Consiglio Nazionale delle Ricerche
Istituto per l'Energetica e le Interfasi

Geopolymer Camp 2014 Saint Quentin

July 8, 2014

CHALLENGING MATERIALS FOR RESTORATION OF CULTURAL HERITAGE

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Part A: Strengthening and repair with Fiber Reinforced GEOPolymers (FRGP)

Strengthening and repair of both modern and historic masonry constructions (buildings, bridges, towers) and structural components (walls, arches and vaults, piers and columns) by Fiber Reinforced Polymers (FRP) technique.

Recently, inorganic matrices like cement or lime based mortars have been proposed as an alternative choice to epoxy resin.

GEOPOLYMERIC MATRICES

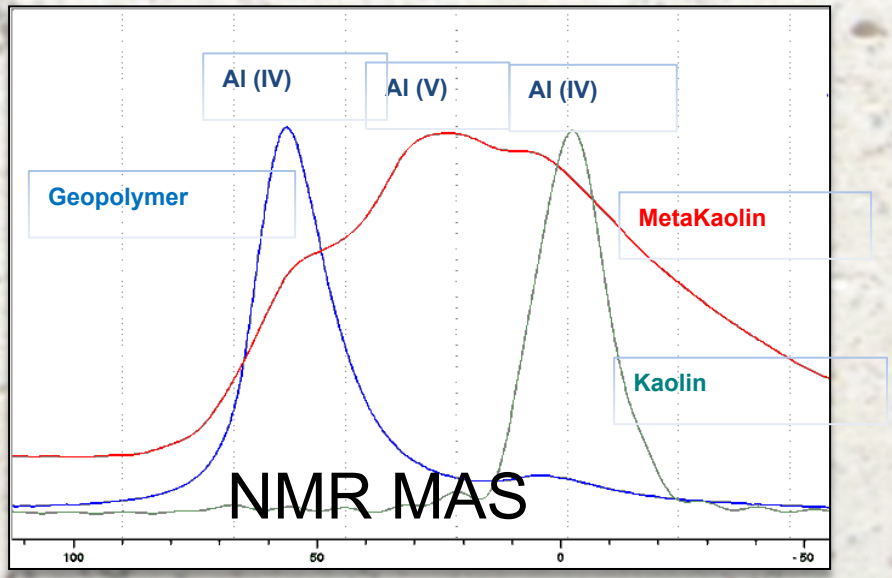
- combination of the best characteristics of ceramic and cement based materials;
- potential ability to reduce from 20 to 80% the emission of CO2;
- reduction of the raw materials consumption;
- excellent fire resistance.

GEOPOLYMER FORMULATION:

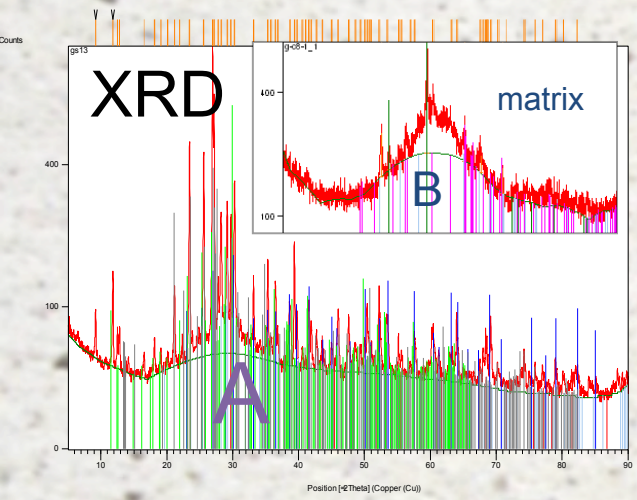
Metakaolin (MK): (medium particle size 0.8-10 um, BET 16.31 ± 0.09 m2/g) calcinated at 780°C
SLAG (GBF): Granulated Blast Furnace SLAG, reduced at the appropriate grain size (10-500um
Base sol. (SiO2/Na2O=1.5) LUDOX® TM-50 colloidal silica, NaOH pellets, and Water
Wollastonite: (grain size < 45um)
Fine Granulated Sand: (grain size of 0,2-0,6 mm)

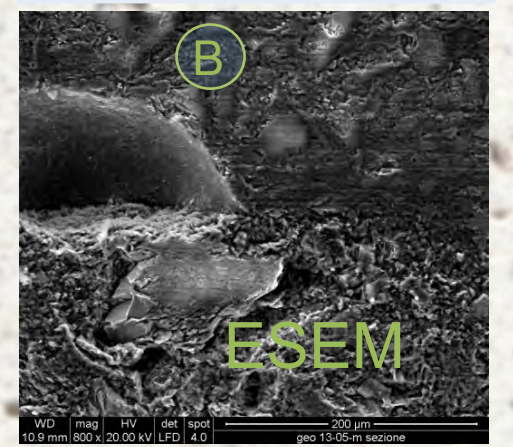
Chemical Characterization

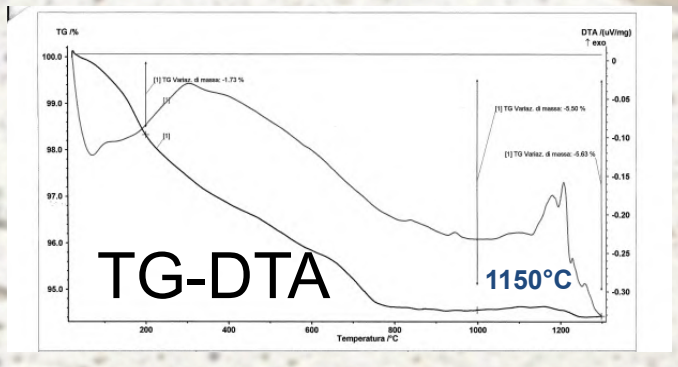
Wt%	Al_2O_3	SiO_2	Na_2O	CaO	K_2O	Fe_2O_3	TiO_2	MgO	Other	LOI
MK1	41.5	55.2	-	0.32	1.0	0.81	1.0	-	-	1.6
GBF	11.6	35.6	7.23	42.0	0.4	0.32	0.29	7,41	1,9	0.7
Geo	15,1	59,66	9,73	11,37	0,68	1,5	0,40	1,54		

