Laboratory of Industrial Chemistry (LCI-II)

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Institut Géopolymère

Structural, thermal, and dielectric characterization of « green » phosphoric acid-based geopolymers

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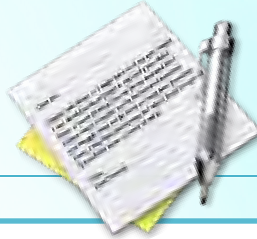
Plan

1. Introduction
2. Objectives
3. Elaboration of the phosphoric acid-based geopolymers
4. Structural characterization of phosphoric acid-based geopolymers
5. Thermal and dielectric characterization of phosphoric acid-based geopolymers
6. Conclusion and perspective

Introduction



Introduction: In the 70's, Mr. Joseph Davidovits, invented and developed new inorganic polymeric material called **geopolymers.**

geopolymers

Properties

- **Good chemical and thermal behavior**
- **Good compressive strength**
- **Low density**
- **Excellent fire resistance…**

Applications

- **Building**
- **Refractory ceramic**
- **Biomaterial**
- **Isolated packaging materials, aviation …**

Introduction

geopolymers

↓

Obtained by activating an aluminosilicate (metakaolinite) with:

- **alkali metal hydroxide (Na+, K+)** *
- **Phosphoric acid** *,°

↓

Acid-based geopolymer have a higher strength than that of the basic-based geopolymer

- *Davidovits et al.,
- °CAO D et al., 2005

Objectives

The synthesis of an environmentally friendly construction material called phosphoric acid-based geopolymers from metakaolin by etching with phosphoric acid.

Portland cement

1 ton of the Portland cement

Produces about 1 ton of CO2 in the atmosphere

Consumes 4GJ energy ↗

Geopolymers

Emission of CO_2 80 times lower

Consolidated at room temperature (T°<80)

Elaboration of “green” phosphoric acid-based geopolymers

mixture

Metakaolinite

water

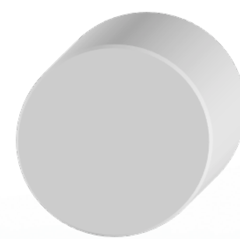
Phosphoric acid 85 wt%

molding

Mold used

Oven at 60°C

Some days at room temperature



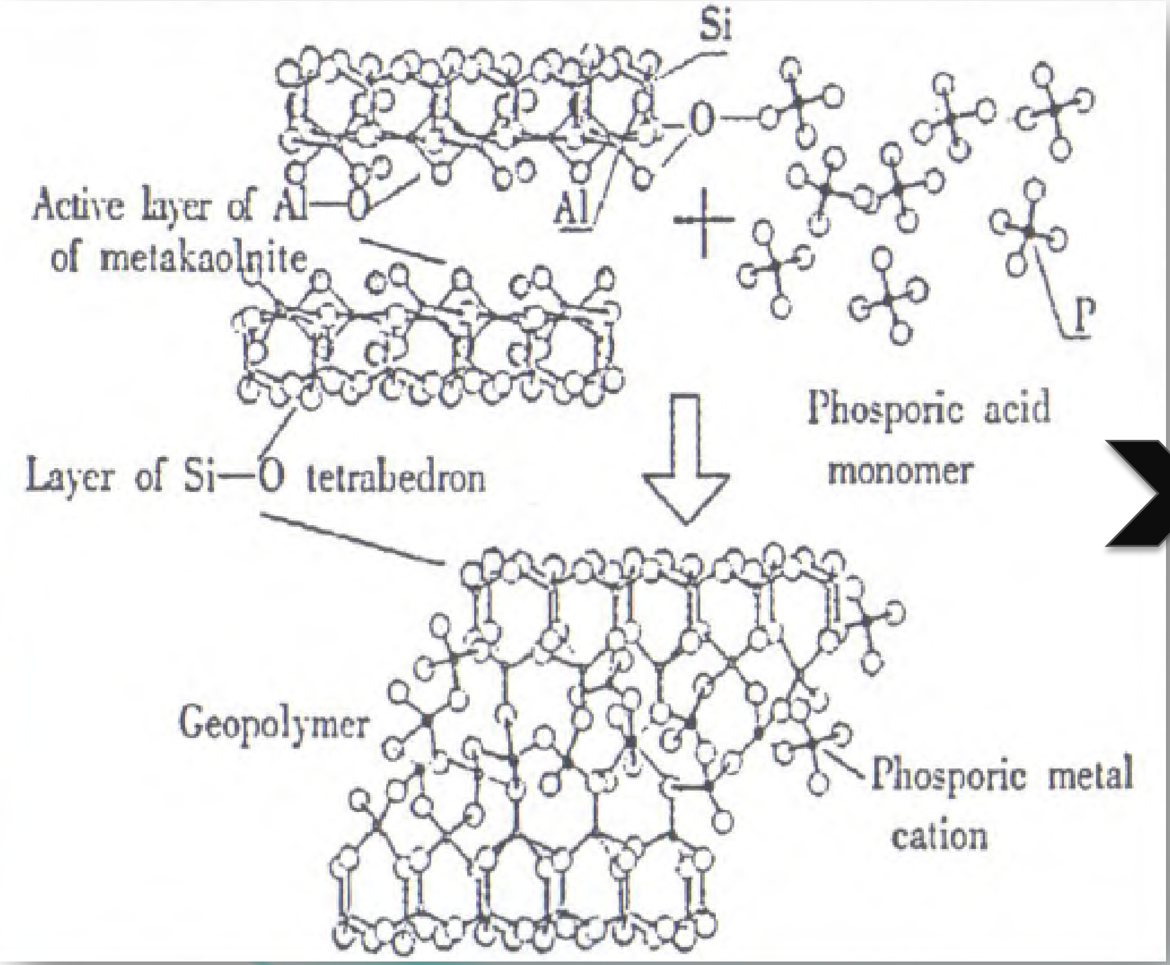
Geopolymers specimen

mechanical and structural characterization

Seven types of geopolymers were synthesized from metakaolinite at 700 ° C with different molar ratios Si / P ranging between 0.5 and 2

Geopolymerization mechanism of the phosphoric acid-based geopolymers

Geopolymerization mechanism



Dissociation of silicate material with phosphoric acid

Polymerization reaction between the low-polymeric **P-O** tetrahedral (phosphoric acid) and the active layer in metakaolinite **Al-O**, **Si-O** → Al-O-P bonds

3D structure Si-O-Al-O-P

* CAO D et al., 2005

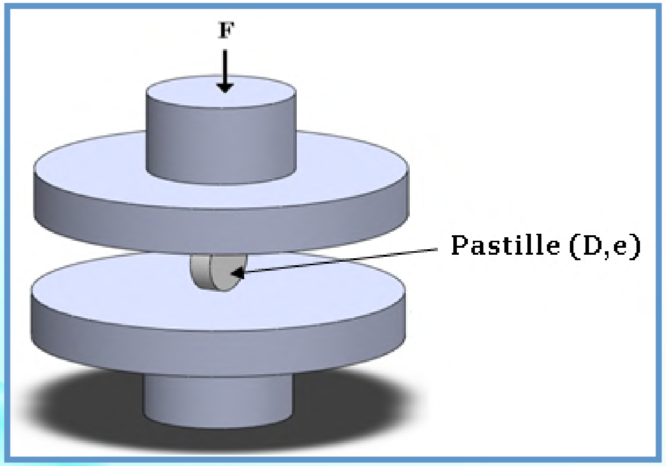
Structural characterization of the phosphoric acid-based geopolymers

Mechanical properties: Brazilian test

Mechanical strength

↓

Brazilian test



$$\sigma_r = \frac{F}{S} = \frac{2 \times F}{\Pi \times D \times e}$$

F : maximum compressive load

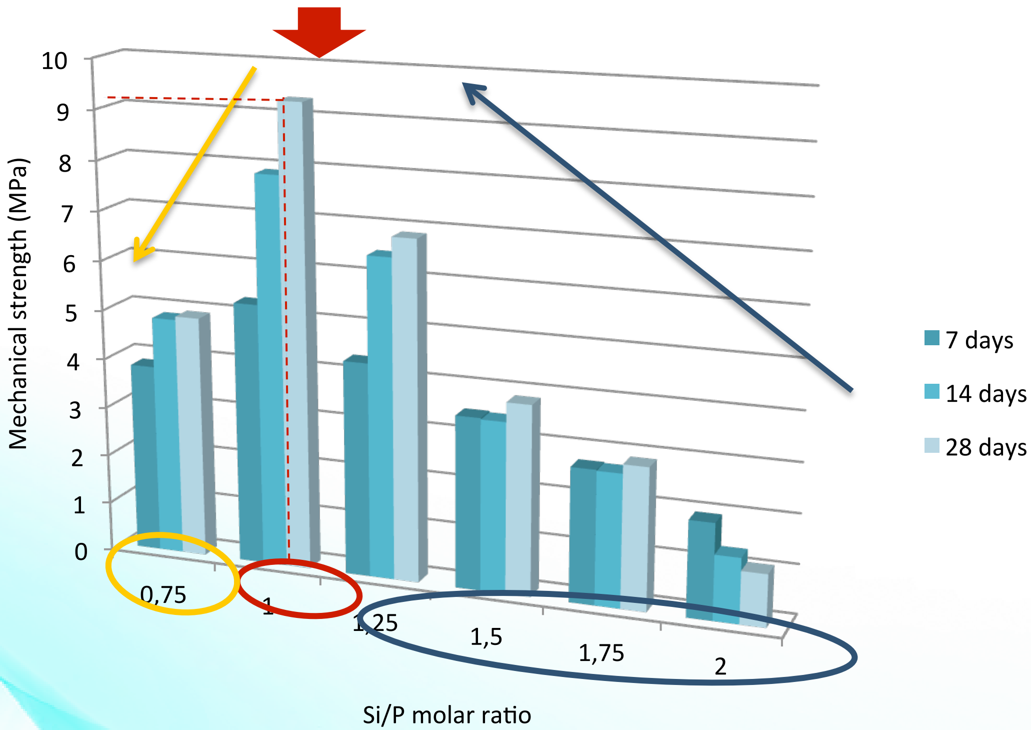
D : diameter of the sample (32mm)

e : Thickness (7mm)

