taille à Rome à l'époque républicaine et impériale. Dans la région des monts Albains, on trouve le site de Segni (la Signia antique). Cette colonie romaine était fameuse dans l'Antiquité pour la fabrication de tuiles et d'un mortier imperméable nommé *opus signinum*, composé de chaux et de *testa*.

<sup>10</sup> *Op. Cit.* p. 317.

La *testa* est faite d'argile kaolinite calcinée. Mais le dégraissant local pour cuire cette tuile est constitué de *peperino* en poudre. C'est l'emploi de ce dégraissant pour la tuile qui permet un mortier aussi excellent que le *signinum*. En effet, avec le *peperino* celui-ci atteint des résultats à la compression (au bout de 28 jours) de 20 à 30 MPa, alors que un mortier de *testa* normal a 14,5 MPa.

Le *peperino* de Segni est utilisé comme dégraissant pour la *testa* locale et comme pierre de construction. Il y a une structure archéologique à Segni qui réunit les deux emplois: la grande citerne proche du Capitole<sup>11</sup>. Celle-ci est d'un grand diamètre et faite de *peperino* en pierre de taille. Le fond de la citerne est constitué d'*opus signinum*.

Segni et le *peperino* de Viterbo constituent un exemple pouvant expliquer la façon dont les Romains faisaient une corrélation. Ainsi, sous le nom moderne et générique de *peperino*, se regroupent différents tufs volcaniques de couleurs noires et grises (aspect "poivré") mais pouvant avoir des compositions diverses. Le *peperino* d'origine était celui des Monts Albains, puis ce nom s'est étendu à des tufs volcaniques de même apparence. De même, peut on imaginer que le nom de *carbunculus* désignait un tuf bien particulier, puis plus tard d'autres tufs, car on découvrit d'autres sources possibles pour faire du *carbunculus*.

### Prochaine étape

La prochaine étape est celle de la prospection archéologique et géologique. Il faudra choisir les sites archéologiques et les monuments datant de l'époque de César, d'Auguste, jusqu'à Néron. Les monuments restés en place (c'est-à-dire

ceux qui n'auront pas été dégagés par une fouille archéologique) doivent comporter un mortier rouge ou brun qui ne soit pas de la *testa*. C'est justement ce mortier rouge que l'on supposera fait d'éléments cuits, du *carbunculus*. Dès lors, ces mortiers seront analysés par les géologues qui travaillent avec nous dans le GEOCISTEM. Cela implique aussi que l'on connaisse géologiquement les environs des sites archéologiques prospectés.

\* ▼ ◆ □ □

## Rapport Juillet 1995 - Janvier 1996

Le voyage d'étude que nous avons effectué du 7 au 12 octobre 1995 s'est déroulé en Etrurie Méridionale. Ce voyage avait pour but de relier les données géologiques avec le contexte archéologique et vitruvien.

### L'Etrurie Meridionale

Les géologues du GEOCISTEM ont fait en 1994 des prélèvements dans la région de Viterbo, à 80 km. au nord de Rome, et ont considéré que les deux échantillons prélevés (nommés LA 01 et LA 02) étaient les plus représentatifs dans le Latium pour le GEOCISTEM. L'Etrurie Méridionale, qui se caractérise par une géologie volcanique, se situe administrativement dans le Latium.

Nous sommes allés dans les environs de Tarquinia et de Norchia, dans les lieux où, précisément, les échantillons géologiques avaient été prélevés.

Le La 01 se présente sous la forme d'un tuf volcanique gris blanc et contenant des inclusions de roches un peu plus foncées. Il se situe dans un site appelé "La Rocca" entre Tuscania et

<sup>11</sup> A. L. FROTHINGHAM, *Roman cities in Italy and Dalmatia*, p. 64-65, New York, 1910.

Norchia. Quel emploi a-t-on fait dans l'antiquité de cette pierre? Le musée nationale de Tarquinia possède des sarcophages étrusques faits en tuf volcanique gris ou brun appelé *nenfro*. Le plus célèbre d'entre eux, le "sarcophage du magistrat"<sup>12</sup> est en *nenfro* gris.

La cité antique et l'acropole (*l'Ara della Regina*) de Tarquinia sont sur un site calcaire, comme d'ailleurs les fameuses tombes étrusques<sup>13</sup>. Mais les tufs volcaniques sont plus au nord et à l'est à l'intérieur des terres.

### Le tuf de Norchia

En visitant quelques kilomètres plus loin le site des hypogées de Norchia, la géologie change du tout au tout. Il ne s'agit plus de calcaire mais de tufs volcaniques, le fameux *nenfro* qui est, suivant les endroits, gris (La Rocca) ou rouge. A Norchia, près de Tuscania, des hypogées sont creusés dans des falaises de tuf rouge-brun. La zone archéologique de Norchia constitue certainement le complexe rupestre le plus ample et le mieux conservé de la région. On date la tombe Lattanzi de la fin du IV<sup>e</sup> siècle B.C. et les célèbres tombes à temples du III<sup>e</sup> s. B.C.

En accédant à la voie carrossable qui débute sur la route secondaire entre Tarquinia et Vetralla et qui mène à Norchia, l'on peut examiner plus à loisir les caractéristiques géologiques de ce tuf. Celui-ci est rouge-brun contient ce qui ressemble à du charbon et des petits morceaux de calcaire.

### Le *nenfro* de Lugli.

Ce tuf ressemble à la description

<sup>12</sup> célèbre en épigraphie étrusque, car le magistrat montre un *volumen* où est inscrit sa vie et sa carrière.

<sup>13</sup> Citons, entre autres, les tombes des lionnes, des danseuses, des léopards, du *triclinium*.

que donne G. Lugli<sup>14</sup> et correspondrait selon lui au *carbunculus*. Il cite une traduction de Vitruve<sup>15</sup> qui décrit le *nenfro*. Ce tuf poreux est semblable au *cappellaccio* qu'on trouve en Etrurie Méridionale. Contrairement à celui-ci, il a la qualité de résister à l'érosion même taillé. Si on le laisse dehors durant un an, de tendre qu'il était au moment de la taille, il devient dur aux agents atmosphériques comme beaucoup de grès et de tufs légers. Sa couleur est brune avec souvent des morceaux de charbon, comme le tuf de Fidène. G. Lugli conclut: "Je ne sais pas si, réduit en poudre ou taillé en petit morceaux, il est apte à remplacer la pouzzolane dans la composition du mortier."<sup>16</sup>

Ce *nenfro* brun ressemble au LA 02 récolté près de Civitá Castellana. C'est avec ce tuf brun rouge, qui contient des inclusions de "charbon", qu'est bâti *Faleri Novii* construite par les Romains après la prise de la ville étrusque de *Faleri Veteres* (-241). De plus la plupart des maisons de la région de Civitá Castellana sont construites avec ce tuf.

### Le transport du *carbunculus*

Si le *carbunculus* vient effectivement d'une région volcanique, comment aurait-il été transporté vers des sites comme Rome, par exemple, lors d'une période d'édification importante (époque de Sylla, de César, d'Auguste)?

Mauro CRISTOFANI apporte une réponse. Il existe en effet un portulan, attribué à l'époque de Caracalla et qui donne les points d'accostage (*positiones*) entre Portus Augusti, le port de Rome

<sup>14</sup> G. LUGLI, *La tecnica edilizia Romana con particolare riguardo a Roma e Lazio*, 2 tomes, Rome, 1957, p. 398-399.

<sup>15</sup> Prestel, *Zehn Bücher über Architektur, des Vitr. P.*, strasbourg, 1912, p. 73.

<sup>16</sup> G. Lugli, *La tecnica...*, p. 398: "Non so se ridotto in polvere o triturato in piccoli frammenti sia adatto a sostituire la pozzolana nella composizione della malta."

jusqu'à l'embouchure du fleuve Magra, c'est-à-dire le long de l'Etrurie Méridionale. Ce portulan fait partie du *Itenirarium Maritimum Antonini imperatoris*. Dans la région de Tarquinia, le portulan indique que les sites sont Algae (Torre Valdaliga), Rapinium (Foce del Mignone), Gravisca, Martanum (Foce del Marta). Tous ces points sont situés entre eux de 4 à 5 km. et sont quasi certainement autant d'escales d'époque étrusque<sup>17</sup>.

De plus, un matériau comme le LA 01 est idéalement situé pour être descendu par le fleuve Marta vers la mer et être transporté vers Rome, ou vers le Nord. La Marta, la plus importante rivière de la région de Tarquinia, prend sa source au lac de Bolsena et se jette dans la mer tyrrhénienne. M. CRISTIFANI indique que la Marta constituait un autre itinéraire commercial pour la région de Tarquinia<sup>18</sup>. Le transport d'un matériau pouvait donc se faire sur la Marta et de là, être expédié vers Gravisca et Ostie, puisque de Martanum, l'on pouvait naviguer vers Gravisca.

En -181, cette colonie romaine fut fondée sur l'escale étrusque; elle était destinée à être une étape commerciale vers l'Espagne et une défense contre la piraterie ligure et insulaire. L'envoi de nouveaux colons par Auguste et par Tibère n'empêchera pas la décadence de la cité<sup>19</sup>.

De même, si le carbunculus vient de la région de *Faleri Novii*, il pourra descendre le Tibre vers Rome. Le transport fluvial par le Tibre est attesté dans l'histoire de Rome. Les tufs du Grotta-Oscura atteignent Rome par le

fleuve au IV<sup>e</sup> siècle grâce à la prise de Véies<sup>20</sup>. Quand en 204 av. J. -C., Scipion est désigné par le Sénat pour diriger une expédition contre Carthage, Tite-Live (Liv. XXVIII, 45, 16-18) écrit que les gens de Pérouse, de Clusium, et de Rutella promettent de livrer des sapins pour construire des navires et une grande quantité de blé. J. LE GALL conclut que le seul transport de masse disponible était le Tibre<sup>21</sup>.

Sous quelle forme pouvait être transporté le *carbunculus*? Certainement pas comme une pierre de taille. En effet, pour ses grands travaux, Rome a, d'une manière générale, employé des tufs dont les carrières étaient situées assez près. Le *peperino* se trouve aux Monts Albains, le tuf de Gabi est à 19 km de Rome, celui de l'Aniene était près de Rome, celui de Monteverde était proche pour être descendu grâce au Tibre vers Ostie. Par contre le *peperino* de Viterbo bien qu'il fût meilleur que celui des Monts Albains, fut rarement employé à Rome à cause des difficultés de transport<sup>22</sup>.

#### L'origine du *carbunculus*.

C. F. Giuliani<sup>23</sup> rapporte que Caton (*De Agr.* 38, 2; Pline l'Ancien, *N. H.* 36, 174) déconseille la chaux obtenue par des pierres différentes entre elles, et celle dérivée du *silex* (pierre trop dure ou le basalte?) et ajoute que les tufs ne sont d'aucune utilité pour faire de la chaux.

Pour Caton et Pline, le choix de la pierre à chaux se fait seulement sur le critère de la couleur: la pierre la plus blanche (*quam candidissimum*) et la moins tacheté possible (*quam minime vario*). Vitruve (2, 5, 1) conseille de cuire des

<sup>17</sup> Mauro CRISTOFANI, *Gli etruschi del mare*, biblioteca di archeologia, Longanesi & C., seconda edizione, Milan, 1989, p. 37.

<sup>18</sup> *Id.*

<sup>19</sup> *Guida ai luoghi etruschi*, guide archeologiche De Agostini, Istituto geografico De Agostini, Novara, 1993, article Gravisca; p. 114-115.

<sup>20</sup> J. LE GALL, *Le Tibre, fleuve de Rome dans l'Antiquité*, Presses Universitaires de France, Paris, 1953, p. 57.

<sup>21</sup> *Op. Cit.* p. 58.

<sup>22</sup> G. LUGLI, p. 303.

<sup>23</sup> C. F. Giuliani, *L'edilizia nell'antichità*, La Nuova Italia Scientifica, Rome, 1989, p. 163.

pierres blanches (*saxo albo*) et des cailloux (*silice*).

Palladius (10, 1, 3) donne une liste plus longue: la pierre blanche dure, le travertin, le caillou gris de rivière, la pierre rouge et la pierre ponce. La sélection se fonde sur la provenance et la couleur de la pierre. Mais la nature minéralogique de la pierre n'est pas indiquée. Comme pour l'*harena fossicia*, la géologie fait de cette *harena*, un sable volcanique à propriété pouzzolanique. De même, la pierre rouge (*saxo rubro*) peut être un tuf volcanique ou une pierre calcaire.

Donc on peut émettre l'hypothèse suivante: les chauffourniers, pouvant confondre un calcaire gris et un tuf volcanique de la même couleur, quand ils chauffaient le tout à 800°C, obtenaient certes une chaux issue du calcaire mais aussi un tuf rouge brique, impropre à la vente! Cet accident pourrait être à l'invention du *carbunculus*.

Mais le plus curieux, Palladius (10, 1, 3) conseille de calciner de la pierre ponce (*spongea*) pour la chaux! C'est donc la preuve que les Anciens cuisaient des pierres volcaniques.