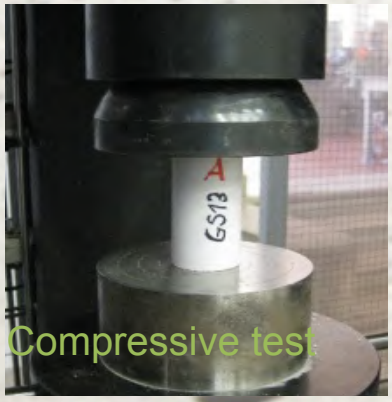


Geopolymer Matrix Characterization

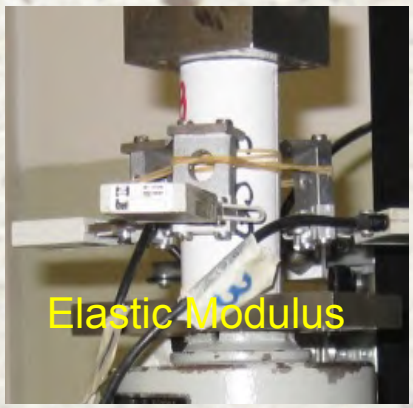




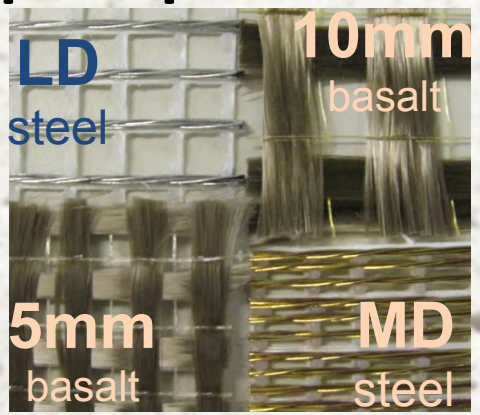


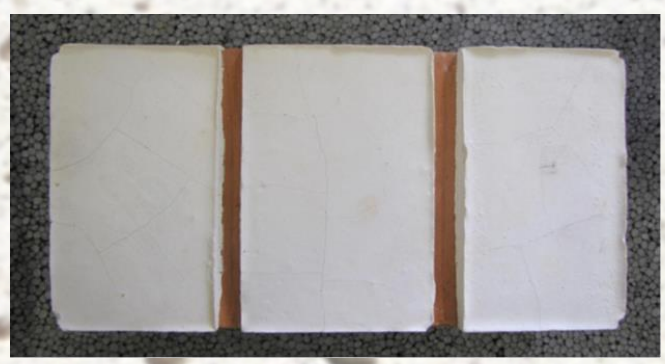


H_2O Adsorb 70°C	Density g/cm³	Porosity	Hardness (Barcol)	Rc N/mm²	E N/mm²
14%	1.8	31%	61	38,24	11428

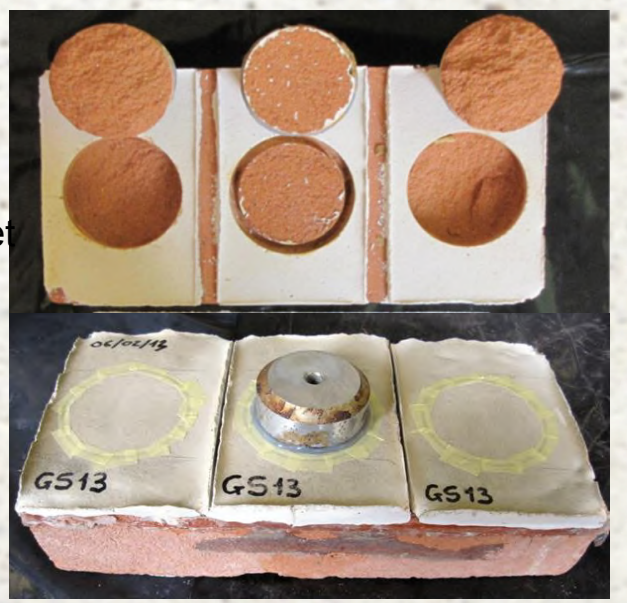


FRGP
Sample preparation and Test





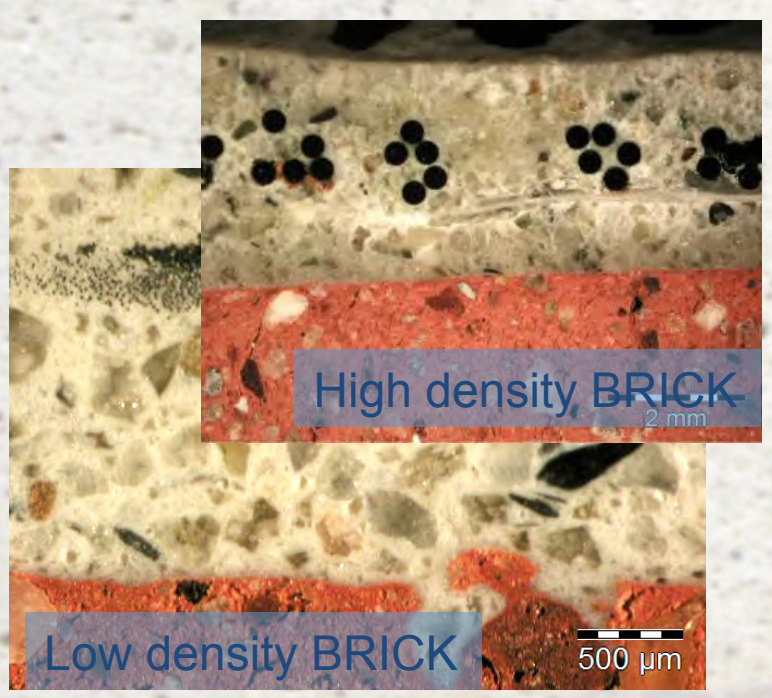
- ✓ Two type of bricks: solid soft clay (SanMarco) and High density clay (Solava)
- ✓ the geopolymeric resin with embedded basalt and steel fiber net was vibrated to ensure a good distribution of the geopolimer into the fibers.
- ✓ The binding performance of reinforcements was qualitatively and quantitatively evaluated by means of **pull-off tests**.