Structural characterization of the phosphoric acid-based geopolymers

Si/P molar ratio and curing age

Mechanical properties: Brazilian test

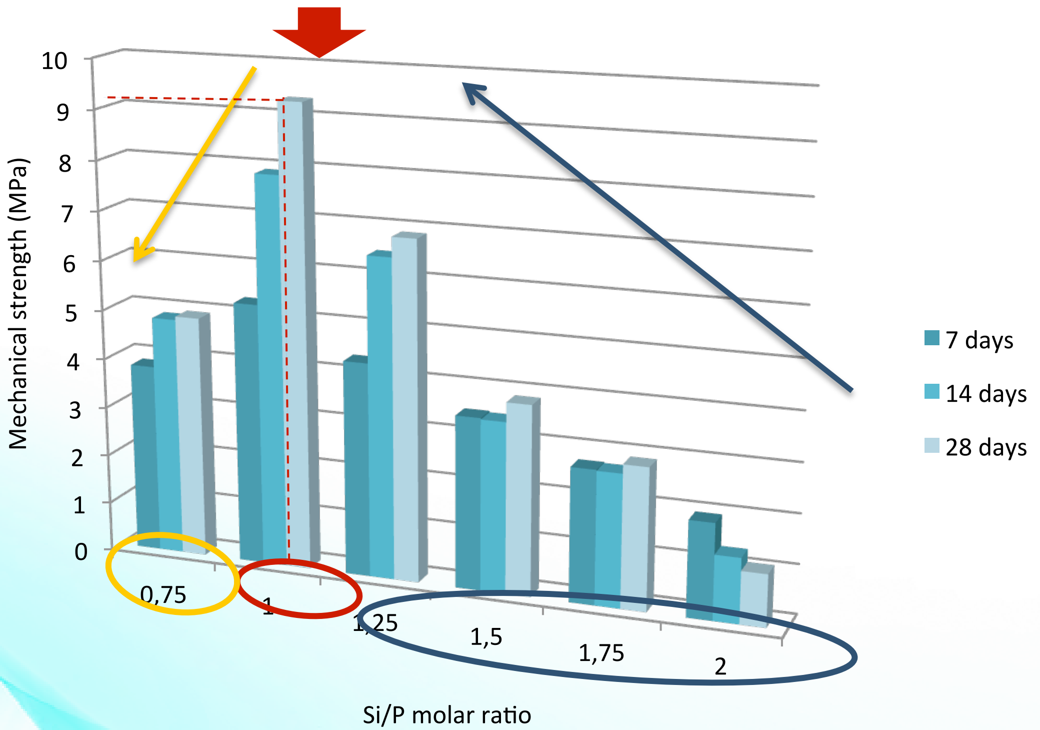


Mechanical strength evolution of the product phosphoric acid-based geopolymers with the <u>different</u> Si/P molar ratio and curing time

- **Si/P>1:** Small amounts of phosphoric acid → the dissolution step is not complete : → <u>low</u> mechanical properties.
- **Si/P=1:** resistance is maximum → the amount of phosphoric acid is just sufficient to complete the dissolution step, ($[AlO_4] / [PO_4] = 1$) the charge balance is assured
- **Si/P <1:** the large amounts of phosphoric acid → lead to an excess in $[PO_4]^{3-}$ ---→ which weakens geopolymers structure because of <u>Unbalanced charges</u> → <u>mechanical properties drop</u>

Structural characterization of the phosphoric acid-based geopolymers

Mechanical properties: Brazilian test



Mechanical strength evolution of the product phosphoric acid-based geopolymers with the different Si/P molar ratio and curing time

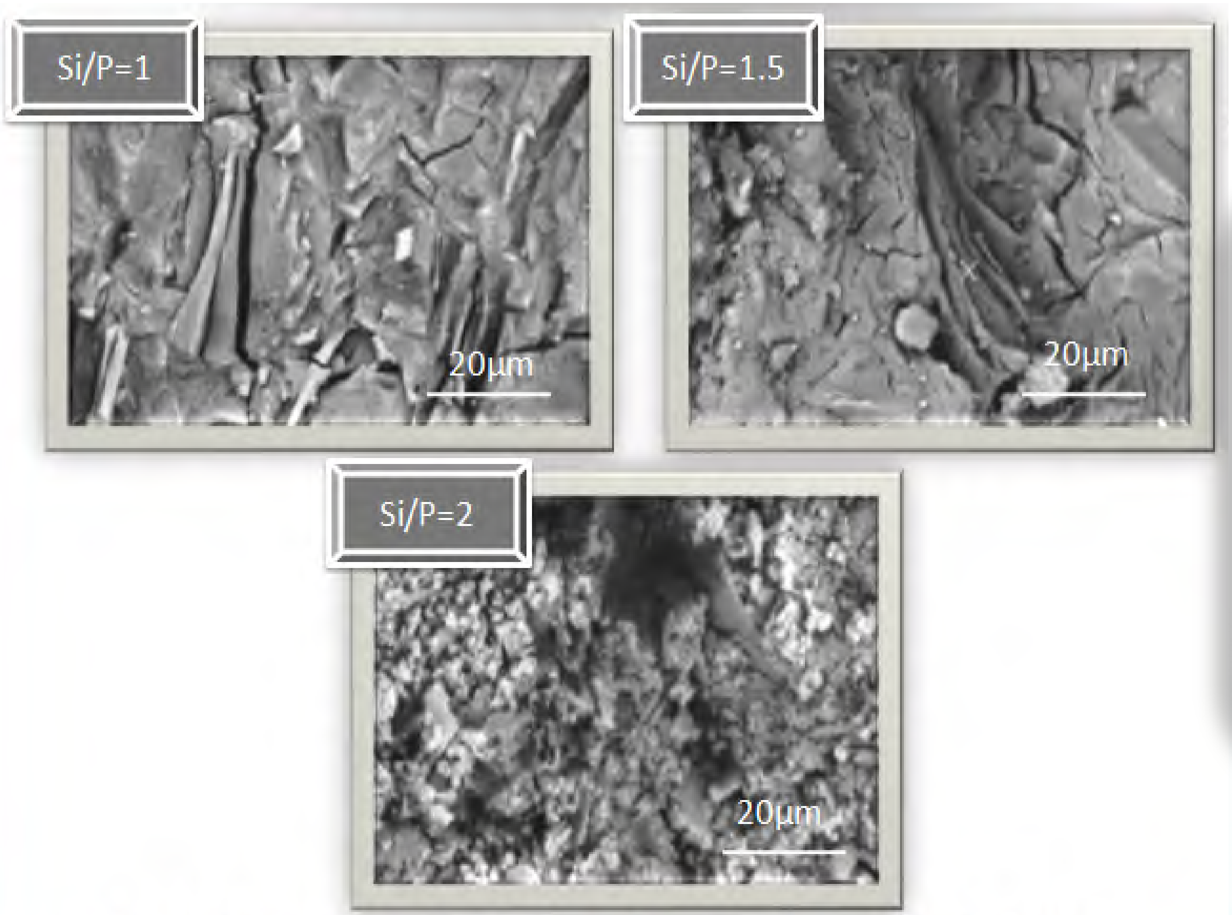
The Curing age

- The mechanical strength of geopolymers samples increases with curing age whatever the molar ratio Si/P