### *Harena fossicia rubra*

Dans notre précédent rapport du 30 juin 1995, nous avons rapporté que l'*harena* rouge qui apparaît au temps de César et dont parle M. E. Blake<sup>24</sup> est une vraie pouzzolane aux angles pointus et possède des tailles différentes (fine poudre et une granulométrie supérieure): "His later buildings reveal a grayish-red mortar. The lime is much

<sup>24</sup> M. E. Blake, *Ancient roman construction in Italy from the prehistoric period to Augustus*, Carnegie Institution of Washington, Washington, 1947, p. 317: "In the days of Julius Caesar, Rome discovered, probably by accident, that the local red pozzolana made a superior mortar, but she had associated hydraulic properties with pulvis Puteolanus for too long a time to think of testing her new discovery for possible water-resisting powers."

cleaner and more abundant; the "arena" is a true pozzolana, consisting of a sharp-angled particles which vary greatly in size and are often very large. This pozzolana is predominantly reddish brown and dark gray with some admixture of red. Although there is still a slight earthiness, the friability, which was the curse of the earlier mortars, has largely been eradicated."<sup>25</sup>

Nous avons rapproché cette pouzzolane rouge avec le *carbunculus*. G. Lugli<sup>26</sup> prétend que cette pouzzolane rouge, employée aussi au temps d'Auguste, correspond aux carrières de Tre Fontane, à Rome, qui fournit encore aujourd'hui une des meilleures pouzzolanes du territoire romain. Cette affirmation est contredite par M. E. Blake<sup>27</sup> qui indique: "Pozzalana is so abundant in and about Rome that it is quite impossible to locate the sources from which most of the used in ancient buildings came." A San Paolo, non loin de là, il y a aussi des carrières de pouzzolanes rouges, mais l'on est pas sûr qu'il s'agisse de l'unique source d'*harena fossicia rubra*.

Dans une lettre que nous a adressée le prof. Giuliani de l'université *La Sapienza*, celui-ci écrit qu'il est douteux de rapprocher la pouzzolane rouge des carrières de Tre Fontane. Il pense, comme Blake, qu'il est pratiquement impossible de retrouver les carrières de provenance des pouzzolanes employées dans les murs simples. Il arrive qu'une carrière fournisse des pouzzolanes rouges ou noires sur le même site ou que les monuments, construits à la même époque, emploient ces deux couleurs de pouzzolanes, qui sont peut-être des résidus de différentes fournitures.

Il faudrait en conclure que la seule méthode probante pour établir une

<sup>25</sup> *Op. Cit.* p. 317.

<sup>26</sup> G. Lugli, *La tecnica...*, 426-427.

<sup>27</sup> M. E. Blake, *Roman...* p.44-45.

provenance serait une étude géologique approfondie.

### Les ports romains

Durant ce voyage en octobre 95 en Etrurie, nous avons été déçu par le fait que des sites romains importants comme Ferento, où se trouvent des thermes et un théâtre, n'emploient que des sables de tufs locaux et que ces sites, à l'air libre depuis assez longtemps, ont été restaurés. Du carboncle rouge, point de trace semble-t-il en Etrurie. Il a été peut-être utilisé à Rome, mais Rome est grande. A une échelle plus réduite, il est possible qu'il ait été employé dans un port comme Ostie.

Vitruve consacre le chapitre 6 du livre II à la pouzzolane des environs du Vésuve, cette poudre merveilleuse qui fait durcir le mortier sous l'eau et décrit son emploi dans le chapitre 12 du livre 5. Vitruve (2, 6, 6) compare le *carbunculus* et la pouzzolane de Baïa et indique que celle-ci est bonne pour les constructions qui se font dans la mer et le *carbunculus* pour celle qui se font sur terre. Dans ce cas, on peut imaginer que dans ce contexte de deux produits complémentaires (l'un sur la terre, l'autre dans la mer), ils soient réunis sur un même site, un port comme Ostie ou la région de Naples.

A Ostie, selon l'époque, on distingue une pouzzolane rouge et noire dans l'*opus caementicium*. G. LUGLI a établi les listes suivantes qui contiennent les monuments en *opus caementium* les plus caractéristiques.

#### Liste des monuments caractéristiques pour la période de -100 à -44 av. J. -C. :

La pouzzolane dominante est la noire pour la période de -100 à -44, c'est-à-dire de Sylla à César. Mais la rouge y est quand même attestée<sup>28</sup> dans le *caementicium* du mur d'enceinte en

*opus quasi reticulatum*.

Mure Sillane in opera quasi reticulata (*Ostia*, I, p.79 sgg.; tav. XLVI, 1-3).

Tempio di Ercole (*Ostia*, I, p. 233; tav. XLVII, I).

Tempio tetrastilo (*Ostia*, I, p. 205).

Quattro tempietti ("Monum. Ant. Lincei", XXIII, (1916), col. 441 sgg.; *Ostia*, I, p. 233).

Magazzini repubblicani (reg. II, ins. II, n. 2) - (*Ostia*, I, p.190, tav. XLVII, 3).

Case sotto angipoto delle taberne finestrate, di Giove Fulminatore, dei capitelli di stucco, nel vico di Dioniso, sotto la Basilica, sotto il tempio dei fabri navales, ecc. (*Ostia*, I, pp. 190 sgg., 233).

Seconde taberne sotto gli horrea di Ortensio (*Ostia* I, p. 233; tav. XLV, 3).

Lungo muro sotto la fronte del portico della a "lucerna" (*Ostia*, I, p. 233).

Tombe fuori porta Romana (*Ostia*, I, p.233, tav. XLVI, 2).

Mercato di via della Foce (reg. III, ins. I, n.7) - (*Ostia*, I, p. 233; tav. XLVII, 2).

#### Liste pour la période de la fin de la République et le début de l'Empire:

Entre la fin de la République et le début de l'empire, les murs d'Ostie ne diffèrent pas beaucoup de ceux de Rome. Le tuf de Monteverde prévaut car il est facile à transporter par le fleuve; le mortier est plutôt maigre, confectionnée avec une pouzzolane rouge, riche de *cretoni* (grains de dimensions supérieures par rapport au reste). Dans les réalisations augustéennes (théâtre), la noire domine<sup>29</sup>.

Circ. 12 av. Cr. - Teatro (I fase). (*Scavi di Ostia*, I, p. 191, tav. XLVIII, I).

14-20 d. Cr. - Tempio di Roma e Augusto (*Ostia*, I, p. 191, tav. XLVIII, 5).

Augusto? Tempio della Bona Dea (*Ostia*, I, p. 192).

Case dell' atrio tetrastile, di Giove Fulminatore (2<sup>a</sup> fase) e nel cardine degli

<sup>28</sup> G. LUGLI, *La tecnica...*, p. 418-419.

<sup>29</sup> *Op. Cit.*, p. 429-430.

Aurighi (*Ostia*, I, p. 191).

Grandi horrea (*Ostia*, I, p. 234, tav. XLIX, 4).

Horrea nella Semita dei Cippi (*Ostia*, I, p. 234).

Horrea di Ortensio (*Ostia*, I, p. 234, tav. XLIX, 4).

Edificio sotto l'insula delle Trifore (*Ostia*, I, p. 234, tav. XLVIII, 2).

Tomba del Pretoriano (*Ostia*, I, p. 234; tav. XLVIII, 4).

Grande tomba fuori porta Marina (reg. VIII, ins. VII, n. 2).

Pour la période de 41 à 79 ap. J. C., on note toujours la présence des agrégats de tufs de l'Aniene et de Monteverde même pour les parements en *opera quadrata* et *reticulata*. Le mortier est à base de pouzzolane rouge riche de *cretoni*. La noire est présente dans certaines constructions (*horrea* d'Ortensius); elle a été passée au crible quand elle devait servir pour des joints subtiles<sup>30</sup>.

La bibliographie précise pour Ostie est : *Scavi di Ostia*, Libreria dello Stato, Rome, 1953.

Une étude dans le même ouvrage sur les matériaux volcaniques: Gio. De Angelis, *Nota sui materiali vulcanici litoidi da costruzione in Roma ed Ostia Antiche*, in "Scavi di Ostia", I, p. 209 sq.

#### Autres sites possibles:

Segni: la citerne avec *opus signinum*.

Villa Hadriana: on note une alternance dans le mortier d'une pouzzolane noire et rouge. Dans ce gigantesque palais où le reticulatum domine, les mortiers de mortiers rouges et noirs y sont présents en grande quantité.

Les sites de Torre Astura, Anzio, Villa Hadriana, Porto possèdent un mortier qui a mieux résisté à l'érosion que les briques de tufs.

#### Prochaine étape

La prochaine étape est celle de la prospection archéologique et géologique. Il faudra choisir les sites archéologiques et les monuments datant de l'époque de César, d'Auguste, jusqu'à Néron. En particulier, il semble que nous devrions nous concentrer sur Ostie et la Villa Hadriana. Les autres sites, que nous avons indiqués, seront à prospecter car ils sont intéressants pour servir de comparaison. Une fois les autorisations de prélèvements accordées, il faudra choisir les mortiers sur les sites archéologiques et les analyser.

Frédéric Davidovits

<sup>30</sup> *Op. Cit.* p. 434.

## Rapport Longterm 1, Phase 2:

### Échantillons archéologiques

Avec les géologues de Cagliari, nous sommes allés à Rome et à Ostia Antica du 16 au 21 juillet pour effectuer les prises d'échantillon de mortiers romains pour analyse. Pour compléter notre étude, il était intéressant d'ajouter à nos prélèvements des morceaux d'*opus signinum*. Pour cela je demandai à la Dot.ssa Sartorio, directrice du Museo della Civiltà Romana, de nous suggérer à Rome les sites les plus représentatifs pour les époques républicaines et impériales.

En effet, il était intéressant de comparer les deux ingrédients qui sont à la base de la pérennité du béton romain, à savoir:

- la *testa*, appelé aussi par les Italiens le *coccio pesto* et qui serait une argile kaolinite calcinée de type *kandoxi*;

- le *carbunculus*, notre sable pouzzolanique calciné, objet de cet étude.

Ces deux ingrédients, aussi différents sur le plan chimique et minéralogique, lorsqu'ils sont mêlés à de la chaux, font un ciment hydraulique.

A Rome, donc, nous sommes allés avec la Dot. ssa Sartorio sur le site de l'Aire Sacrée de Santo Omobono et nous y avons prélevés 4 échantillons d'*opus signinum* pour la période républicaine.

ROM 1: Aire Sacrée de Santo Omobono: sous-couche du pavement de *tessera* de terre cuite, elle est réalisé en mortier de *testa* et date de la seconde moitié du 3<sup>e</sup> s. avant notre ère.

ROM 2: Aire Sacrée de Santo Omobono. Mortier de la fondation du Compitum augustéen.

ROM 2a: comme 2, mais en un bloc isolé, dans un petit tas.

ROM 3: Aire Sacrée de Santo Omobono: troisième couche du mortier du pavage de la citerne du côté oriental, près du Compitum.

Pour la période impériale, nous sommes allés dans la citerne dite "des Sept Salles", qui alimentait les Thermes de Trajan. Nous y avons prélevés 3 échantillons d'*opus signinum*.

ROM 4: Thermes de Trajan: "cisterna delle 7 Salle"; enduit du mur de la salle 5, près de la troisième porte.

ROM 5: Cisterna delle 7 Salle: pavement de la quatrième salle.

ROM 6: Cisterna delle 7 Salle: enduit de la voûte de citerne pris au sol dans la troisième salle.

Nous nous sommes ensuite rendus à Ostie pour rechercher et prélever les mortiers qui pourraient contenir le *carbunculus*. La liste des monuments à examiner pour les périodes républicaines et impériales est inspirée par celle de G. Lugli (cf. rapport précédent). L'archéologue travaillant sur le site et qui nous accompagnait avait cette liste, nous menait sur les lieux d'époque romaine, qui n'avaient pas été restaurés. Car entre les années 50 et 1996, le site d'Ostie ne présente plus le même aspect et tous les monuments de la liste n'ont pas pu faire l'objet de prélèvement: soit ceux-ci furent restaurés, soit certaines parties de ces monuments ne sont plus accessibles, car elles avaient été révélés lors de fouilles, qui ont été rebouchés depuis.

C'est pourquoi les échantillons viennent de monuments "sûrs" et qui n'ont pas subi de modifications majeures. Nous avons aussi échantillonné dans des lieux typiques de l'époque trajane et tardo-impériale. En tout nous avons 11 échantillons.

OST 1: Magasins Républicains; mortier de liaison du *reticulatum* gris clair. R. 2, Is. 2, 1

OST 2: Nécropole Républicaine en dehors de la Porta Romana; *Caementicium* et *reticulatum* d'un *columbarium*; *opus reticulatum* de lave et de tuf volcaniques.

OST 3: *Caementicium* du "castellum" de l'aqueduc romain (époque claudienne?); béton très dure.

OST 4: "Horrea di Ortensio": entrepôts républicains.

4 r: Restauration en mortier rouge sur l'*opus reticulatum*.

4 g: mortier gris du *reticulatum*.

OST 5: "4 tempietti": *quasi reticulatum* du *podium*; prélèvement d'un mortier de couleur terreuse à la bases d'un congé du *podium*; présence de *cretoni*;

OST 6: chambre associée au Temple d'Auguste; Mortier gris et friable du *reticulatum*.