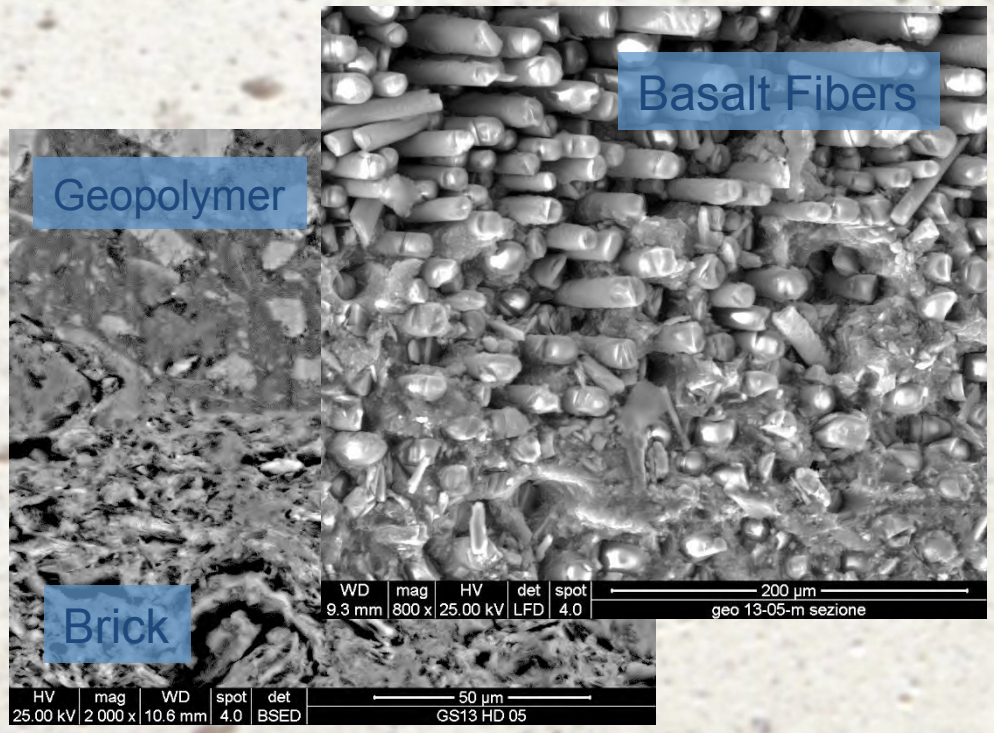


An aluminium dolly able to be connected through a spherical joint to a dynamometer that applies a force, normal to the surface itself, increasing until failure occures, was glued on an isolated area on the renforcement's surface

Adhesion

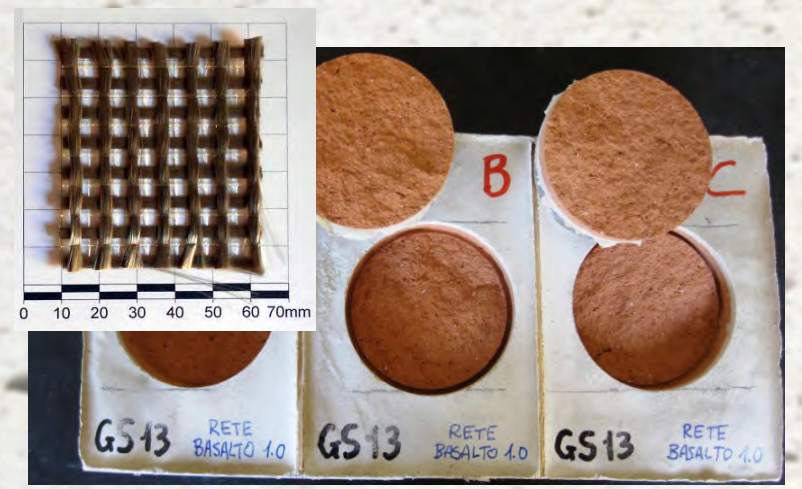
Morphological investigations at the **interfaces** (brick-geopolymer matrix-fiber).
NO fissures or cracking during geopolymer setting,
NO cracking and detachments induced by the mechanical stress of the pull-off tests.





Images of the fiber embedded in the geopolymeric matrix and the interfacial region between the geopolymer and the brick.

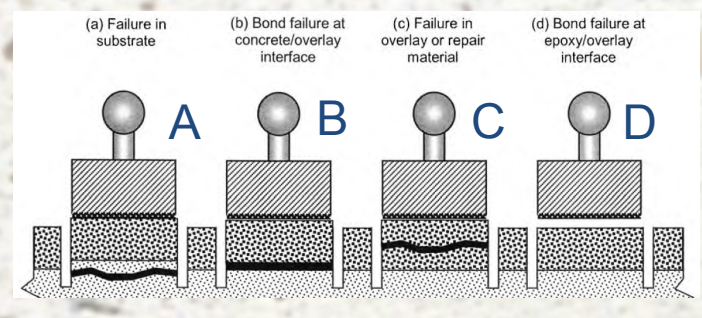
Results of Mechanical Tests



Basalt Fiber Net

Steel Fiber

Failure Type



	Soft San Marco brick			HD Solava brick	
	Failure Type	f_{P-O} N/mm²		Failure Type	f_{P-O} N/mm²
Brick		0.97			2.72
GS13 no net	A	0.89		A	2.69
GS13 + F Basalt 5mm	A	0.94		C	2.32
GS13 + F Basalt 10mm	A	1.02		A/C	2.12
GS13 + LD steel	A	1.19		A/C	2.81

FRGP Conclusions

- **This paper presents a first assessment of Fibre-Reinforced Geopolymers (FRGP) as strengthening material for masonry buildings: three geopolymeric matrices were coupled with either bidirectional basalt nets or unidirectional high-strength steel cords, then applied to soft and strong clay bricks.**
- **The formulation of the geopolymeric matrix is effective for a complete geopolymerization reaction.**
- **Optimum adhesion of the geopolymer matrix to porous soft mud and extruded clay brick also in presence of reinforcing fibers**
- **Pull-off tests confirm the very good binding performance from a mechanical point of view of geopolymers with building materials**
- **Good compatibility of the Fiber Reinforced Geopolymers with these kind of materials for structural strengthening of masonry buildings**

Part B: Restoration of pottery, ceramics or bricks

Restoration and reconstruction of missing parts of pottery, ceramics or bricks actually done with the use of organic (paraloyd B72) or inorganic (gypsum, polyfilla etc…) materials

Principles on Restoration of Cultural Heritage:

- **Compatibility (chemical, physical, mechanical)**
  - Added material must avoid: different thermal expansion, different behavior over time; states of constraint; formation of nuclei hyper-resistant; acceleration of deterioration on the edge of the renovated areas etc
- **Durability**
  - The same duration of the material to restore
- **Reversibility**
  - additions and integrations must be removable at any time
- **Retractability**
  - Use of materials/systems that do not impede the possibility of further future restoration actions
- **Interdiction**
  - Use modern binders based on Portland Cement

OBJECTIVES: Assessment of **geopolymeric** materials as alternative choice for traditional materials

Experimental: Development of geopolymer composites able to bind different ceramic materials and relative tests of flexural strength and removability

Classification of Samples:

Medieval Ceramics :

Rough Medieval (10): GM
Rough Roman (10): GR
Purified Amphora (10): DA
Purified Common (12): DC

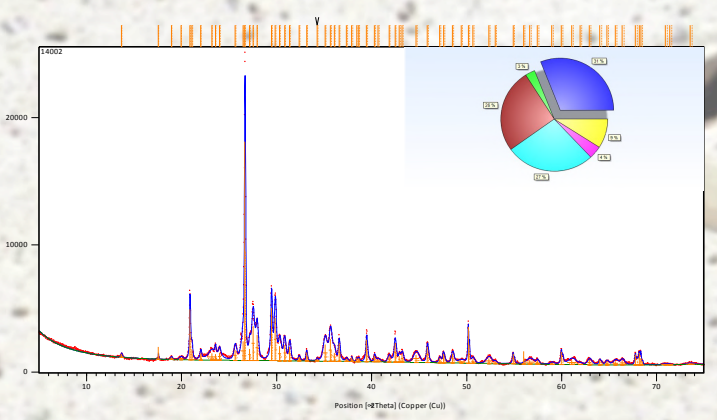
Roman Bricks

Roof Tiles A (7): LC
Roof Tiles B (7): LT
Bricks (7): LM

High density modern Brick: solava

SAMPLES: CERAMIC FIRING TEMPERATURE

X-ray diffraction analyses:



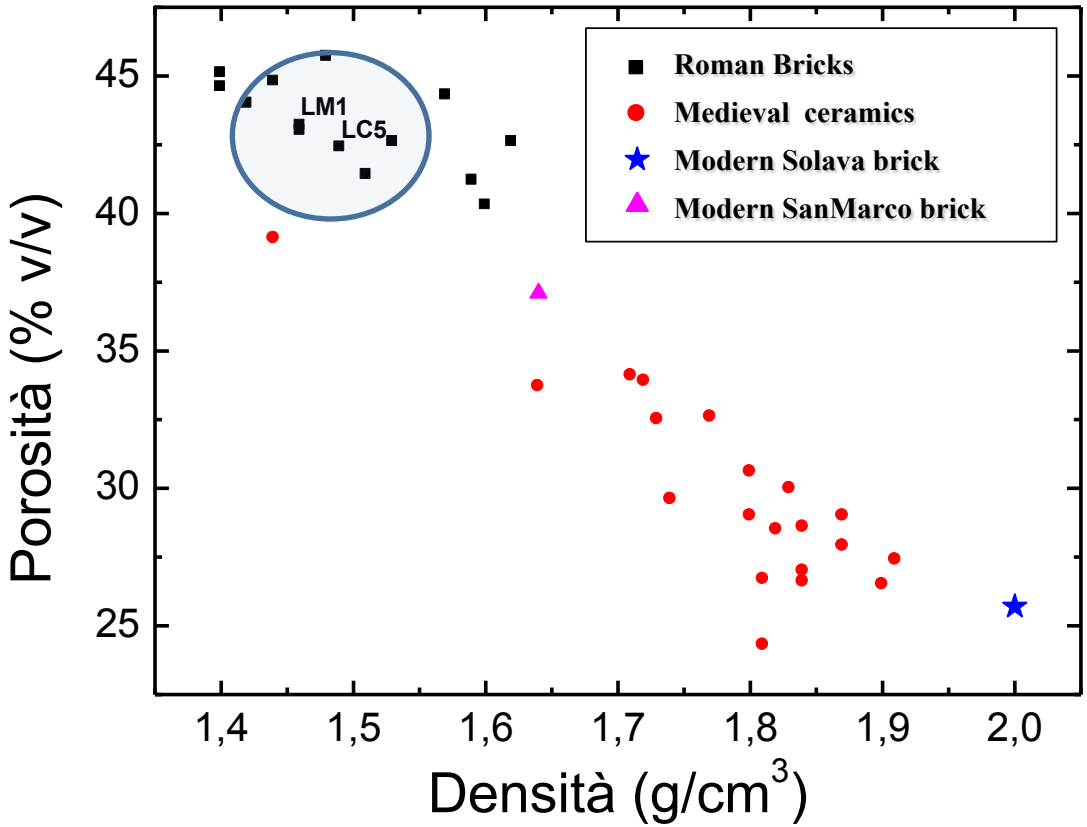
Recognition of phases of neoformation

- Diopside
- Ghelenite
- Anortite

Estimating Firing Temperature

T>800-850°C roman bricks

SAMPLES: POROSITY AND DENSITY



Measured by ASTM C20-00

GEOPOLYMER FORMULATION:

Example application: geopolymer as glue to assemble pieces of broken ceramics

Objectives

1) Very thin layer of ligand between the broken pieces
2) Strength of adhesion between the interface ceramic-geopolymer lower than the geopolymer itself
3) Strength of the geopolymeric connection lower than the ceramics itself
4) Good removability of the geopolymer layer from the ceramic

Metakaolin (MK): MK1 (medium particle size 1.2 um) calcining kaolinite at 750°C - MK2 (medium particle size 0.8-10 um, BET 16.31 ± 0.09 m2/g) precalcinated at 780°C
SLAG (GBF): Granulated Blast Furnace SLAG, reduced at the appropriate grain size (10-63um)
Base Sol.: (SiO2/Na2O=1.5 or 2,5) LUDOX® TM-50 colloidal silica, NaOH pellets, and Water
Wollastonite: (grain size < 45um)
Quartz: (grain size <75um)
Kaolin (K): K1 (medium particle size 1.2um)