Structural characterization of the phosphoric acid-based geopolymers

SEM micrographs

Si/P molar ratio

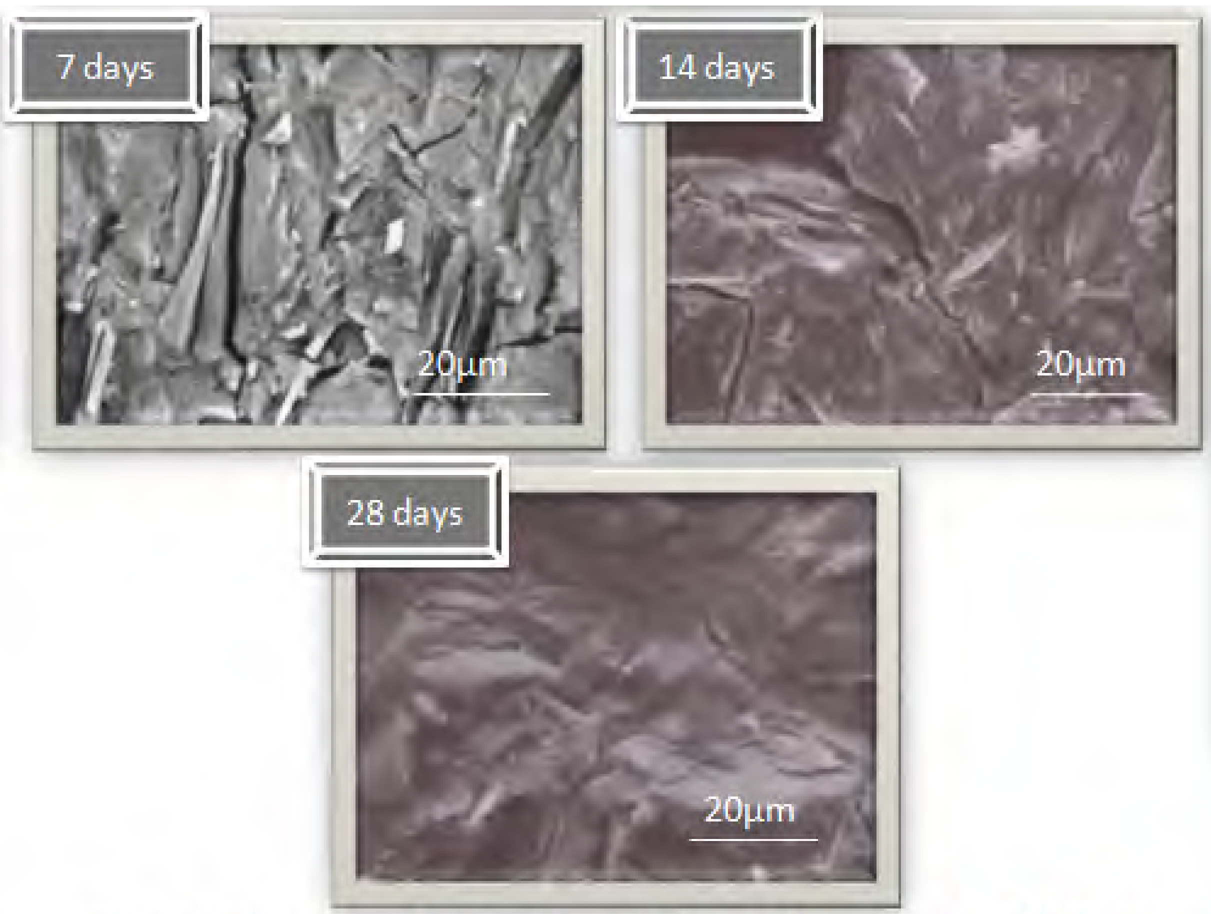


The SEM micrographs of acid-based geopolymers shows that decreasing the molar ratio Si / P, the structure becomes more and more dense

SEM micrographs of phosphoric acid-based geopolymers with different molar ratio Si/P

Structural characterization of the phosphoric acid-based geopolymers

SEM micrographs



SEM micrographs of phosphoric acid-based geopolymers (Si/P=1) with a curing age

Curing ages influence

Structure → becomes denser at 28 days than 7 days, which means that the geopolymerization reaction progresses in time.

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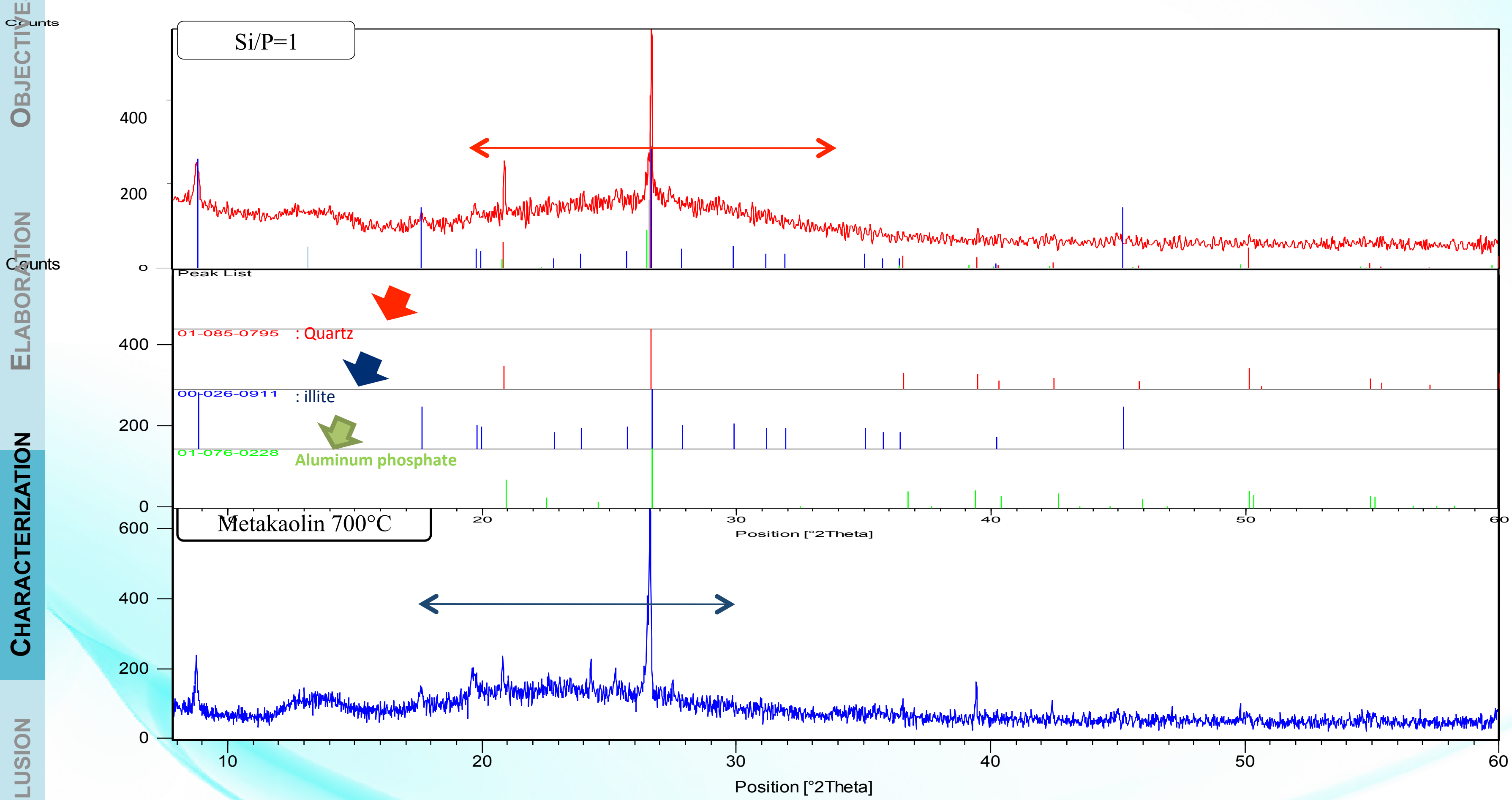
Structural characterization of the phosphoric acid-based geopolymers