Les échantillons suivants sont d'époque impériale.

OST 7: Intérieur du *Capitolium*; Réfection impériale.

7 r: parement du *testaceum*; mortier rouge.

7 g: parement du *testaceum*; mortier gris.

OST 8: Basilique de Trajan (1, 11, 5).

8 a: *caementicium* gris.

8 b: joint rouge solide du *testaceum*.

OST 9: Temple Rond: première moitié du 3<sup>e</sup> s; *caementicium* gris avec des éléments de marbre et de *testa*.

OST 10: Monument funéraire en dehors de la Porta Marina: *caementicium* de ce monument: seconde moitié de 1<sup>er</sup> s. avant notre ère; *caementicium* terreux très friable.

OST 11: "Domus tardive sur le decumanus", en face de l'école de Trajan. Joint gris du mur de la fontaine.

Les 17 prélèvements, que l'équipe scientifique a effectués, compareront les différences chimiques entre la *testa* et si les analyses le trouve, le *carbunculus*.

Frédéric Davidovits, 25 Août 1996

### Archaeological Analogues

This task was aimed at providing longevity prediction from archaeological materials studies. Two thousand years are generally accepted as a sufficient amount of time to permit decay of fission products that represent the most hazardous fraction in low-level radwaste material. Ancient Roman concrete structures (up to 2.000 years old and older) are still functioning today and thereby could provide historical documentation of the extended durability of zeolithic and geopolymere cements.

Fundamental research carried out by GEOPOLYMER scientist at Institute for Applied Archaeological Sciences, Barry University, USA, and studies performed by the University of Amiens, France, on Ancient Roman mortars, especially *Opus Signinum* masonry, in relation with the descriptions by the Roman author Vitruvius in *De Architectura*, provided Background knowledge for this task. *Opus Signinum* mortar involves a hardening mechanism based on the alkali-activation of KANDOXI materials with zeolites and lime. Recent studies performed by the same researcher at University of PARIS-Nanterre, Archaeology Department, on Vitruvius' text have clearly demonstrated the link between Roman Concrete and Italian zeolithic tuffs [ ]. According to the Roman author Vitruvius in *De Architectura*, another raw material for concretes and mortars is a very unique geological material called *carbunculus*. *Carbunculus* was processed at high temperature, i.e. in the range of 800°C. From the study of the Latin text, it has been deduced that *carbunculus* was a volcanic tuff of the ignimbric type. It could be similar to the geological samples LA01 and CA02 tested in task GP-CEMENT («glass» and «carbunculus»).

The linguistic and archaeological approach of this task was carried out in Italy, by the same researcher now at CERLA (Caen University). A sampling of archaeological mortars and concretes

dating back to the 3rd century BC and later was carried out in Rome and Ostia, Italy. Two series of artefacts: *Opus Signinum* (in Rome), *Opus Caementicum /Testacaem*: mortars and concretes (*carbunculus?*), (in Ostia):

*Opus Signinum*: 7 samples (Rome). The *Opus Signinum* contains the element *testa*, which is a calcined kaolinitic clay equivalent to the Kandoxi used in the GEOCISTEM cements, and carbonated lime.

*Opus Caementicum /Testacaem*: (Rome and Ostia): 15 samples of mortars and concretes. The mortar usually contains carbonated lime and volcanic tuff aggregates and sand called in Italian *cretoni*. Some of the *cretoni* could be the element *carbunculus*, which is equivalent to the calcined volcanic tuffs used in the GEOCISTEM cements.

The elementary chemical and mineralogical analysis carried out by the geologist team at Cagliari on these ancient mortars, does not provide detailed information on the make-up of the lime-cement (see the complete report in the Annex). Comparative NMR spectra made on the coarse aggregates (*testa* and *cretoni*) on one part, and on lime-cement on the other part are providing some very interesting clues. We found at least two specimens of Roman cement (*Opus Signinum* and *Opus Testacaem*) whose  $^{29}\text{Si}$  NMR Spectrum show the same resonance at -86 ppm as those of GEOCISTEM CARBUNCULUS cements. The  $^{29}\text{Si}$  Spectra for the *Opus Signinum* sample ROM 4, and the sample OST 7G, *Opus Testacaem* mortar, are different from those of the aggregates (*testa*, *cretoni*, LA01). This suggests that, at least for these two specimens, the hardening mechanism is not a simple lime carbonation as generally claimed by archaeology (and by the Cagliari team). Rather, the hardening would result from a chemical reaction between the lime and the alumino-silicates, comprising calcined clay *testa* and the volcanic tuff *cretoni*. This chemical reaction yields an alumino-silicate structure with a major resonance at -86 ppm suggesting a structure of the  $\text{Si}(\text{Q}3\text{Si}, 1\text{OH})$  and  $\text{Si}(\text{Q}4)$  types. This chemical reaction could be of the geopolymeric type. The chemically un-reacted lime will then slowly recarbonate into calcite, with time. This explains why the cement matrix of the mortar contains calcium carbonate and alumino-silicates.

We have compared the spectra of these two Roman cements (from 2nd Century AD) with the spectra of the GEOCISTEM CARBUNCULUS cements. The spectrum for the cement ROM 4 (*Opus Signinum*) is similar to the spectra of CA01/CA02 cements and also to LA02. We know that these particular GEOCISTEM cements made of KANDOXI and zeolitic tuffs LA02, CA01, CA02 (philipsite type). We also know that the *Opus Signinum* consists of lime and calcined ceramic, *testa*. The chemical mechanism of the two cement types will be discussed in Chapter 3.5.2..

Concerning the cement OST 7G, the equivalent GEOCISTEM cement is the LA01 cement.

### **The make-up of ROMAN CEMENTS and their modern counterpart GEOCISTEM Carbunculus cements: NMR Spectroscopy (Task LONGTERM 1-2).**

Task Leader: CORDI-GEOPOLYMERE ; NMR Spectroscopy performed at NAMUR University (Belgium); Archaeological/Linguistic part subcontracted to CAEN University (France)

planned start:	January, 1995	actual start:	January, 1995
planned end:	April, 1996	actual end:	December, 1996

From the digging of ancient Roman ruins, one knows that approximately 95% of the concretes and mortars constituting the Roman buildings consist of a very simple lime cement, which hardened slowly through the precipitating action of carbon dioxide  $\text{CO}_2$ , from the atmosphere. This is a very weak material that was used essentially in the making of foundations and in buildings for the populace. But for the building of their "ouvrages d'art", the Roman architects did not refrain from employing more sophisticated and expensive ingredients. These technologies are described by several ancient authors such as Vitruvius (1. Cen-

tury BC) and Plinius (1. Century AD). Technical keywords related to these high-performance cements have not been properly understood before recent linguistic studies shed new light and new interpretation on these texts.

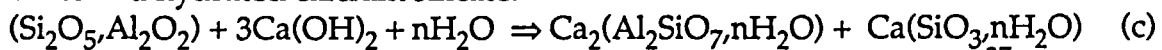
The first high-performance Roman cement. Opus Signinum.

Civil infrastructures, especially works related to water storage (cisterns, aqueducts) required a high-performance material and a special technology. This technology was known under the generic technical term of *Opus Signinum*.

*Opus Signinum* (cf. Vitruvius, Book II, 5,1 and Book VII, 1,3) is obtained by blending crushed and sieved potsherds (in Latin *testa*) with lime, in the proportion of three to one. It yields a high quality plaster that is waterproof and is used to coat the interior of cisterns and aqueducts. According to the Roman author Plinius (Natural History, Book 35, 165), this technology was recognized as: "*..one of the most spectacular invention of mankind.*" The ingredient *testa* is a ceramic powder from calcined kaolinitic clay and therefore very close to the KANDOXI ingredient.

We selected two *Opus Signinum* samples dating to different epoch: ROM 1 (pavement of Santo Omobono, Rome, 3rd c. BC) and ROM 4 (interior coating of Cistern, Trajan Baths, 2nd. c. AD), and performed  $^{29}\text{Si}$  and  $^{27}\text{Al}$  NMR Spectroscopy on the aggregates (the crushed *testa*) and on the fines (the lime cement).

ROM 1  $^{29}\text{Si}$  NMR spectrum is different from the one of ROM 4. ROM 1 spectra for *testa* and cement are similar. This excludes the presence of a new geopolymeric type framework tecto-silicate phase in the cement. However, one knows from studies performed at INSA Lyon [], that lime  $\text{Ca}(\text{OH})_2$  chemically reacts with calcined kaolin ( $\text{Si}_2\text{O}_5, \text{Al}_2\text{O}_2$ ) and yields hydrated gehlinitite and hydrated calcium silicate:

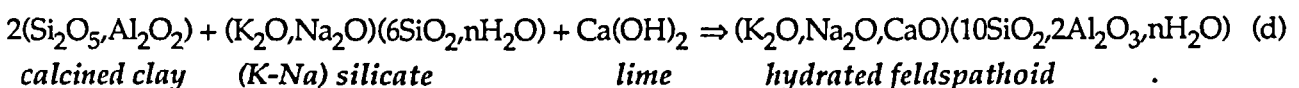
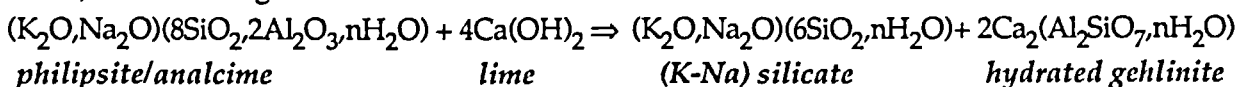


The presence of hydrated gehlinitite in ROM 1 cement is deduced from  $^{27}\text{Al}$  Spectroscopy. The content in Al(6) in the ROM 1 cement (8%) is twice the content of Al(6) in *testa* (4%). In addition to the hydrated gehlinitite, ROM 1 cement contains recarbonated lime.

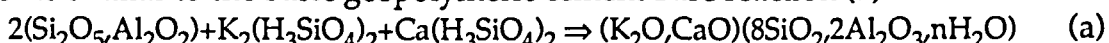
For ROM 4, its spectrum is very close to those of CA01/CA02/LA01 GEOCISTEM Carbunculus cements. We suspected, that a better cement would be achieved if the ceramic *testa* contains a tempering additive of the alkaline zeolithic type, or pozzolan (in Latin *harena fossicia*).

ROM 4 *testa*  $^{29}\text{Si}$  NMR spectrum results from the addition of two ingredients: calcined kaolinitic clay (Kandoxi) and analcime/leucite type pozzolan temper (Cretoni OST 7G). ROM 4 and OST 7G pertain to the same epoch (Emperor Trajan, 2nd c. AD). We assume that the temper ingredient used in ROM 4 *testa* was the pozzolan tuff *cretoni* added to the OST 7G mortar.

It is well known [] that the reaction of lime with alkaline pozzolan causes the alkalis to pass into solution, yielding soluble alkaline silicates. With *testa* and philipsite/analcime type *harena fossicia*, the hardening mechanism would have been:



which is similar to the basic geopolymeric cement base reaction (a)



The presence of hydrated gehlinitite in ROM 4 cement is deduced from  $^{27}\text{Al}$  Spectroscopy. The content in Al(6) in the ROM 4 cement (13%) is three time the content of Al(6) in *testa* (4.5%). The final make-up of ROM 4 cement would be:

- hydrated gehlinitite

- recarbonated lime
- hydrated feldspathoid
- fine grained zeolithic volcanic tuff

Hydrated gehlinites and hydrated feldspathoids are X-rays amorphous. This explains why they are not detected with conventional techniques (see CAGLIARI report in Annex)

The second high-performance Roman cement, with Carbunculus.

Vitruvius outlines that natural pozzolanic tuffs *harena fossicia* may only be used if they are fresh from the pit (*quae sunt de harenariis recentes*). When lying too long, they cannot bind together the aggregates and the walls and vaults collapse. In modern Italian, *harena fossicia* is designated by archaeologists sometimes by *cretoni*. The mortar of ROM 2, dating back to the Republican Era, illustrates Vitruvius teaching. The NMR Spectra for *cretoni* and cement are absolutely identical. This means that the silicates in the *cretoni* fines are acting as inert materials, having not participated into any hardening reaction with lime. Hardening of this mortar would have occurred through regular slow recarbonation. There is a general consensus in the literature [ ] that the products of the lime-pozzolan reaction are:

- a) hydrated calcium silicate  $\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$
- b) hydrated calcium aluminate  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$
- c) ettringite, calcium sulphate.

ROM 2 cement does not exhibit any low molecular silicate Si(Q1-Q2). However, the difference in Al(6) content suggests a remain of hydrated calcium aluminate, i.e. a small chemical reaction.