Starting point: formulation used for FRGP application

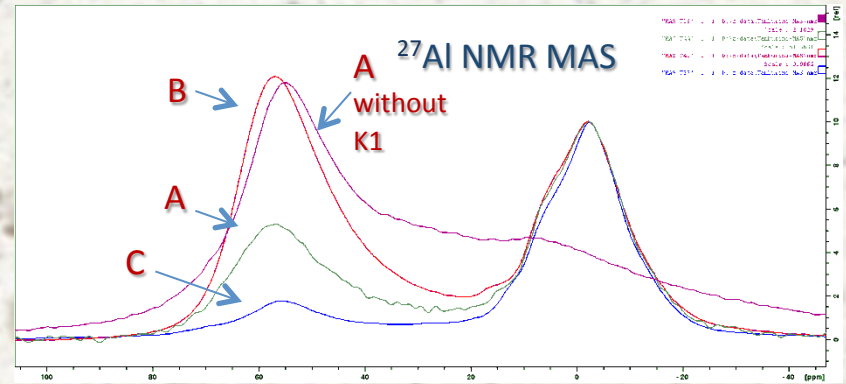
1 MK1/2 GBF/1,5 Wollastonite/2,5 Sand/2 Activator (SiO2/NaO2=1,5 H2O/Na2O=12)/0,47 H2O

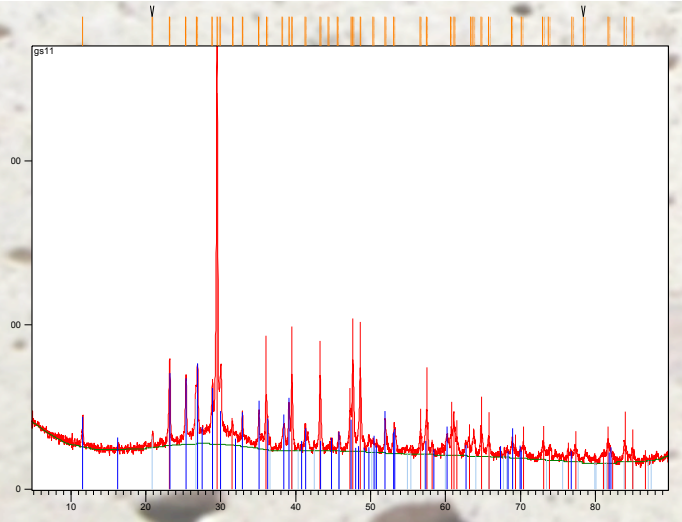
Formulation modification: a) particle size of all components lower than 75 um b) Lower Ratio (MK+GBF)/inerts) no added water d) addition of clays or kaolins c) use of basic NaSilicate solution at high ratio SiO2/Na2O (>2.5)
Pretreatment of the ceramic: wetting the ceramic surface with water or diluited basic solution of NaSilicate, or aceton solution of paraloyd B72 (sacrificial layers)

GEOPOLYMER CHEMICAL CHARACTERIZATION

BLEND A:	1 MK1 + 2 GBF + 1 K1 + 2,5 Base NaSilicate (SiO2/Na2O=1.5)
BLEND B:	1 MK1 + 1 GBF + 0.5 K1 + 1.5 Quartz + 3,5 Base NaSilicate (SiO2/Na2O=1.5)
BLEND C:	1 MK1 + 1 GBF + 1.5 K1 + 0.5 Quartz + 5.0 Base NaSilicate (SiO2/Na2O=2.5)

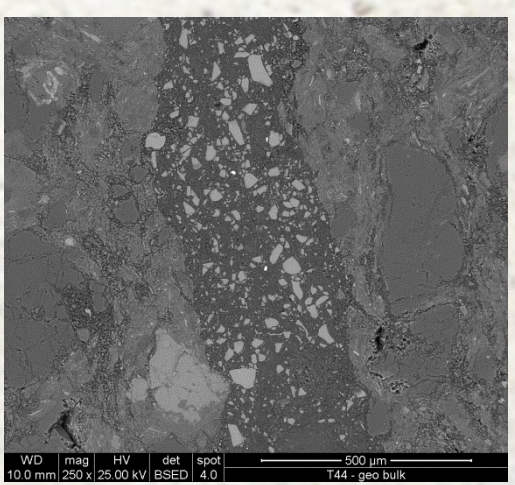
Wt/%	Al_2O_3	SiO_2	Na2O	CaO	K_2O	Fe_2O_3	TiO_2	MgO	Other	LOI
MK1	41.5	55.2	-	0.32	1.0	0.81	1.0		-	1.6
K1	41.5	55.2	-	0.32	1.0	0.81	1.0		-	1.6
GBF	11.6	35.6	7.2	42.0	0.4	0.32	0.29	7,4	0.37	0.7
Quarzo		100								
Geo A	18,1	45,9	5,3	24,0	1,2	1,4	0,88	3,2		
Geo B	14,7	66,4	3,2	11,4	0,9	1,5	0,6	1,4		
Geo C	17,8	63,0	8,2	6,3	1,0	1,5	0,8	1,4		
Geo A (no K1)	22,8	42,7	4,8	21,5	0,9	1,1	0,8	4,2		