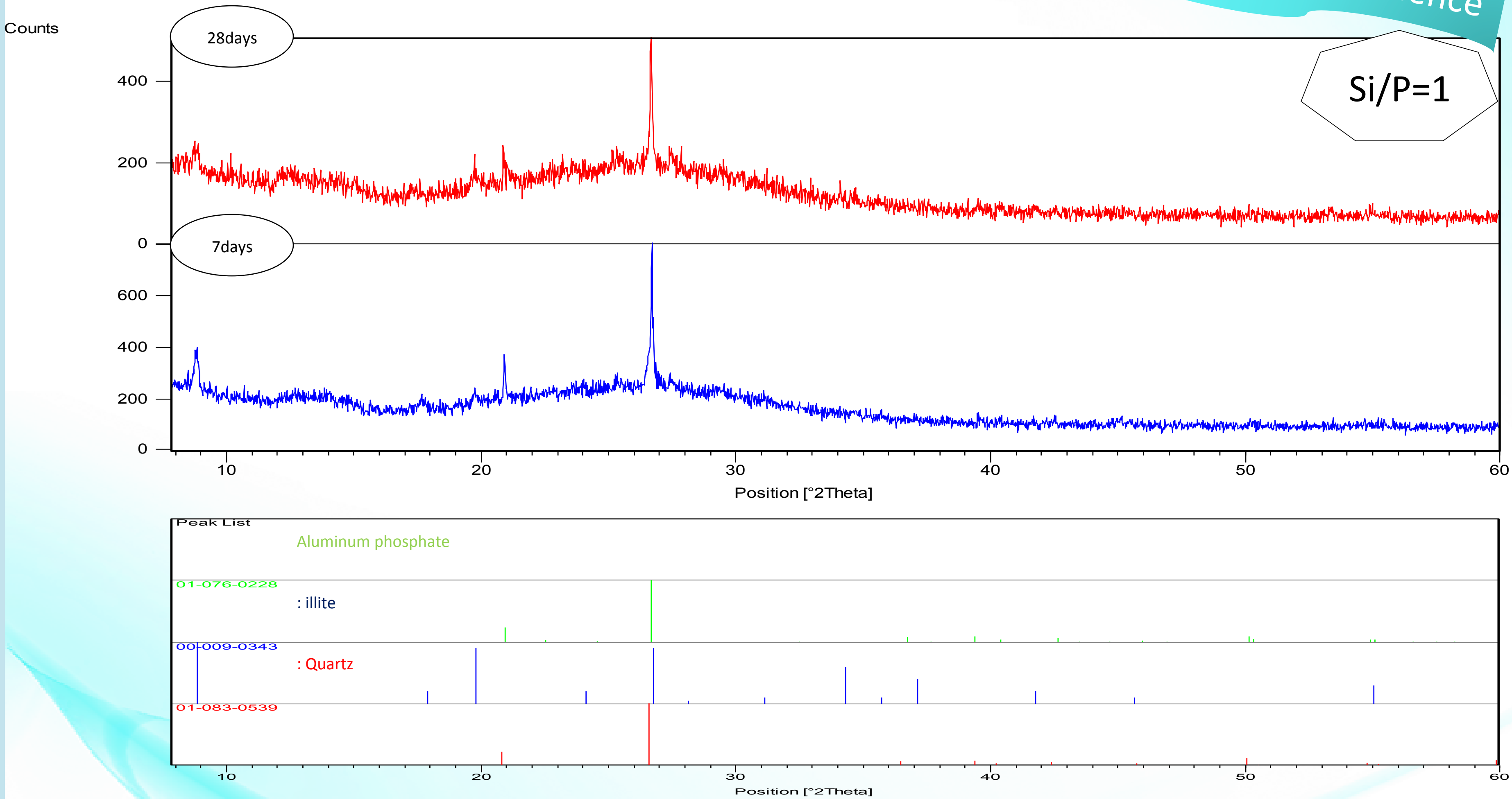
X –Ray Diffraction:



XRD patterns of metakaolinite 700°C and phosphoric acid-based geopolymers (Si/P=1)

Structural characterization of the phosphoric acid-based geopolymers

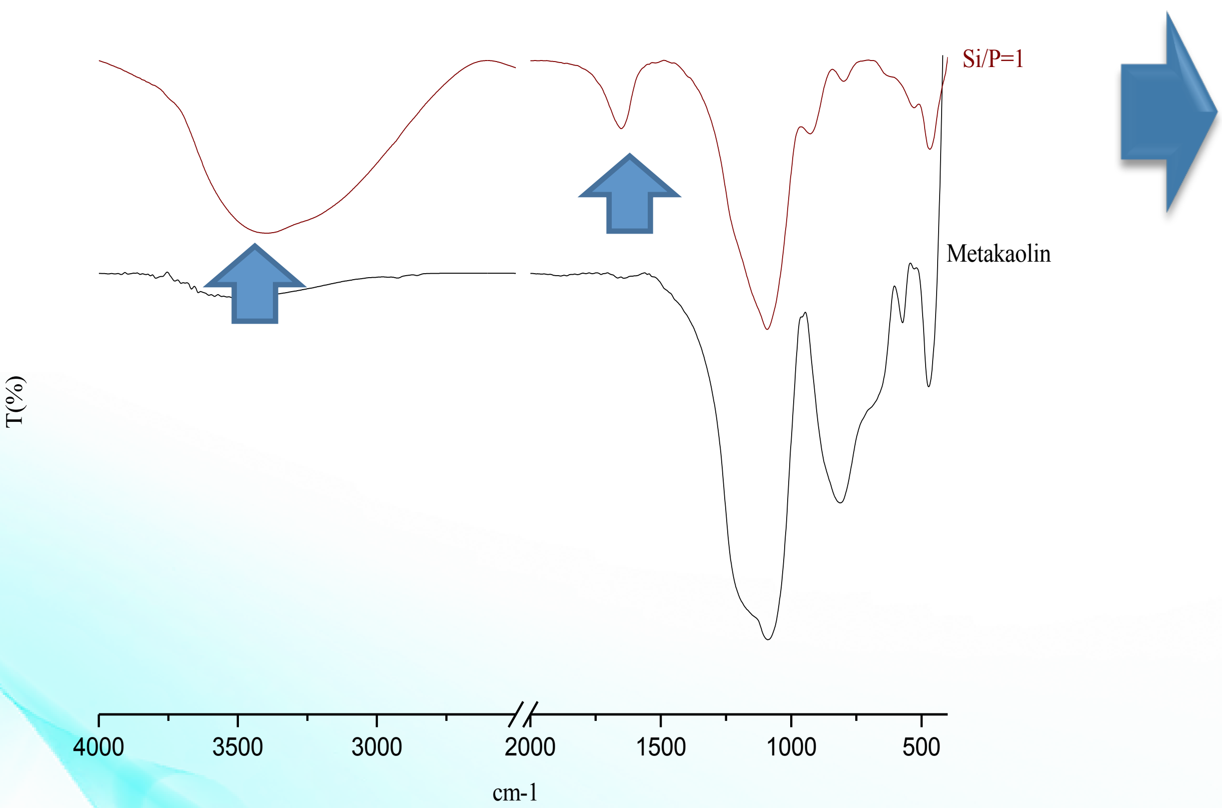
Curing ages influence



XRD patterns of phosphoric acid-based geopolymers (Si/P=1) with curing age

Structural characterization of the phosphoric acid-based geopolymers

Infrared

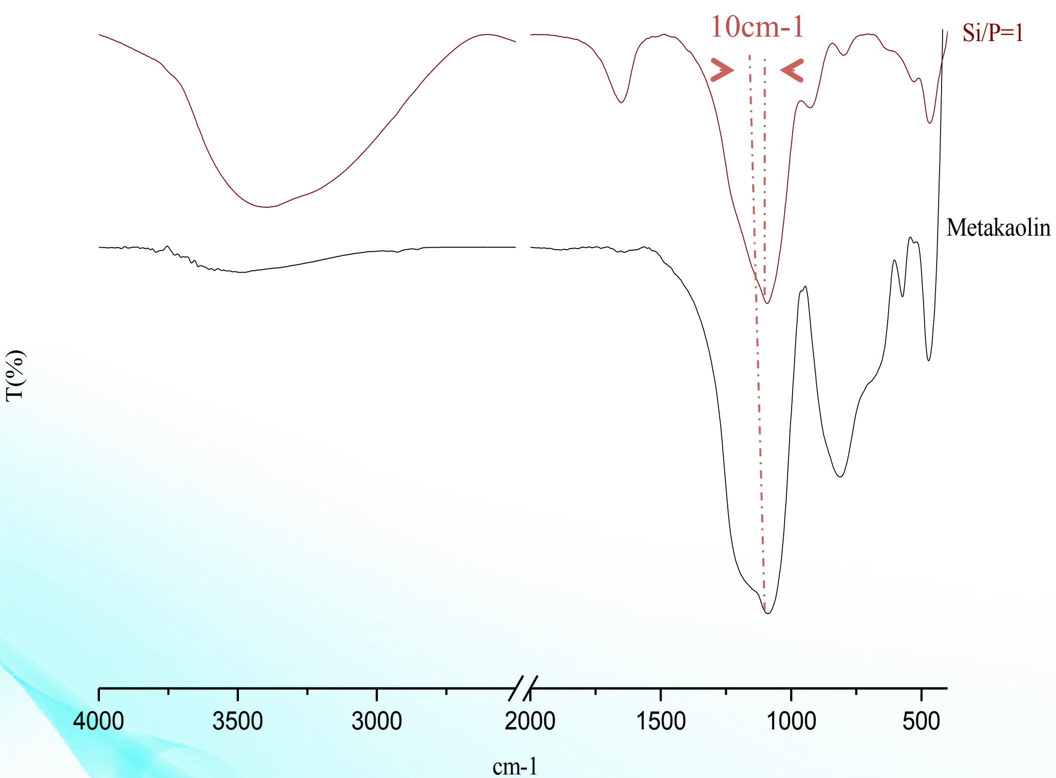


1646cm-1 and 3395cm-1 → stretching and deformation vibration of O-H and H-O-H groups from water

IR spectra of metakaolinite 700°C and phosphoric acid-based geopolymers (Si/P=1)

Structural characterization of the phosphoric acid-based geopolymers

Infrared



The Si-O bands at 1100cm-1 (metakaolin) shifted ~10 cm-1 after geopolymerization reaction to 1089cm-1→the consumption of Si-O monomer in the geopolymerization reaction → Si-O-P oligomers

IR spectra of metakaolinite 700°C and phosphoric acid-based geopolymers (Si/P=1)