Another solution for getting high quality hydraulic mortars is provided by *carbunculus*, In Book II, Chapter VI, Vitruvius compares the properties of the true natural pozzolan from the Bay of Naples around Mount Vesuvius (Pozzuoli), with those of *carbunculus*, a calcined stone from Etruria (North of Rome) (*sic in Etruria excocta materia efficitur carbunculus*). Both are excellent for concrete structures, yet *carbunculus* has advantages in buildings on land, whereas true pozzolan is best for piers built into the sea. We have seen, above that the reaction of lime with alkaline pozzolan yields a soluble alkaline silicate. OST 7G mortar results from the reaction between lime and analcime type *cretoni*. The product of this reaction is an aluminosilicate of type Si(Q3Si, 1OH) and Si(Q4Si) (-86 ppm to -94 ppm range) different to those expected with regular pozzolan. There is no hydrated gehlinites in OST 7G cement deduced from  $^{27}\text{Al}$  Spectroscopy. The content in Al(6) in the OST 7G cement (3%) is equal to the content of Al(6) in *cretoni* (3%). The final make-up of OST 7G cement would be:

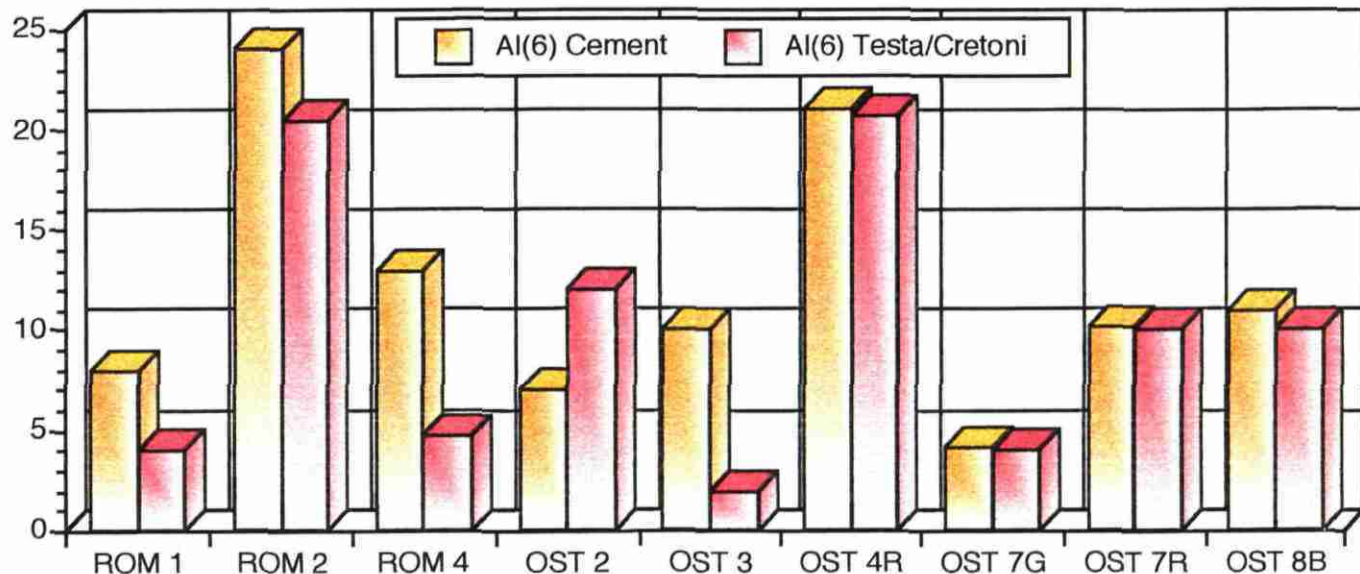
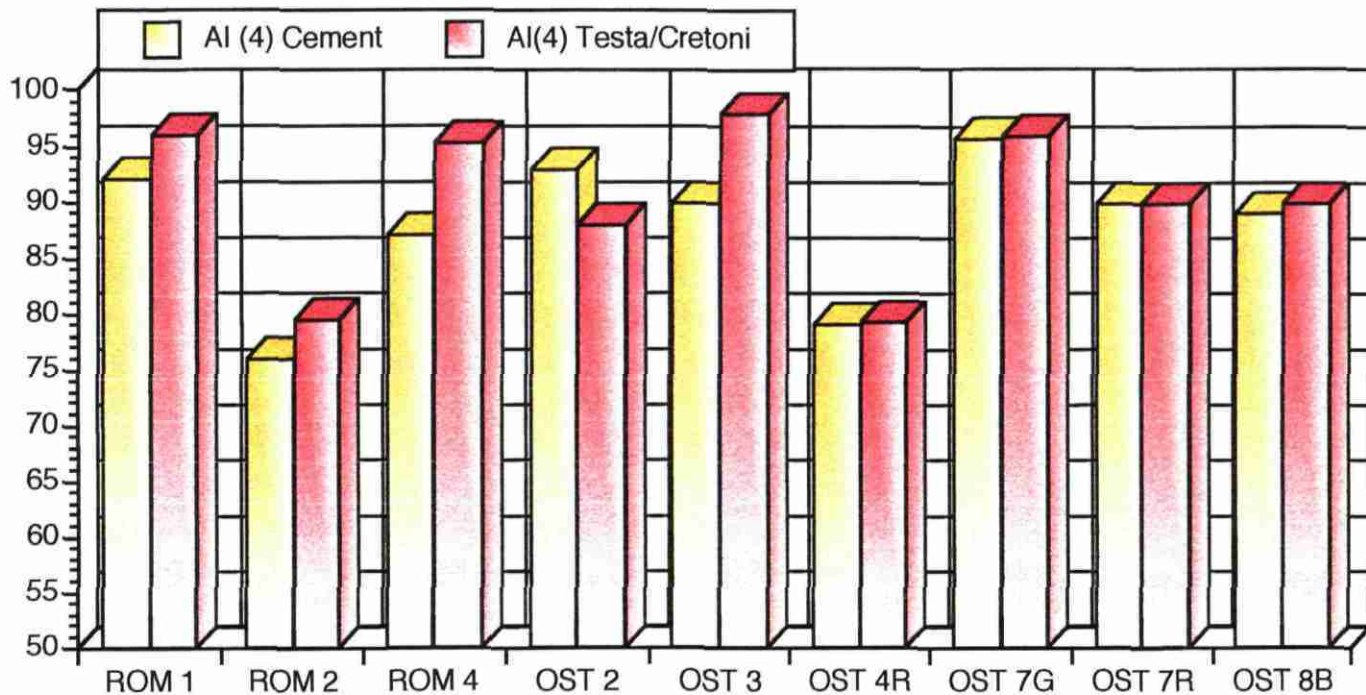
- recarbonated lime
- hydrated feldspathoid
- fine grained zeolithic volcanic tuff

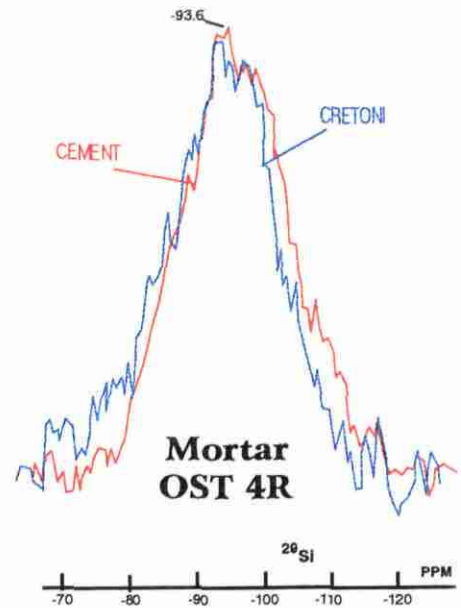
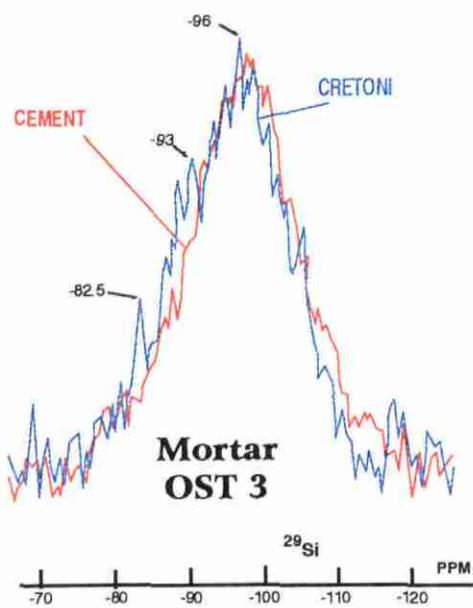
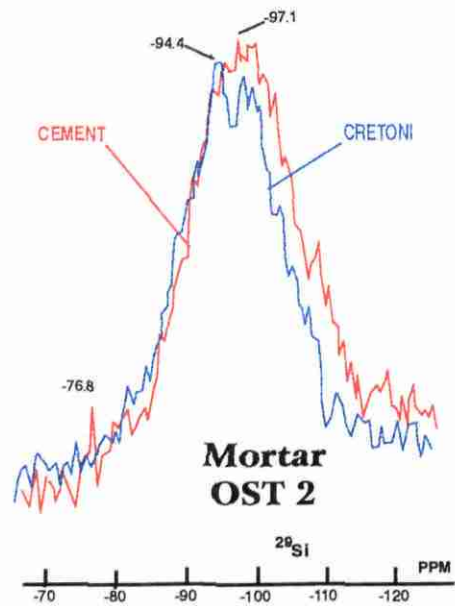
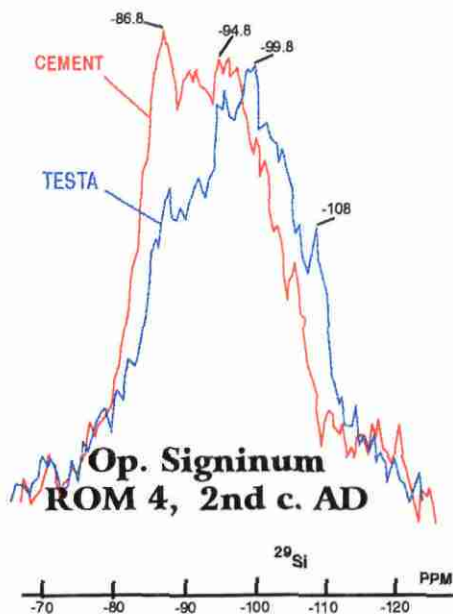
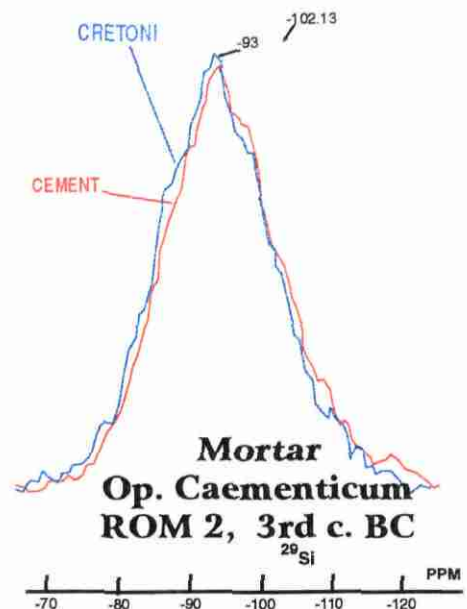
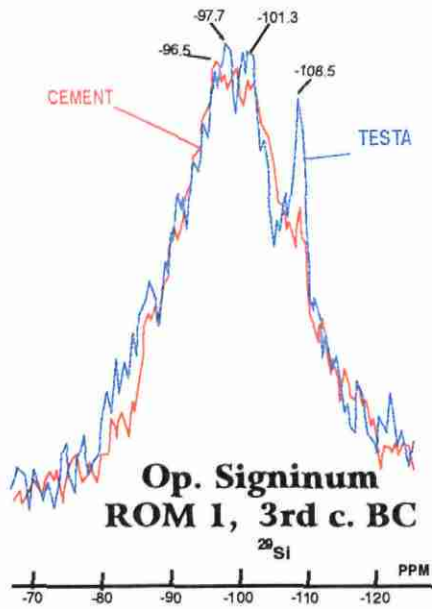
Hydrated feldspathoid is X-rays amorphous. This explains why it was not detected with conventional techniques (see CAGLIARI report in Annex)

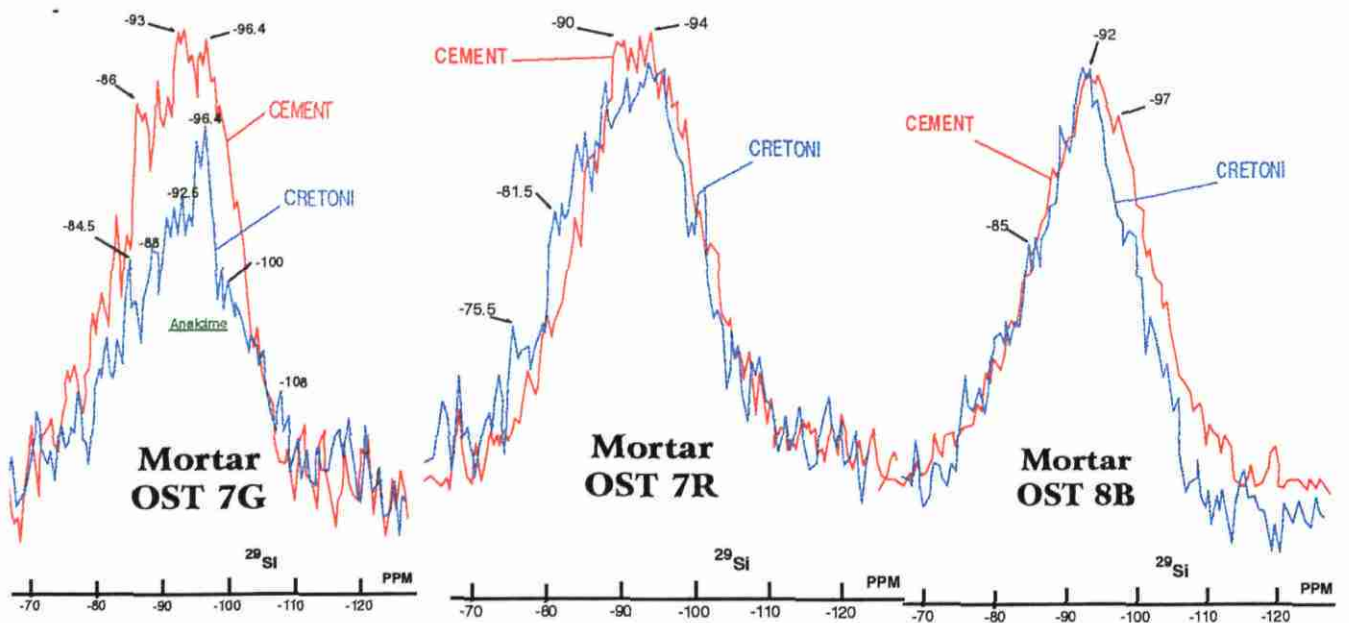
Conclusion:

The two archaeological analogues ROM 4 and OST 7G display NMR spectra similar to those of GEOCISTEM Carbunculus cements. They also have Si(Q3Si, 1OH) (-86 ppm) and Si(Q4Si) (-90 ppm) sites. This would suggest archaeological long-term durability for all GEOCISTEM Carbunculus cements. From an ingredient make-up point of view, we can also state that the archaeological equivalent for the GEOCISTEM Carbunculus cement is the *Opus Signinum* lime-mortar, provided its *testa* does contain a zeolithic temper (analcime-philipsite type). However, GEOCISTEM cements are acid-resistant because they do not contain any calcium carbonate.