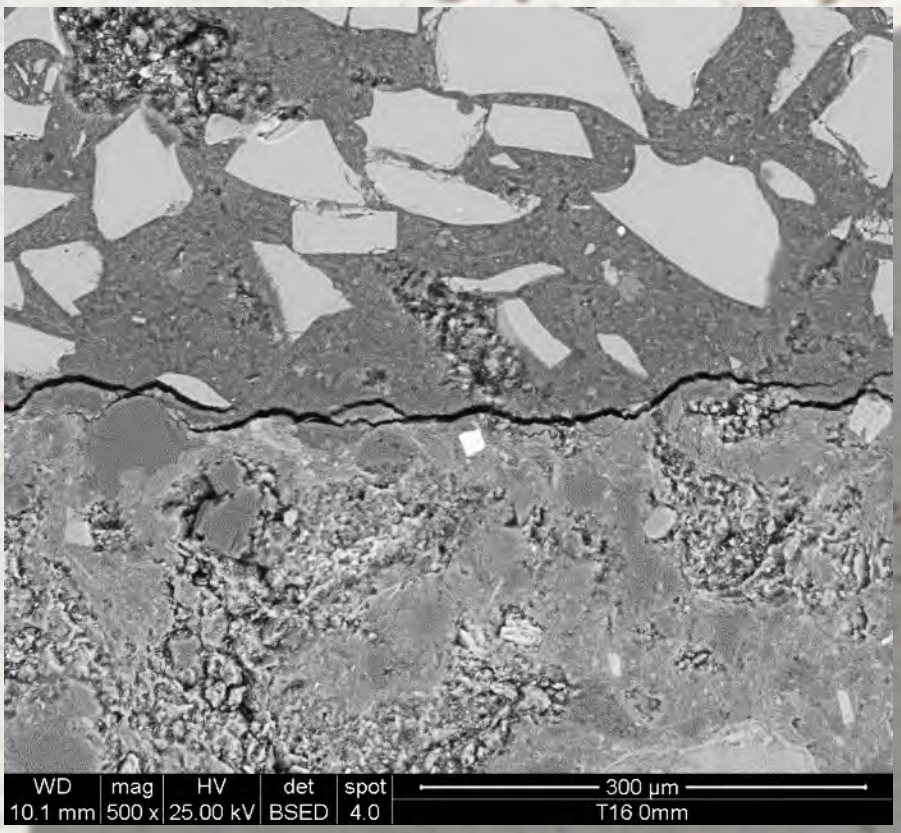


XRD

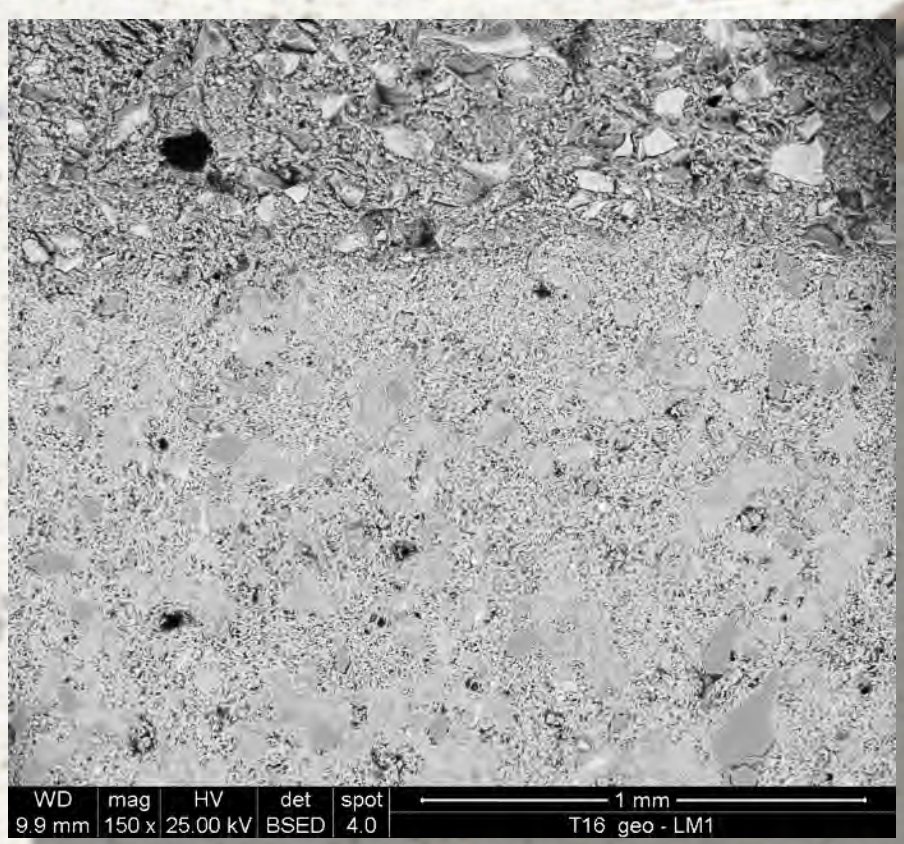
SEM A



SEM morphological investigation



Solava brick and geopolymer after the flexural strenght test: separation between the two phases at the interface



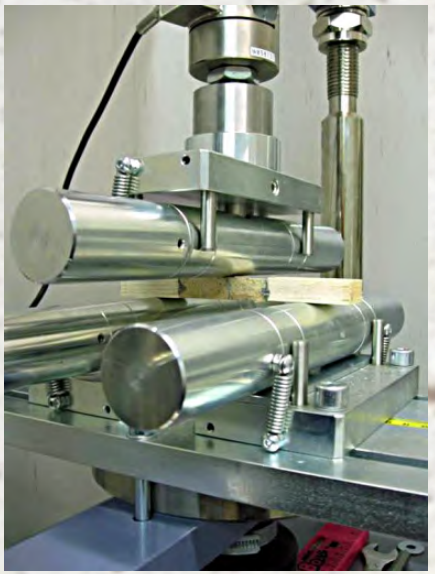
Interface LM1- geoT16

Application steps:

1. Preparation and application of the mixture within 30 min.
2. Pre-treatment of the ceramic (however clean and brushed):
    1. with basic solution at different concentrations
    2. no treatment (dry)
3. Application of the mixture on both sides (layers of different thickness: 1,0 - 0.5 to 0.2 mm)
4. Soft parts approximation with moderate finger pressure
5. At rest for at least 2/3 hours according to the type of blend
6. Manipulable after 10 hours

ADHESION TESTS

MECHANICAL PROPERTIES: FLEXURAL STRENGTH



3-point measuring apparatus
Distance between supports: 10 cm
(elongation of too short samples with wood strongly bond with epoxy resin)

	Roman Bricks		Modern Brick (Solava)
	LM1	LC5	
R_f (MPa)	5.6	5.9	6.0
COV (%)	14	11	22

Example of breakage

	Blend formulation						Pretreatment *	Flexural strenght 6,0 Mpa Solava 5,6Mpa LM1 Rottura su incollaggio = i Rottura fuori incollaggio = p
	MK	Slag C34b R/W	grain size	Activator R/W	Inerts R/W	Extra water		
A (no K1)	1	2	63-125um	1.65	0	0.2	w	3,4 Mpa i 1,0 Mpa i
T18-21	1	2	0-63 d50 20	1.65	0 -2,5		b	6,0 Mpa p 5,5 Mpa p
C	1	1	0-63um	5 *	2	0	no	6,0 Mpa p 5,5 Mpa p
B	1	1	0-63um	3.5	2	0	no	2,5 Mpa i
A	1	2	0-63um	2.5	1	0.7	b	1,8 Mpa i