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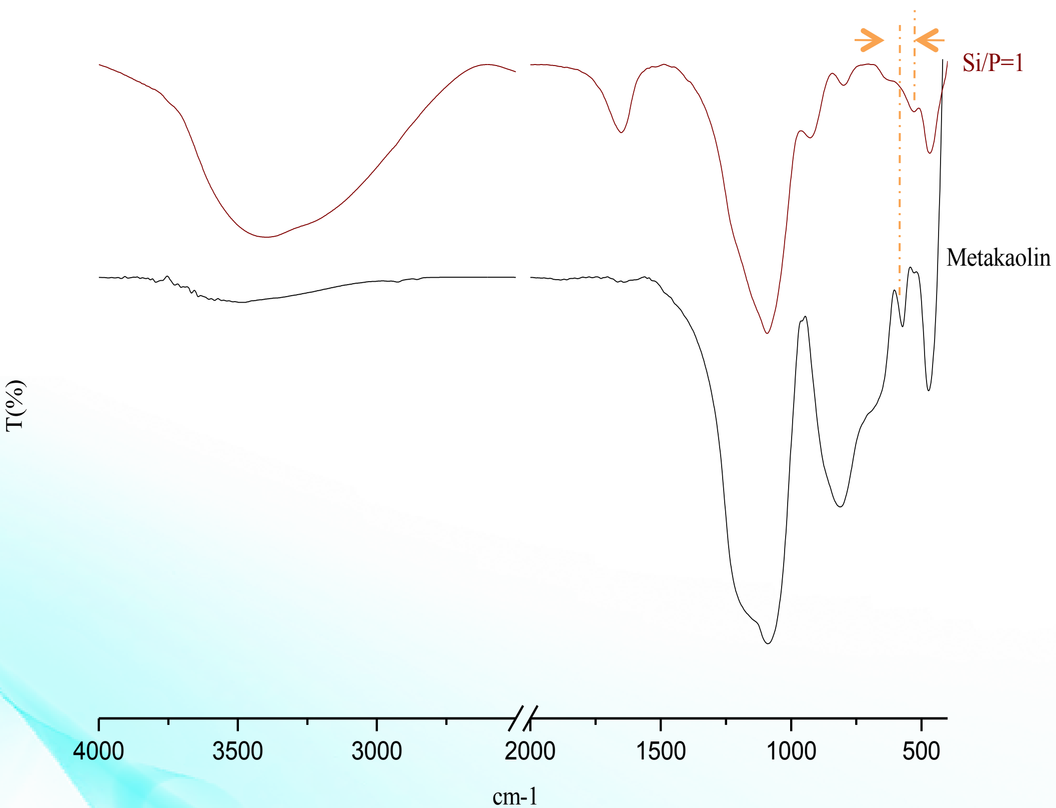
Structural characterization of the phosphoric acid-based geopolymers

Infrared

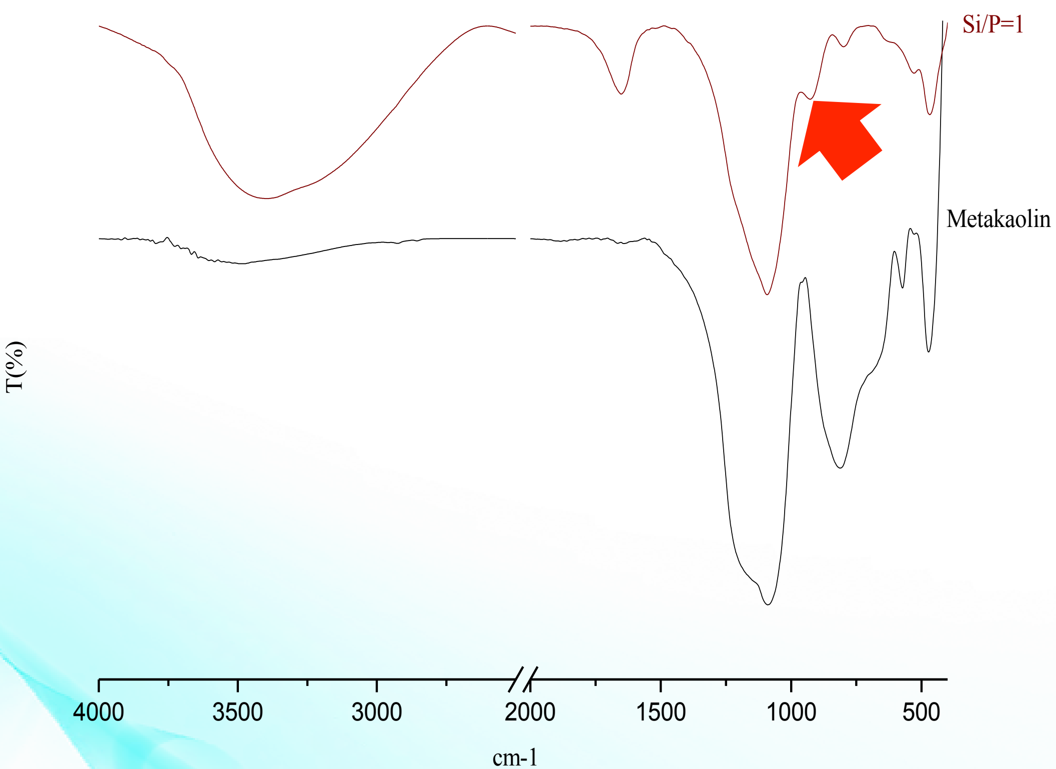


The bands at 570cm-1 (metakaolin)→ Si-O-Al, shifted towards a lower wavenumber after geopolymerization reaction at 533cm-1→Partial substitution of SiO_4 by PO_4 tetrahedral units ,→ resulting a change in the local chemical environment

IR spectra of metakaolinite 700°C and phosphoric acid-based geopolymers (Si/P=1)

Structural characterization of the phosphoric acid-based geopolymers

Infrared



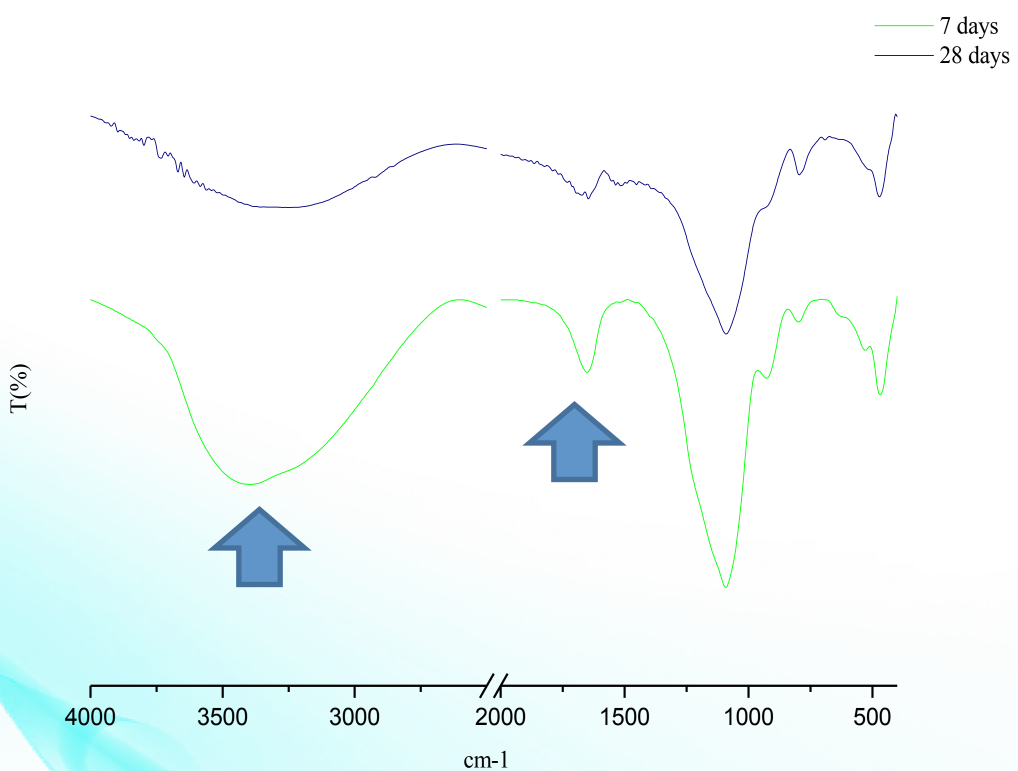
Appearance of new band at 927cm-1 → P-O vibration

IR spectra of metakaolinite 700°C and phosphoric acid-based geopolymers (Si/P=1)

Structural characterization of the phosphoric acid-based geopolymers

Curing ages influence

Infrared



IR spectra of phosphoric acid-based geopolymers for sample (Si/P=1) with curing age