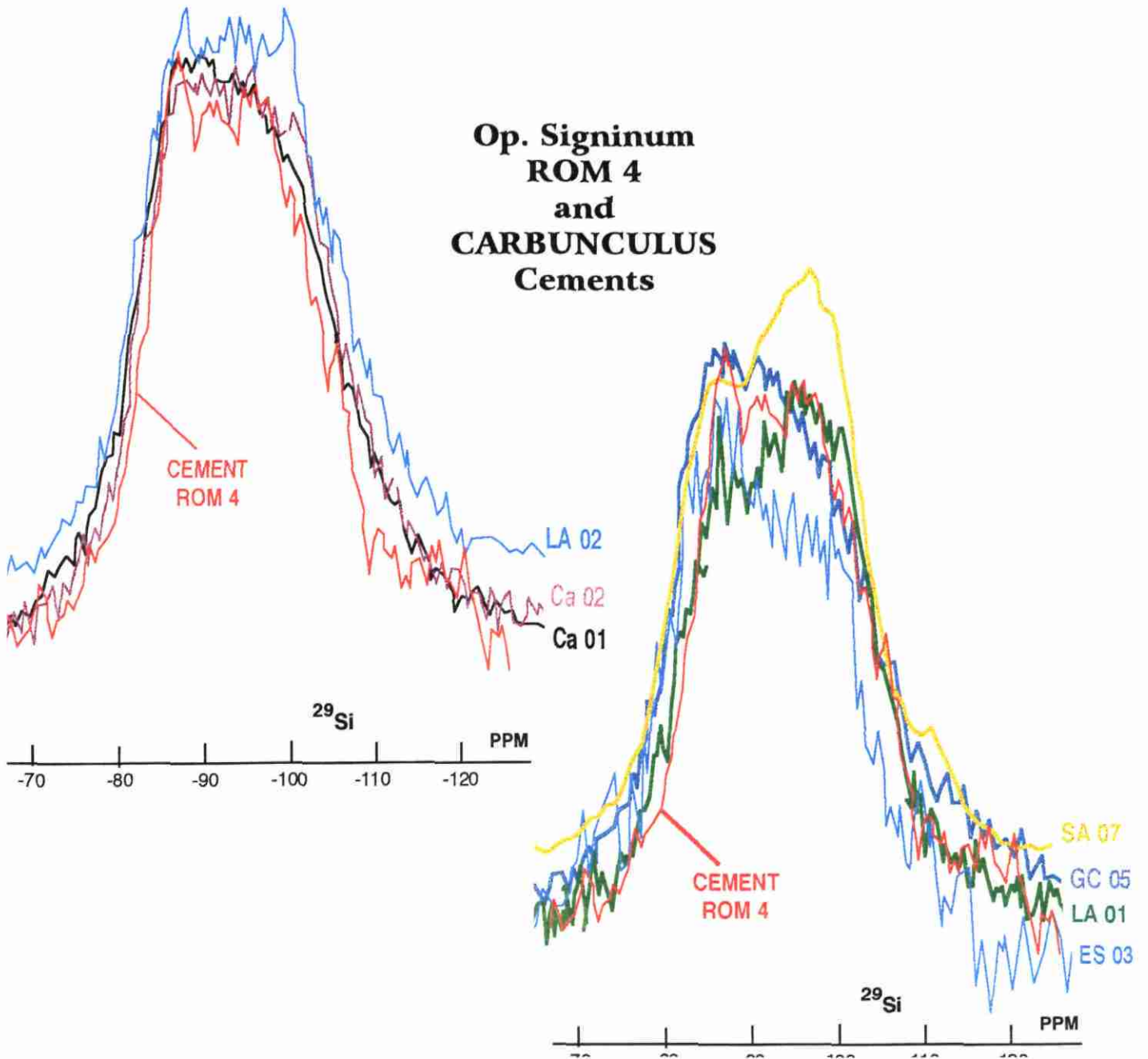
**<sup>27</sup>Al MAS-NMR Spectra  
Roman Mortars  
1) Cement: fines  
2) Aggregates : Testa or Cretoni**