* w = samples are soaked in water; b = surface wetted with basic solution

Results

Blend A

1 MK1 + 2 GBF + 1 K1 + 2,5 Base NaSilicate (SiO_2/Na_2O=1.5)

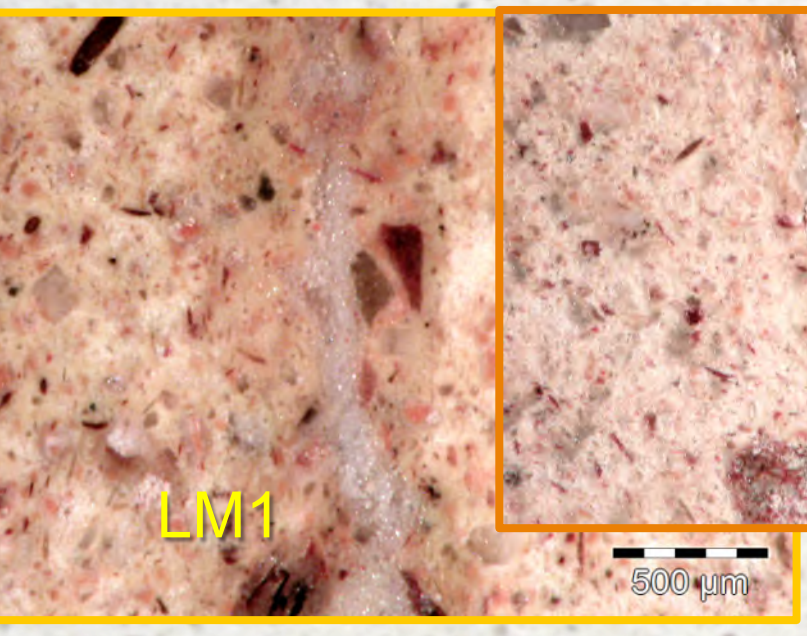
Workability: tolerable – Time w.: good >20'
Pretreatment: wetting with NaSil. Sol.
Thickness: ca 0.3 -0,7 mm
Flexural Strenght: Solava : 1,5- 2,2 Mpa
Removal TEST: good with vibr. tip

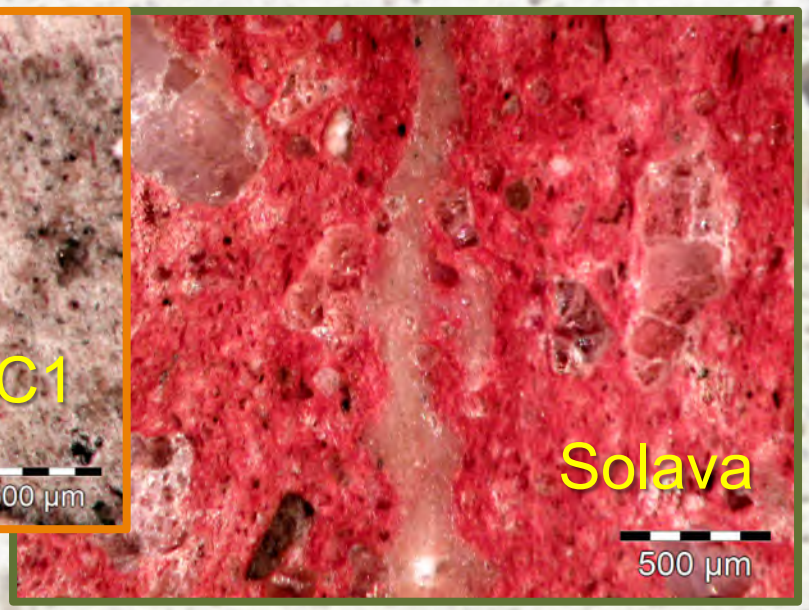
Blend B

1 MK1 + 1 GBF + 0.5 K1 + 1.5 Quartz + 3,5 Base NaSilicate (SiO_2/Na_2O=1.5)

Workability: good – Time w.: good >30'
Pretreatment: **no**
Thickness: ca 0.2 mm
Flexural Strenght: Solava : 2.0- 3.4 Mpa
Removal TEST: difficult with vibr. tip

Results





Blend C

1 MK1 + 1 GBF + 1.5 K1 + 0.5 Quartz + 5.0 Base NaSilicate ($SiO_2/Na_2O=2.5$)

This blend has more the characteristics of WATERGLASS than that a GEOPOLYMER

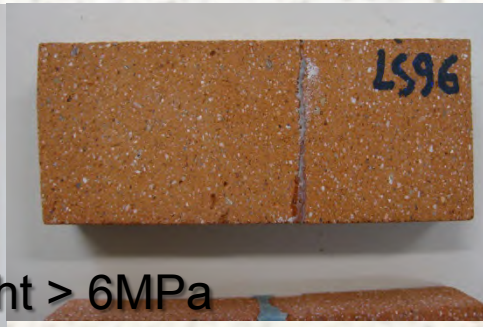
Workability: good – Time w.: good >30'
Pretreatment: **no**
Thickness: ca 0.1 mm
Flexural Strenght: Solava : 6.0 LM1 3.4 Mpa
Removal TEST: excellent removability in WATER.
After 1h treatment with water the binder dissolves and is completely removed

Removability by vibrating tip

Removability by sacrificial layer

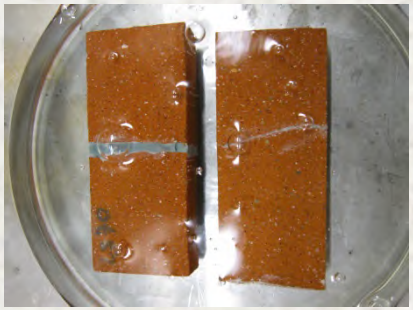
1
Pretreatment: layer of organic paraloyd B72