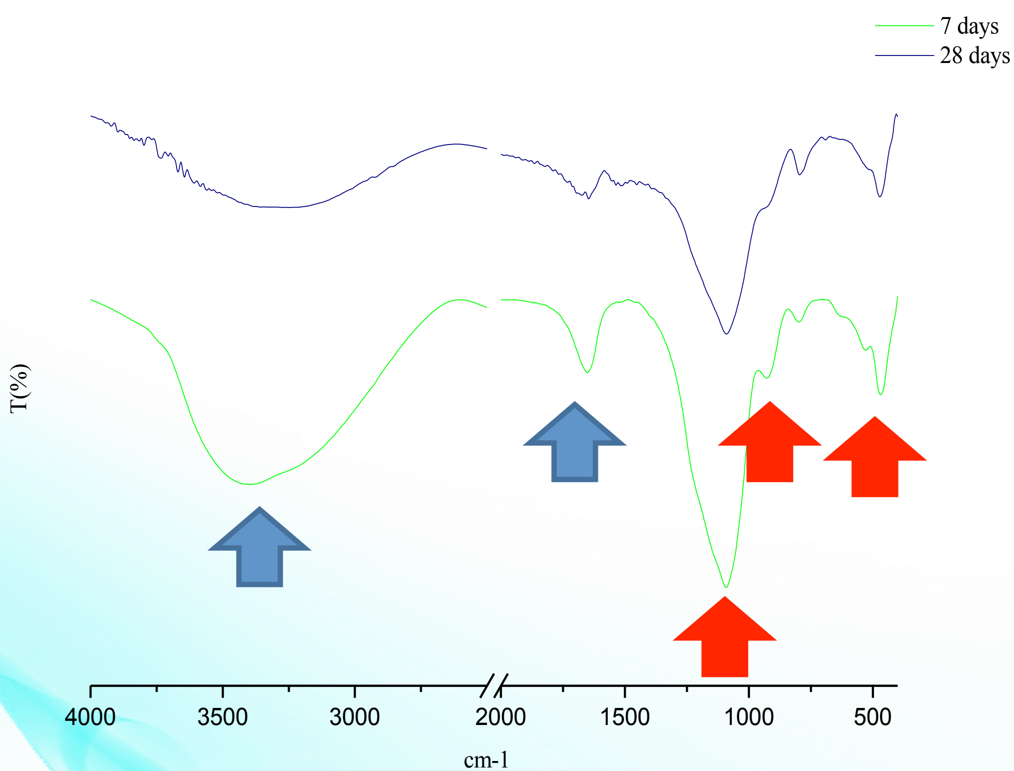
The intensity (1646cm-1 and 3395cm-1) → ↘ between 7 and 28 curing days

The ↘ in intensity provides evidence of the rearrangement of O-H bending inside in the mixture caused by polycondensation reaction

Structural characterization of the phosphoric acid-based geopolymers

Curing ages influence

Infrared



IR spectra of phosphoric acid-based geopolymers for sample (Si/P=1) with curing age

Same trend is observed in geopolymer characteristic bands at 1089cm-1, 570cm-1 and 920cm-1

•At 7 days → intensity is quite high→ abundance of oligomers.

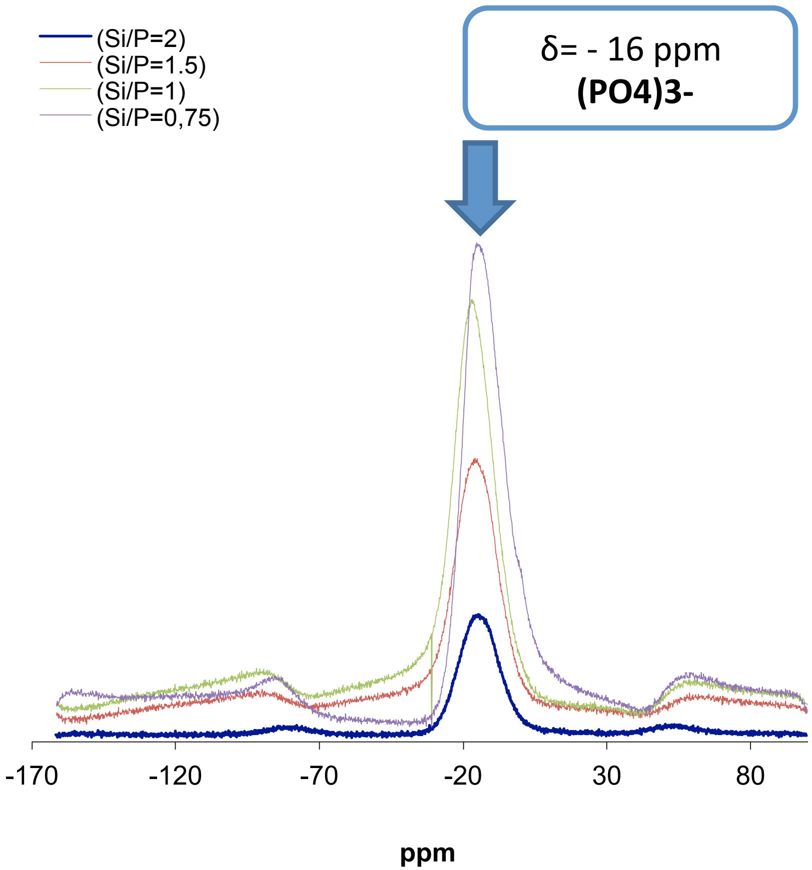
• With curing progress, these oligomers connect together → 3D semi-cristalline aluminosilicate polymers→ intensity ↘

Structural characterization of the phosphoric acid-based geopolymers

Si/P molar ratio

NMR 31P

NMR



31P NMR of phosphoric acid-based geopolymers with different Si/P molar ratio

A slight shift is observed when Si/P increases

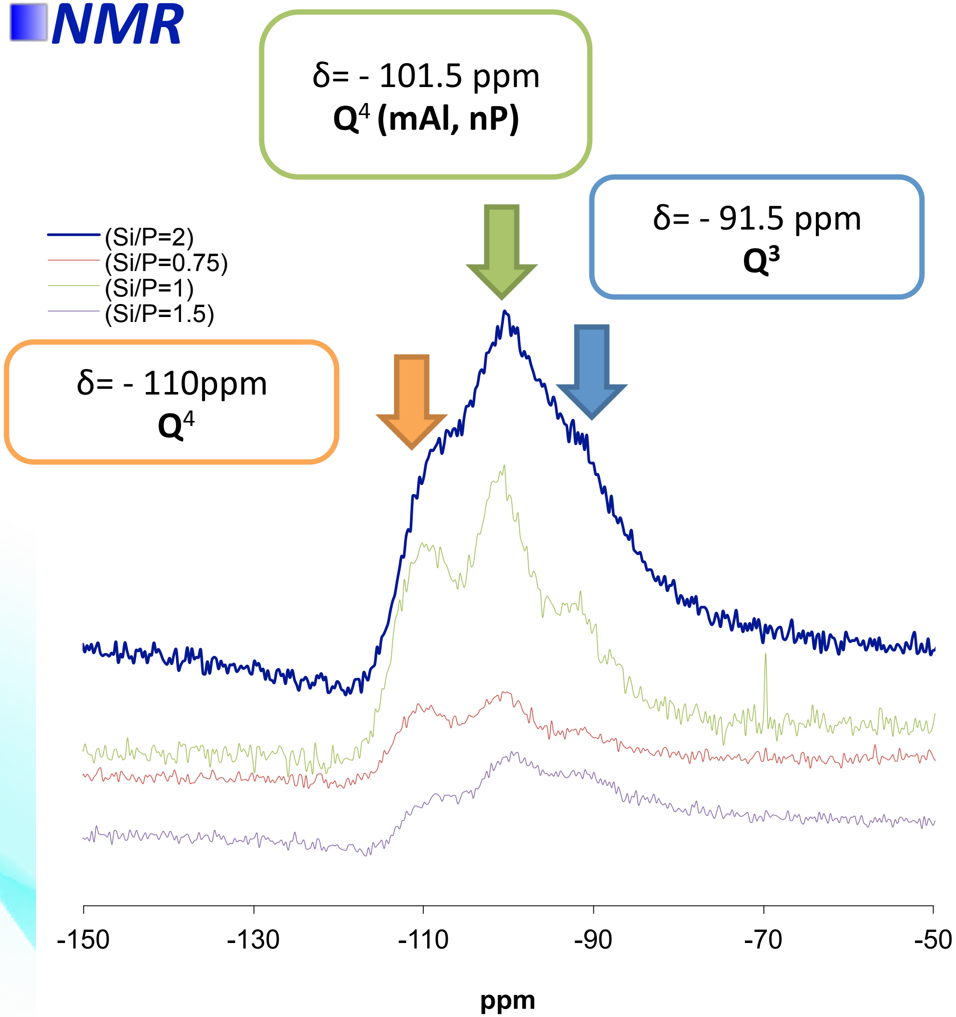
geopolymerization does not change the tetrahedral environment of P