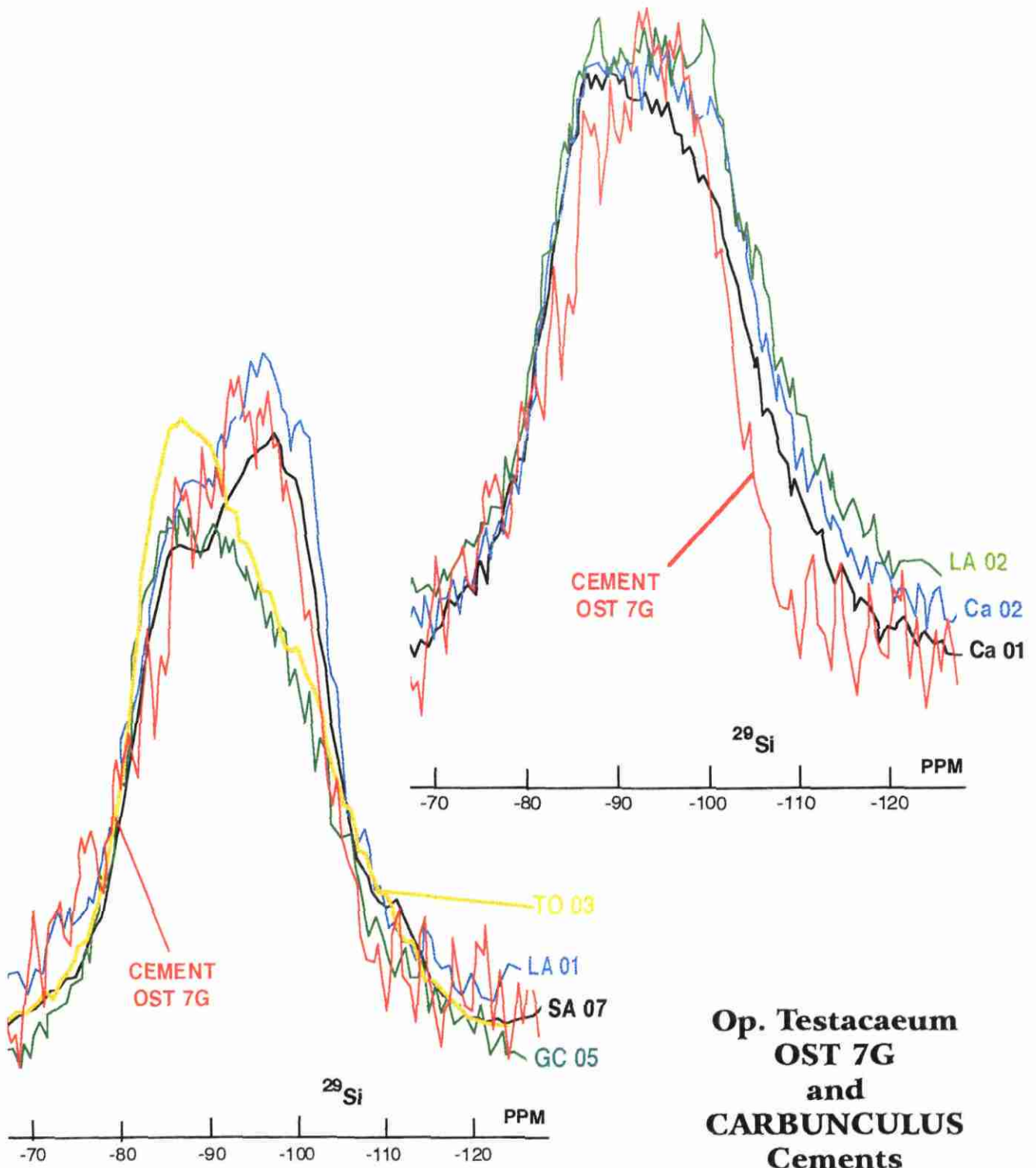


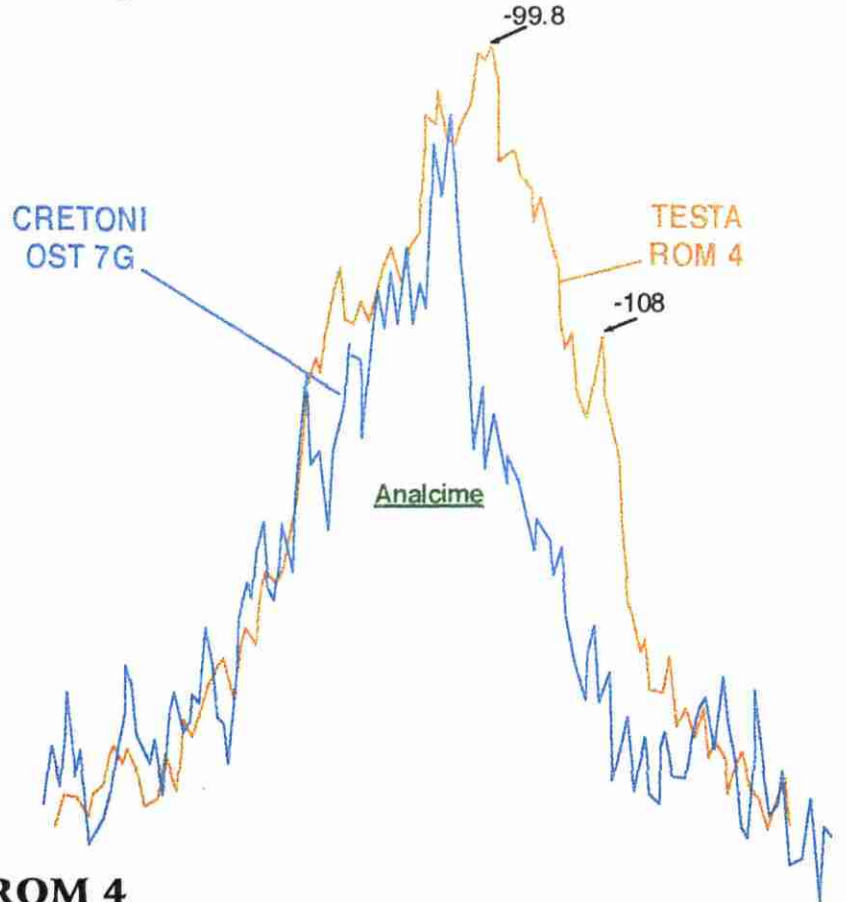




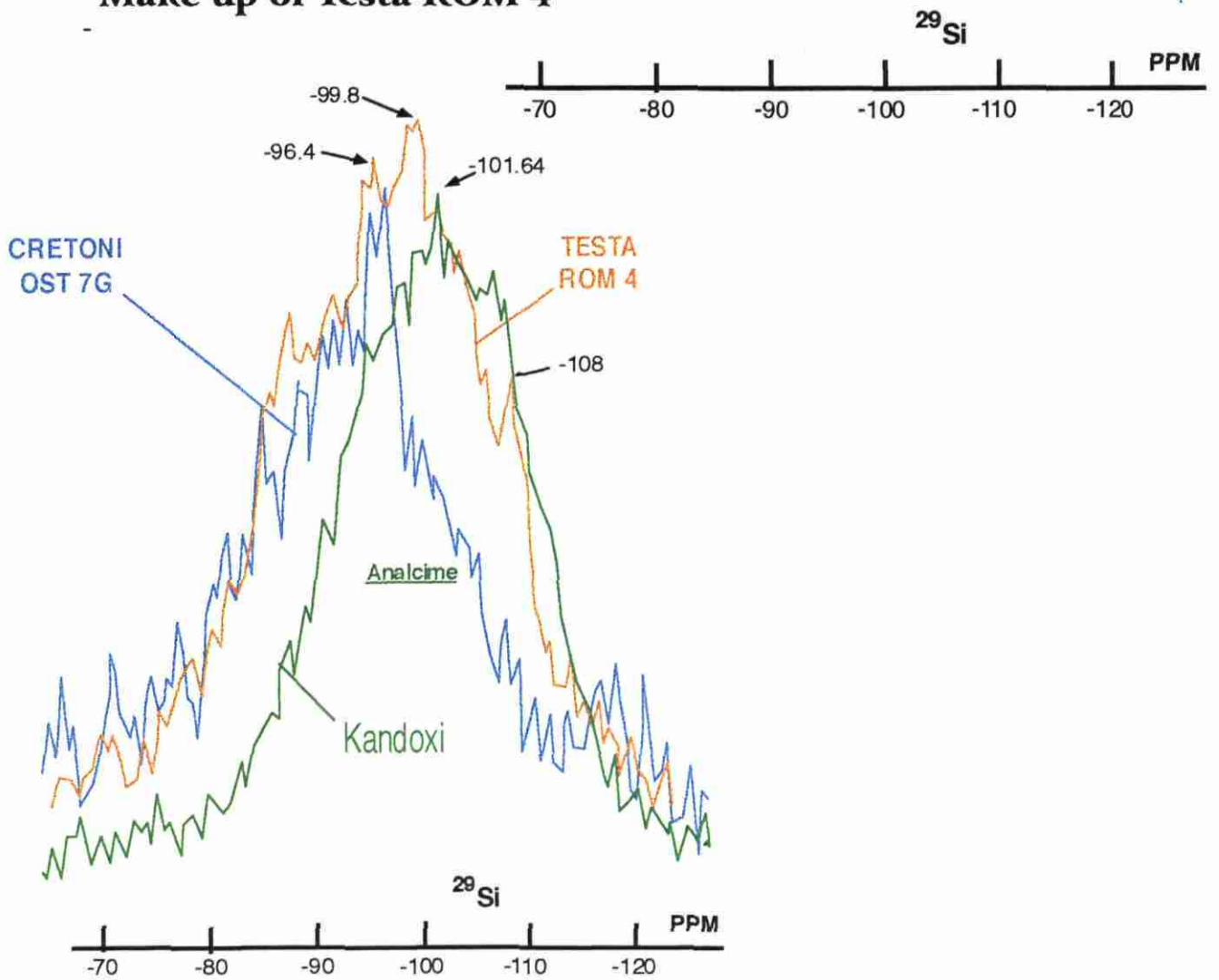
### Op. Signinum ROM 4 and CARBUNCULUS Cements

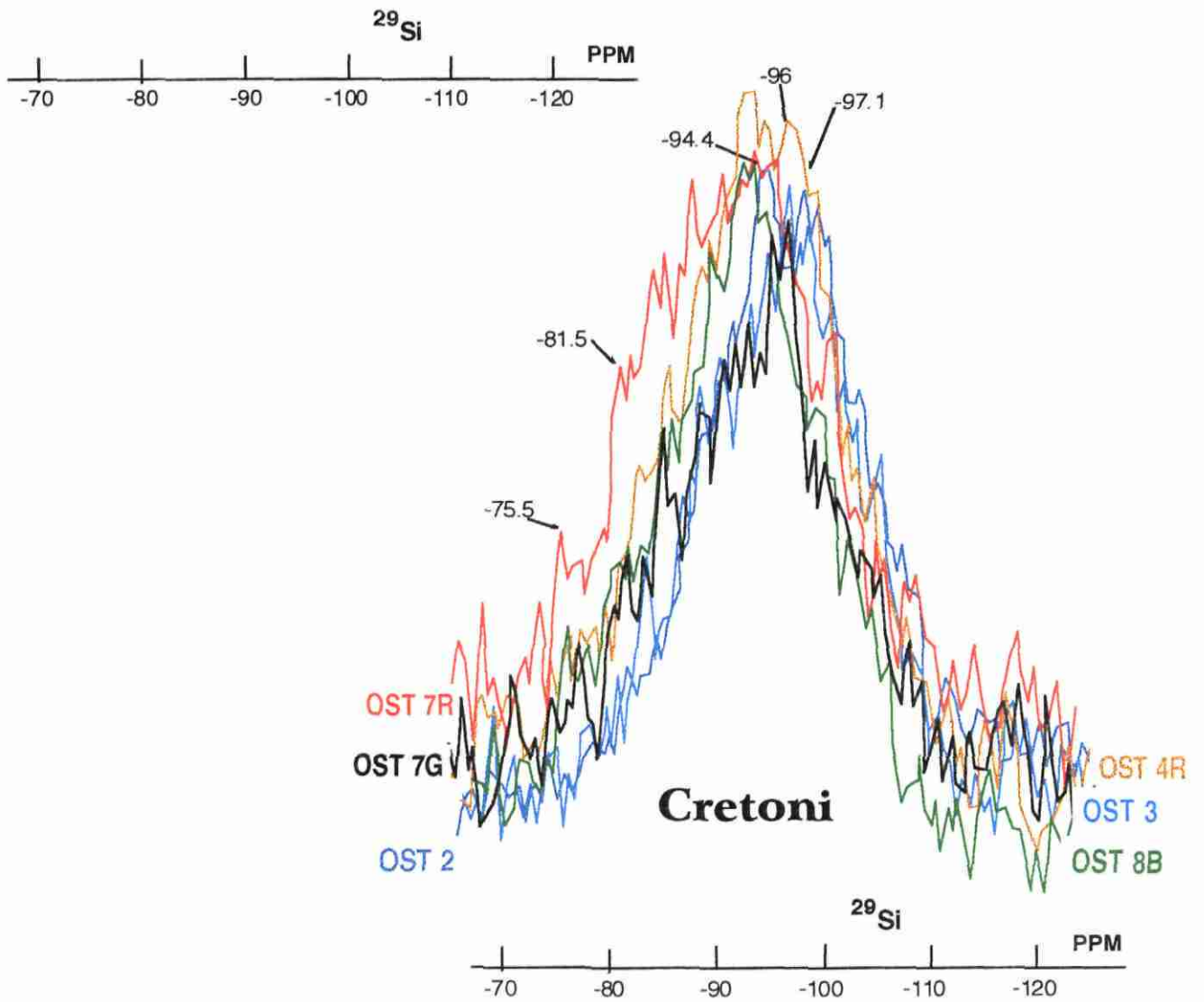
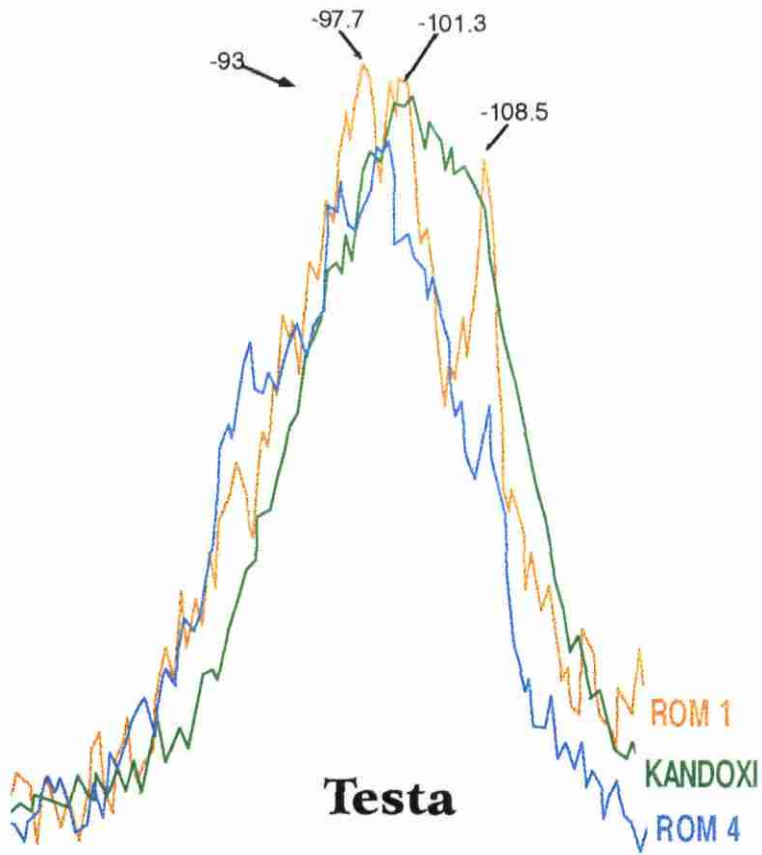






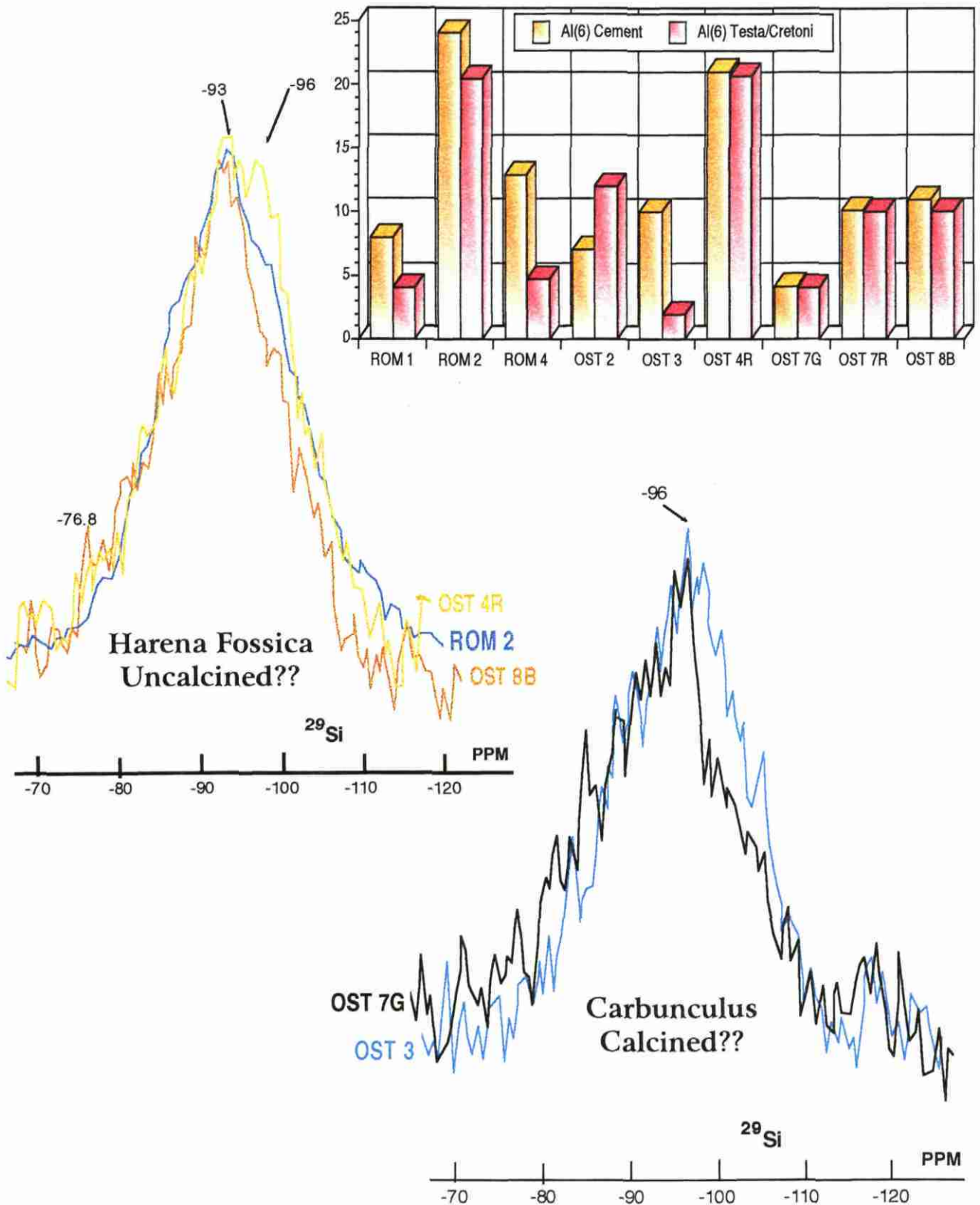
### Make up of Testa ROM 4





### Carbunculus calcined or uncalcined?

Very high amount of Al(6) could suggest uncalcined cretoni, such as ROM 2, OST 4R and OST 8B. On the opposite, very low amount of A(6) could pinpoint on calcined cretoni, i.e. on "carbunculus", such as OST 3 and OST 7G



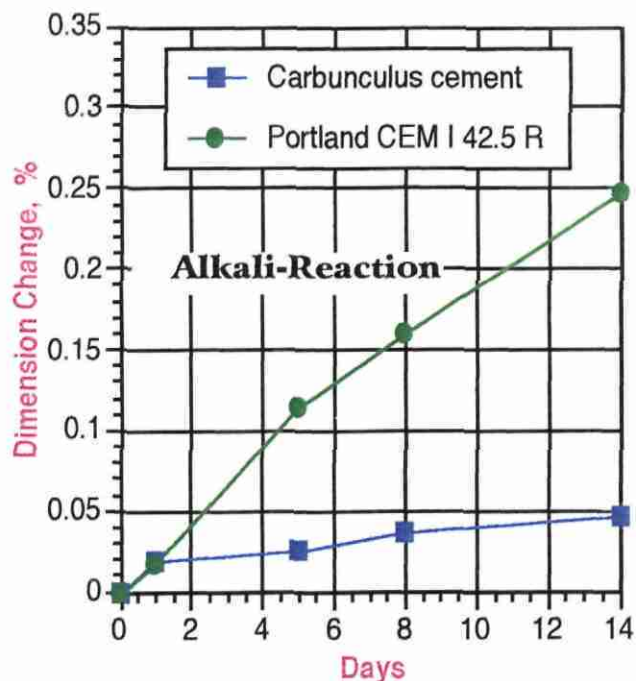
## Subtask n°9.4: PRENORM 2

### Long-term + NMR chemistry mechanism

#### Alkali-Silica-Aggregate reaction

CARBUNCULUS cement contains ca. 10% by weight of alkali  $K_2O/Na_2O$ . This high alkali content poses problem to the concrete industry. It is well known that with Portland cement, any excess in alkali above 1% by weight generates the deleterious Alkali reaction with Silica.