2
Connection with geopolymer blend A

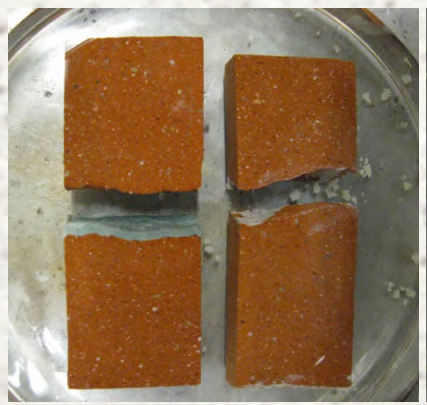


Flexural strenght > 6MPa

3
Immersion in acetone

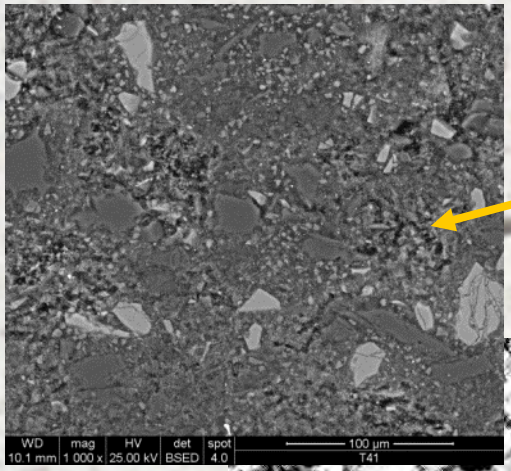


4
Dissolution of paraloyd and detachment of geopolymer layers

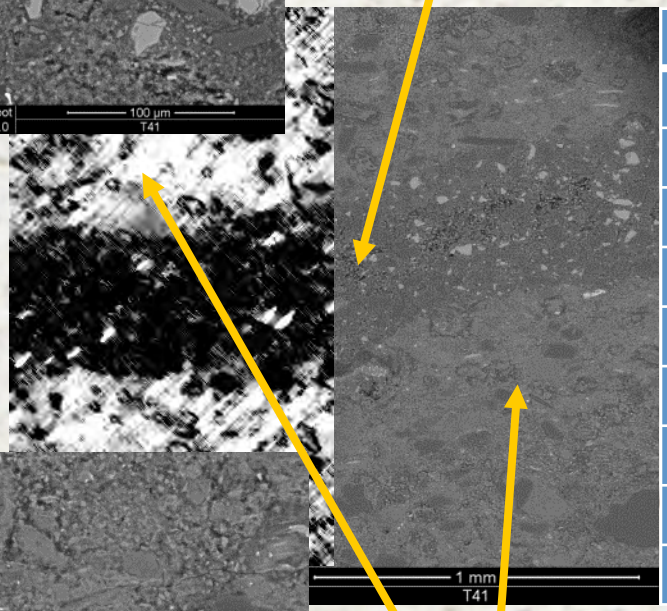


5
Complete removal of geopolymeric layer: Brick at the original state

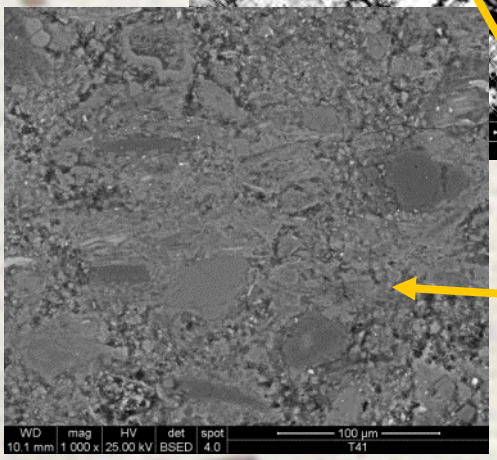
Retractability: chemical compatibility



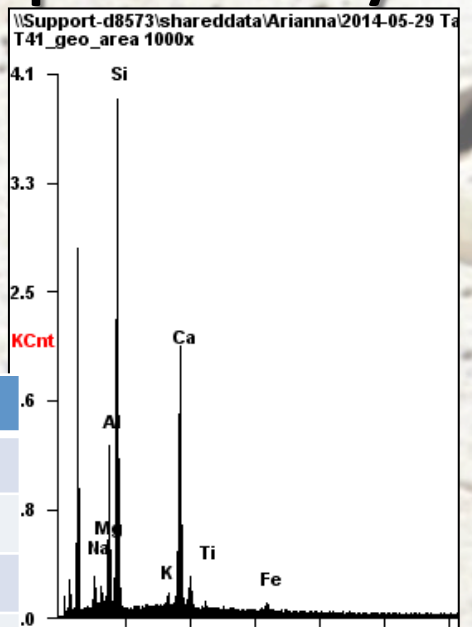
Geopolymer

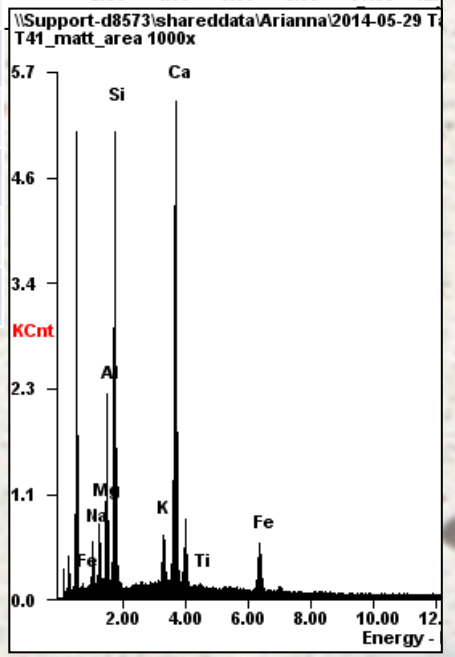


	Geopol	LM2
Element	Wt %	Wt %
NaK	4.51	4.66
MgK	2.18	5.16
AlK	12.80	12.47
SiK	44.50	29.37
K K	1.91	3.70
CaK	30.43	35.84
TiK	1.11	0.51
FeK	2.56	8.28



Roman brick LM1





Restoration - Conclusions

- **The intrinsic quality of the geopolymer matrix assures compatibility and durability to the ceramic historical samples**
- **The formulation of the geopolymeric matrix must be effective for a complete geopolymerization reaction**
- **The adhesion of the geopolymer matrix to ceramic surface can be modulated varyng granulometry, quantity of inert etc**
- **The porosity of the sample can influence the quality of the geopolymer matrix. The problem can be overcome pretreating the sample surface with NaSilicate base solution**
- **The removability problem can be overcame by mechanic way (vibrating tip) or chemical dissolution (acetone solvent) using a "sacrificial layer" (NaSilicate base sol., or Paraloyd B72 organic polymer) between the surface of the historical sample and the geopolymer**

Challenging Materials for Restoration of Cultural Heritage

Sergio Tamburini

Thanks for your kind attention!