Structural characterization of the phosphoric acid-based geopolymers

Si/P molar ratio

NMR 29Si

NMR



29Si NMR of phosphoric acid-based geopolymers with different Si/P molar ratio

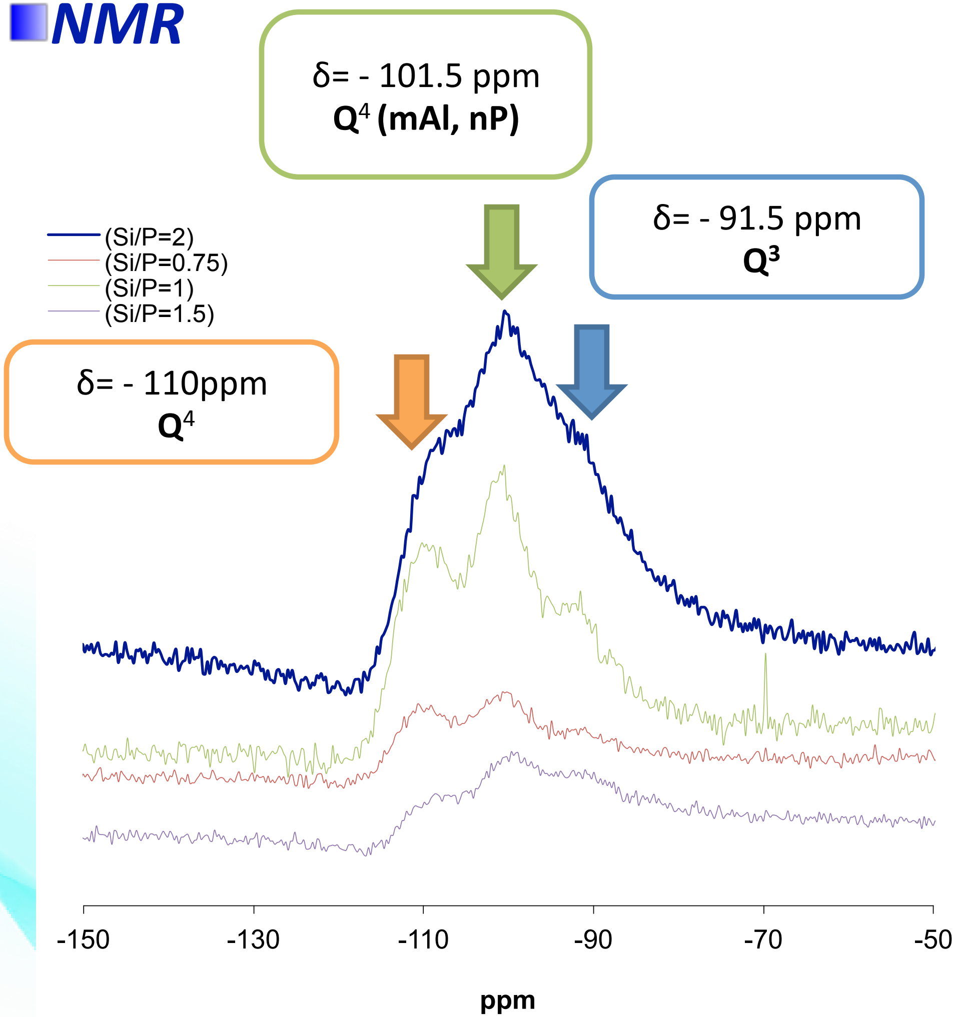
The lowest intensity Q^3 → represent the arrangement of some like kaolin structure segments

Structural characterization of the phosphoric acid-based geopolymers

Si/P molar ratio

NMR 29Si

NMR



29Si NMR of phosphoric acid-based geopolymers with different Si/P molar ratio

The resonance at δ= - 101.5 ppm

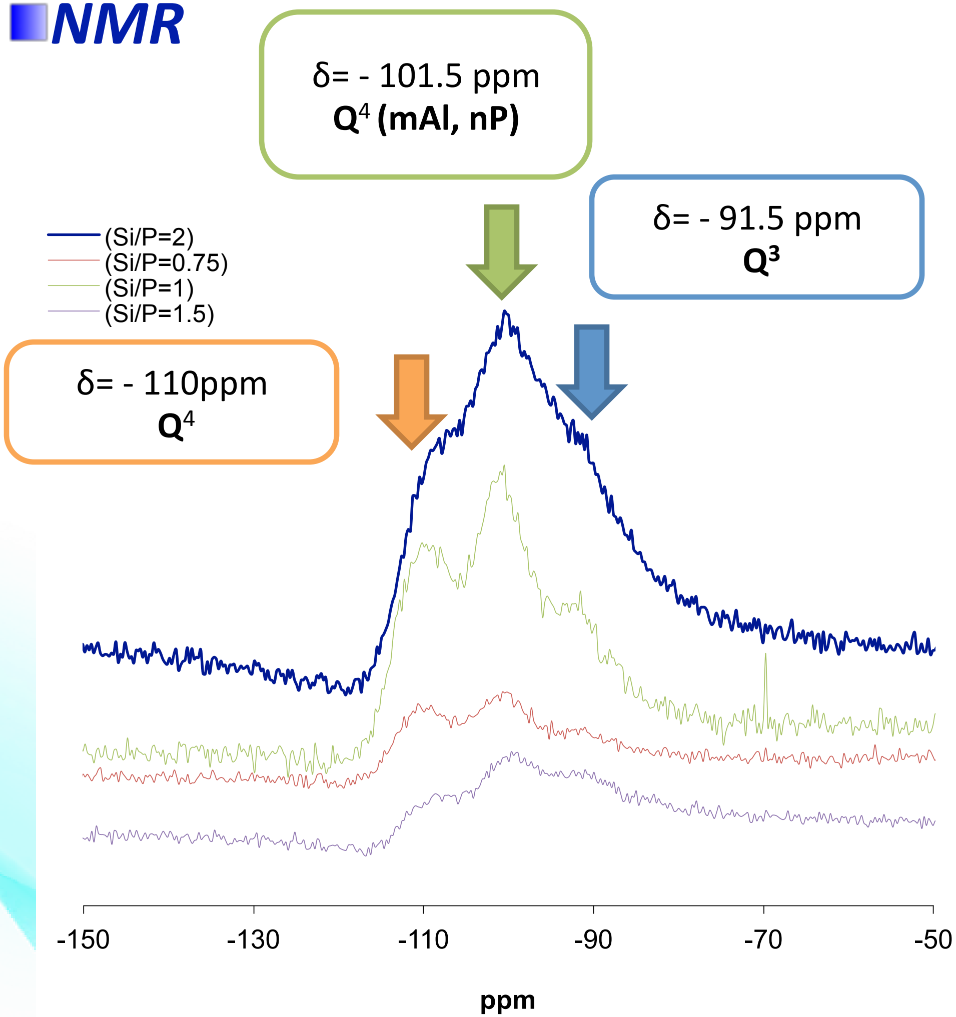
→ describes a mixed environment Q^4 (mAl, nP) species resulting from the phosphoric acid-polymerization of geopolymer

Structural characterization of the phosphoric acid-based geopolymers

Si/P molar ratio

NMR 29Si

NMR



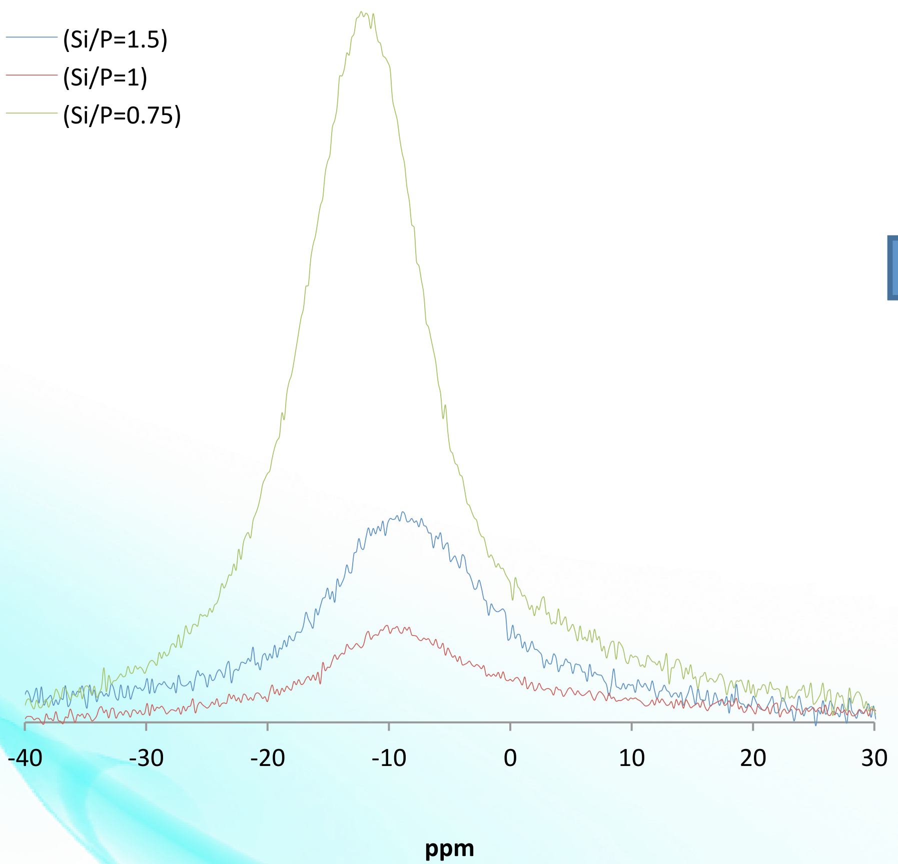
29Si NMR of phosphoric acid-based geopolymers with different Si/P molar ratio