As a consequence, the tendency has been to avoid any addition of alkali in ordinary Portland cement and commonly to require from the cement manufacturers the supply of low-alkali cements. Preliminary studies carried out by CORDI-GEOPOLYMER and associated cement manufacturers, involving  $^{27}Al$  MASNMR and  $^{29}Si$  MASNMR spectroscopy [1], revealed that geopolymeric cements are the synthetic analogs of natural pozzolans which are known to effectively suppress the alkali-aggregate reaction. The chemical make up of geopolymer cement is close to that of Italian pozzolan and Rhineland trass. The Figure displays the results of the tests carried out according to an accelerated expansion test in saturated NaCl bath, developed in Denmark and tested in various Italian cement laboratories, including CEMENTI BUZZI. The results obtained confirm the good properties of CARBUNCULUS cement, which does not show any expansion in comparison to Portland cement. These results are equivalent to the good results obtained previously in the Background Knowledge on laboratory PZ-GEOPOLY binder (see WORKPROGRAMME, pages 5-6). Geopolymer cements, even with alkali contents as high as 10%, do not generate any dangerous alkali-aggregate reaction.



Alkali-Silica-Aggregate reaction;  
NaCl accelerated test

The fostering of alkali-based CARBUNCULUS cements will mean a dramatic change in the normative development presently carried out on Portland cement related concretes.

#### Chemistry mechanism. NMR Spectroscopy

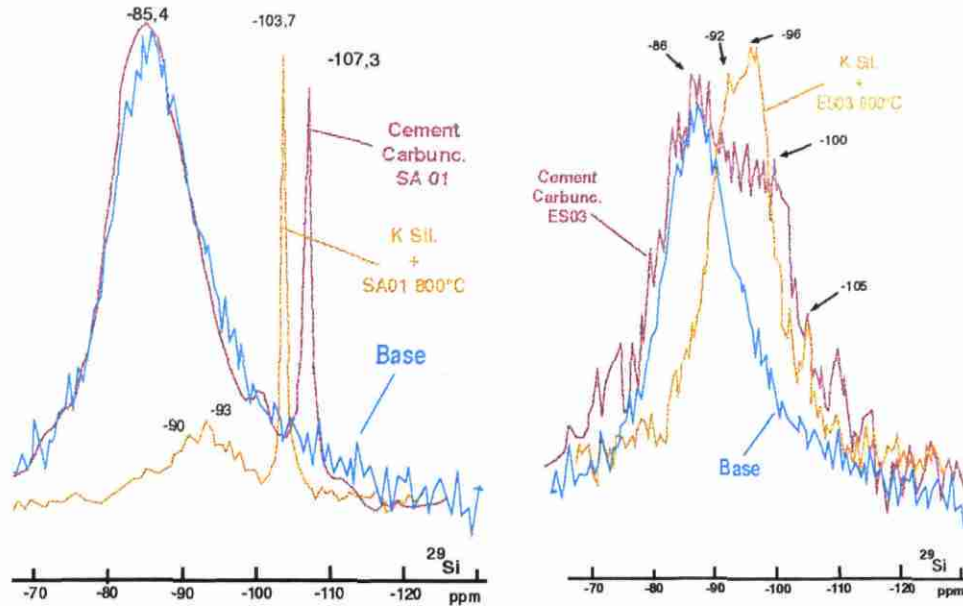
The purpose of the study, in terms of long-term stability, is to demonstrate that the end product of the geopolymeric reaction are always high-molecular silicates or aluminosilicates. Low molecular weight silicates would lead to poor stability and weakness, essentially towards acid medium and biodegradability. It is therefore important to follow the reaction steps between each reactive ingredient of the Cement Base, with the geological elements: glass or calcined  $800^{\circ}C$ .

##### Reaction of K-Silicate ( $K_2O, 1.85SiO_2, nH_2O$ )

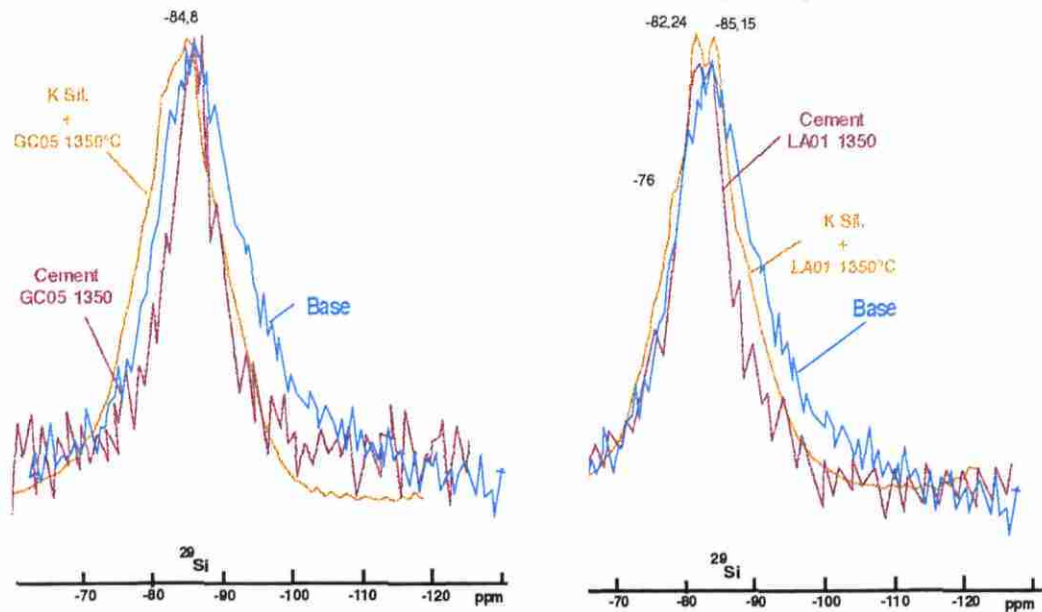
The figure displays  $^{29}Si$  NMR spectra for the reaction of K-Silicate with SA01  $800^{\circ}C$  and GC05  $800^{\circ}C$ ., and the correspondent Carbunculus cements. There is no low molecular K-silicate from type SiQ0, SiQ1 or SiQ2 (-70 to -80 ppm range).

The figure displays  $^{29}Si$  NMR spectra for the reaction of K-Silicate with glasses LA01  $1350^{\circ}C$  and GC05  $1350^{\circ}C$ ., and the correspondent Glass cements. There is no low molecular K-silicate from type SiQ0, SiQ1 or SiQ2 (-70 to -80 ppm range).

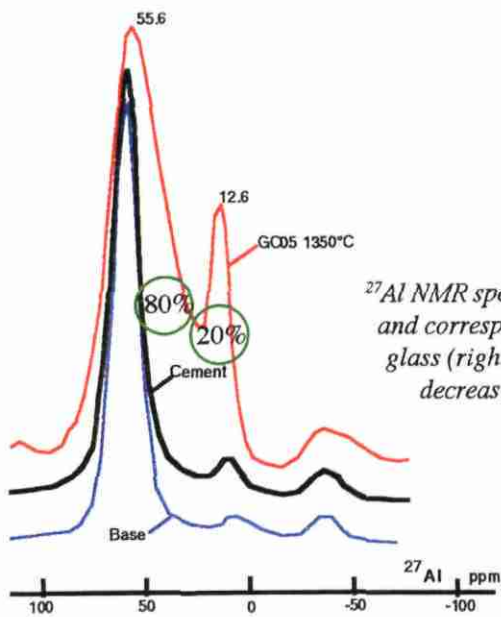
$^{27}Al$  NMR spectra show K-Silicate reacting with the AlO6 sites of LA01/GC05  $1350^{\circ}C$  glass.



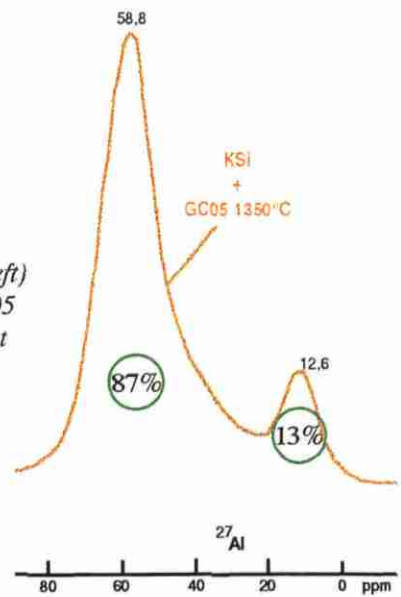
<sup>29</sup>Si NMR spectra for SA01 and GC05 Carbunculus Cements and corresponding K-Silicate reaction

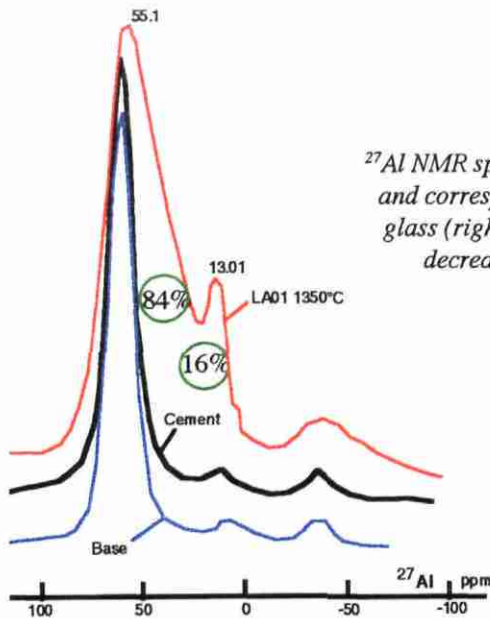


<sup>29</sup>Si NMR spectra for LA01 and GC05 Glass Cements and corresponding K-Silicate reaction

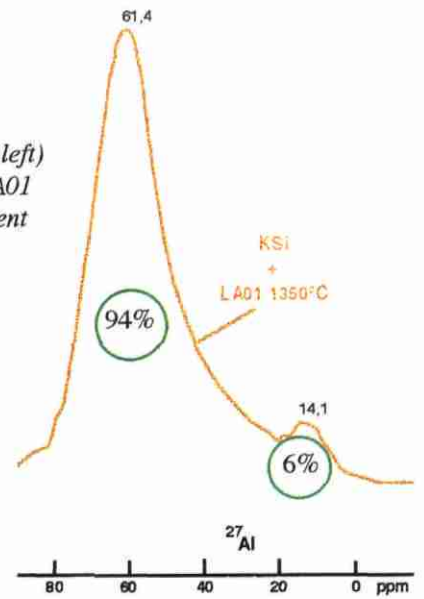


<sup>27</sup>Al NMR spectra for GC05 Glass and Cement (left) and corresponding K-Silicate reaction with GC05 glass (right). The AlO6 sites are reactin, content decreasing from 20% to 13% respectively.





<sup>27</sup>Al NMR spectra for LA01 Glass and Cement (left) and corresponding K-Silicate reaction with LA01 glass (right). The AlO6 sites are reactin, content decreasing from 16% to 6% respectively.



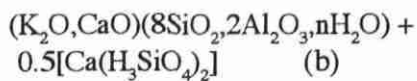
Reaction of Kandoxi on Slag+K-Silicate.

The figure displays the evolution of the alkali activated slag (with K-Silicate) in function of Kandoxi added, namely: 0%, 22%, 36% by weight of the mix slag+K-silicate. The alkali-activated slag shows a main resonance at -82 ppm for a Si(Q2,2OH) low molecular, linear, silicate structure. The addition of Kandoxi generates a shift of the main resonance towards -86, -88 and -92 ppm, for framework silicate structures of the type Si(Q3,1OH) and Si(Q4).

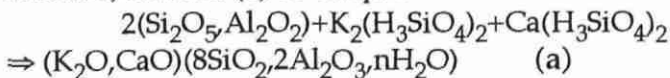
Chemical stability implies a silicate structure from type Si(Q4) found in laboratory GEOPOLYMITE binders of the Background knowledge []. In the present Cement Base, even with the addition of 33% Kandoxi, a substantial quantity of Si(Q3,1OH) sites are still present in the structure. The chemical analysis of the hardened Cement Base performed in Task PRENORM 1 by BRGM, provides an explanation. The chemical composition of the vitreous matrix (Chapt. 2.3.5.2.):

SiO<sub>2</sub>: 37%    Al<sub>2</sub>O<sub>3</sub>: 14%    K<sub>2</sub>O: 7%  
 CaO: 6%    H<sub>2</sub>O: 34%

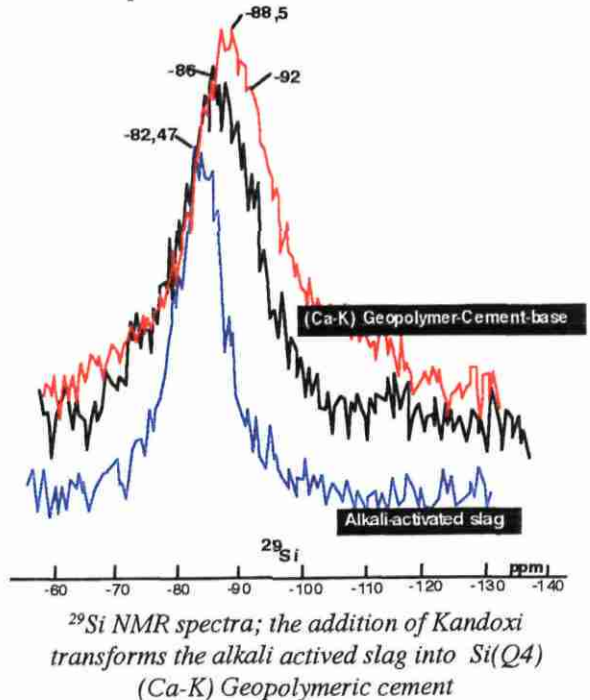
corresponds to a general formula:  
 (K<sub>2</sub>O,1.5CaO)(9SiO<sub>2</sub>,2Al<sub>2</sub>O<sub>3</sub>,27H<sub>2</sub>O) that can also be written:



By comparing it with the basic geopolymeric reaction, formula (a) of Chap. 1

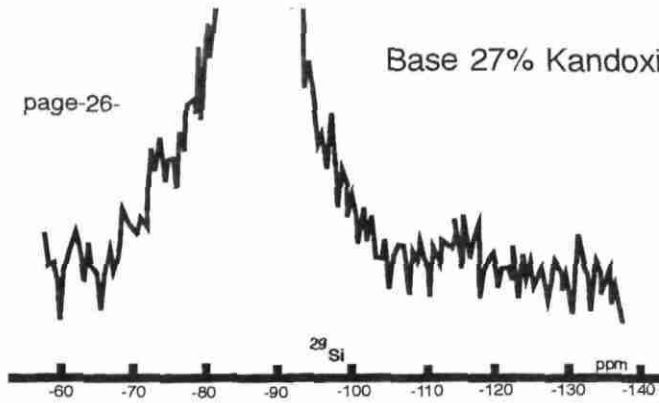


one understands that it is the excess in calcium disilicate Ca(H<sub>3</sub>SiO<sub>4</sub>)<sub>2</sub> produced by the alkali reaction on the melilitic slag, that might induce the Si(Q3, 1OH) structure.



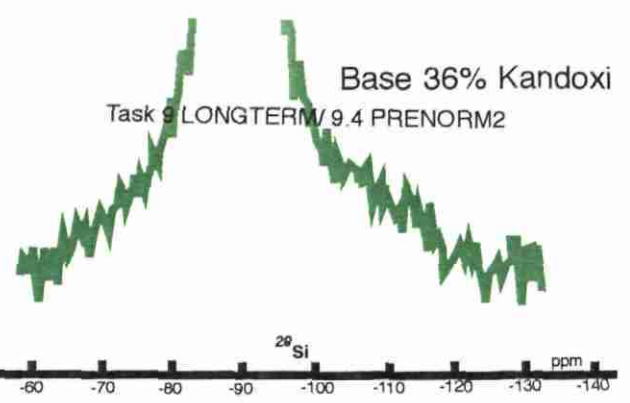
<sup>29</sup>Si NMR spectra; the addition of Kandoxi transforms the alkali activated slag into Si(Q4) (Ca-K) Geopolymeric cement

Base 27% Kandoxi



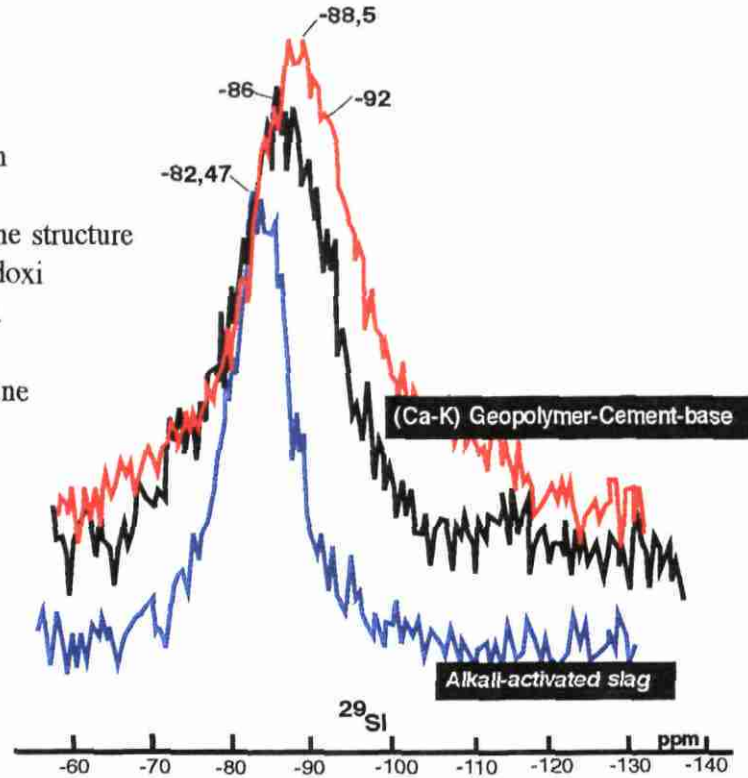
Base 36% Kandoxi

Task 9 LONGTERM/9.4 PRENORM2

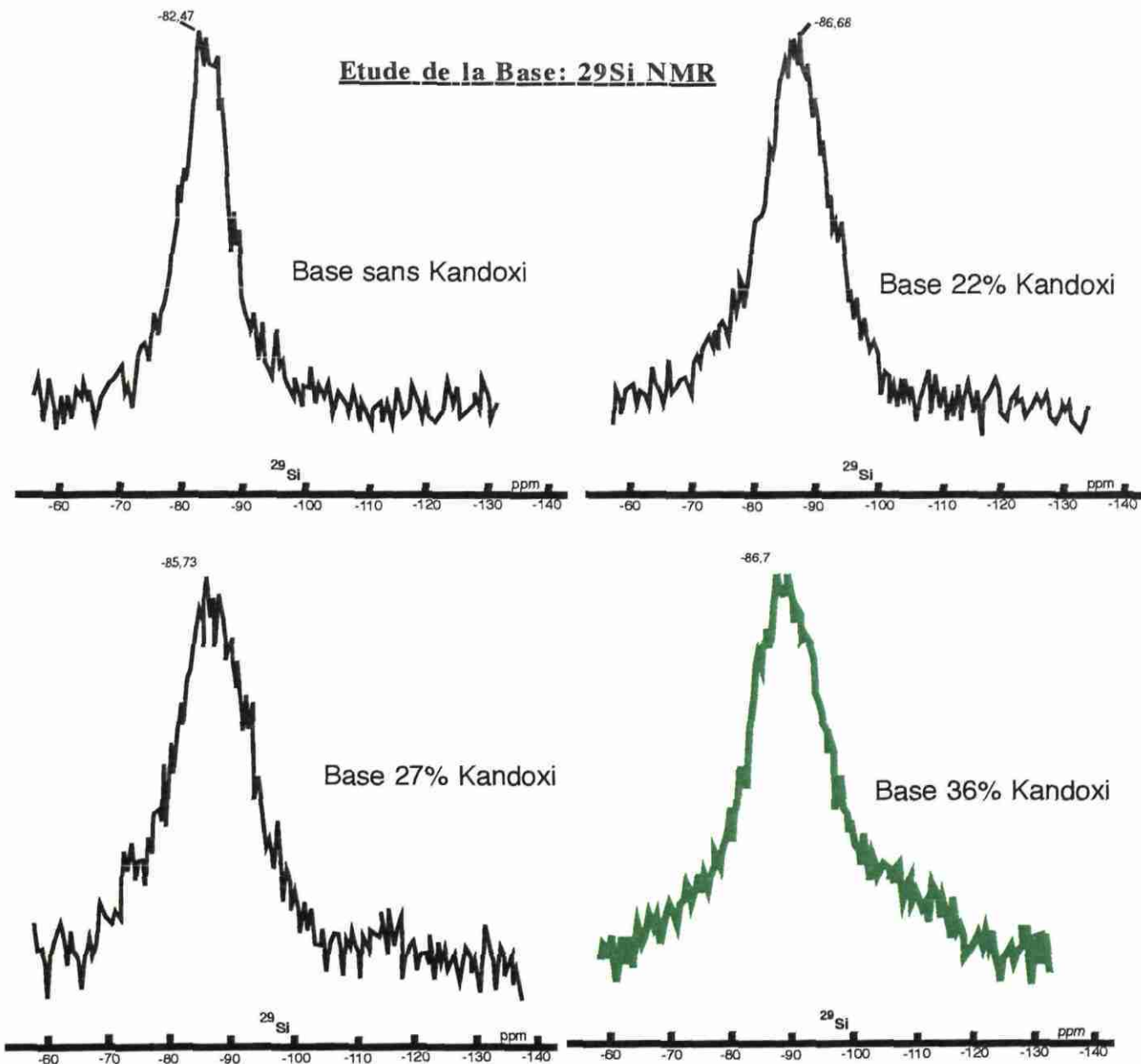


Evolution de la structure de la Base en fonction de la quantité de Kandoxi (0%, 22%, 36%). La base sans Kandoxi (alkali-activated slag) a une structure de type Si(Q2,2OH). L'addition de 22% de Kandoxi transforme la structure en Si(Q3,1OH) et Si(Q4).

La stabilité aux corrosions chimiques implique une structure de type Si(Q4) (33%).



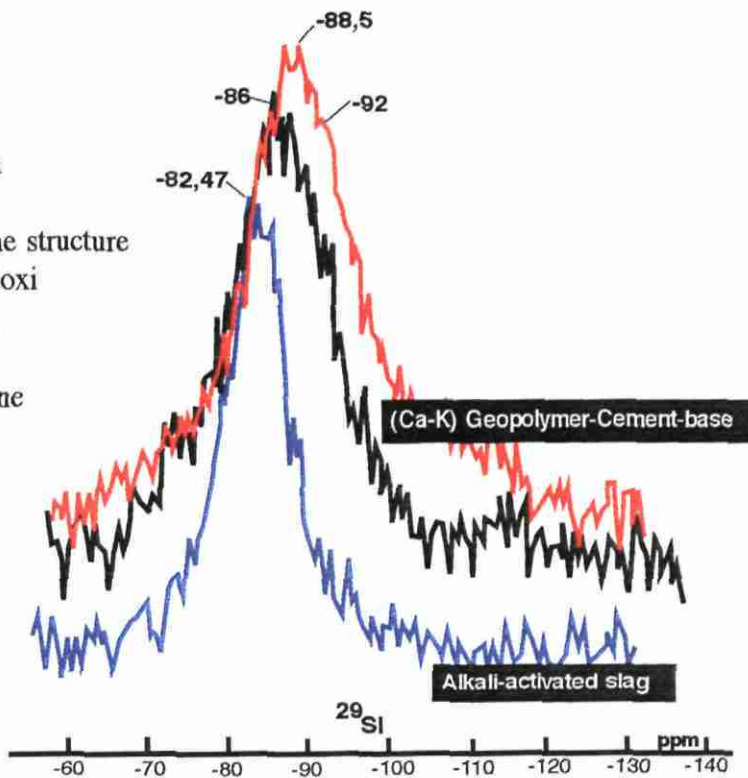
## Etude de la Base: $^{29}\text{Si}$ NMR



Evolution de la structure de la Base en fonction de la quantité de Kandoxi (0%, 22%, 36%).

La base sans Kandoxi (alkali-activated slag) a une structure de type  $\text{Si}(\text{Q}2,2\text{OH})$ . L'addition de 22% de Kandoxi transforme la structure en  $\text{Si}(\text{Q}3,1\text{OH})$  et  $\text{Si}(\text{Q}4)$ .

La stabilité aux corrosions chimiques implique une structure de type  $\text{Si}(\text{Q}4)$  (33%).



Etude de la Base :  $^{27}\text{Al}$  NMR