The resonance at δ= - 110 ppm

→ siliceous, Al-free portions of the original metakaolinite structure and dealuminated structural segments as a result of geopolymerization process

Structural characterization of the phosphoric acid-based geopolymers

NMR



27Al NMR of phosphoric acid-based geopolymers with different Si/P molar ratio

Si/P molar ratio

NMR 27Al

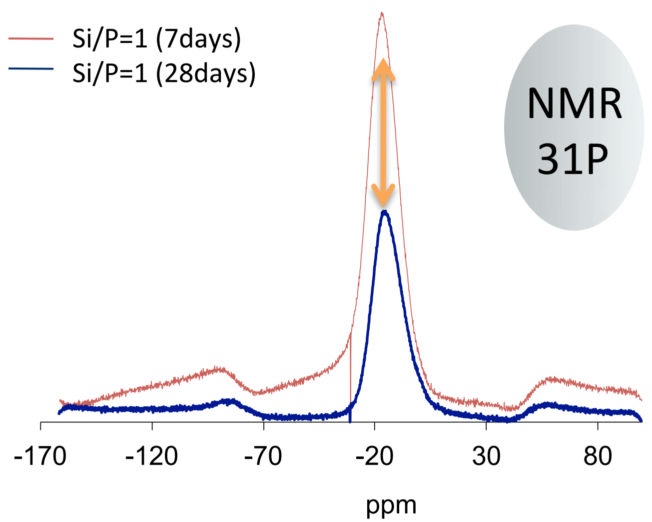
The presence of a single signal to δ=~-12ppm → hexa-coordinated environment of ^{27}Al

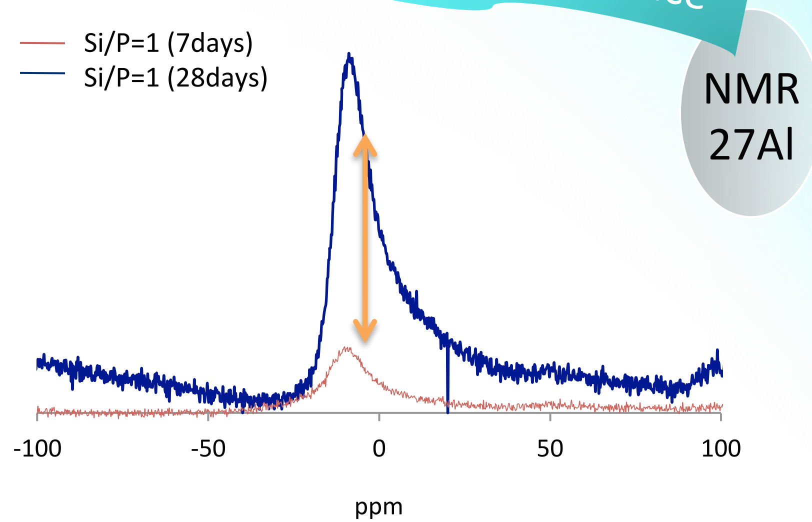
Formulation structure is

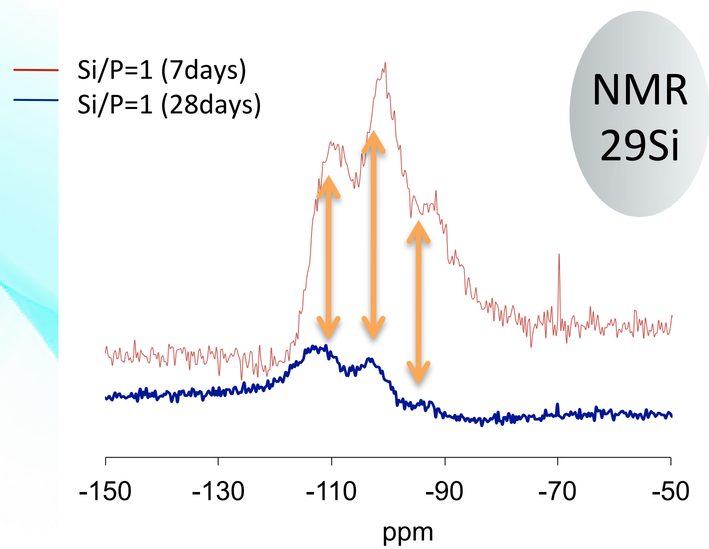
$[Al\ (O\text{-}P)_x(O\text{-}Si)_{6-x}]$

Structural characterization of the phosphoric acid-based geopolymers

Curing ages influence







↘ **the intensity of these signals at 28 days**

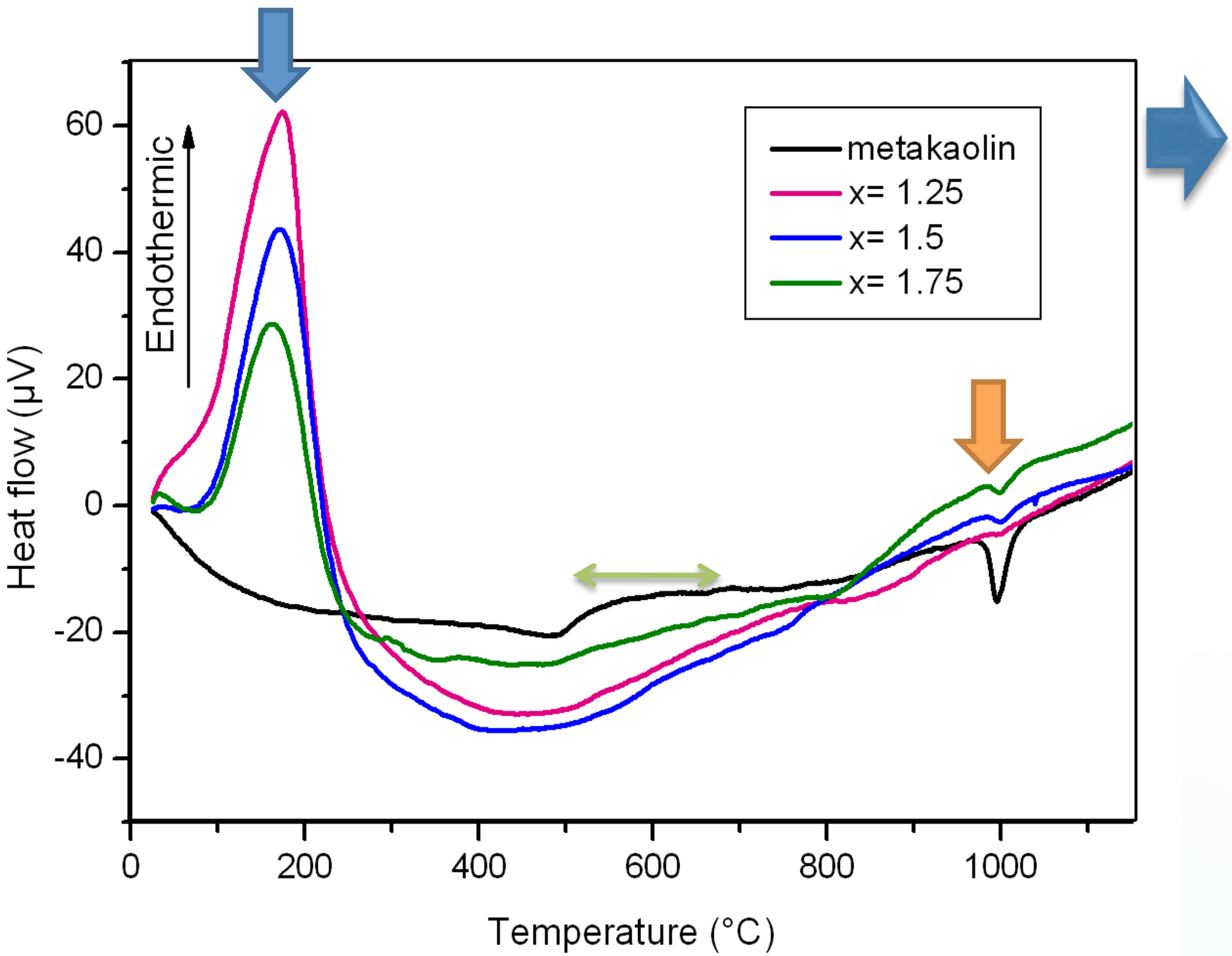
Geopolymerization reaction evolves in time → indicating that 7 days is not sufficient to complete geopolymerization

27Al, 29Si and 31P NMR of phosphoric acid-based geopolymers with curing ages

Thermal and dielectric characterization of the phosphoric acid-based geopolymers

Molar ratio Si/P influence

Thermal Analysis: DTA



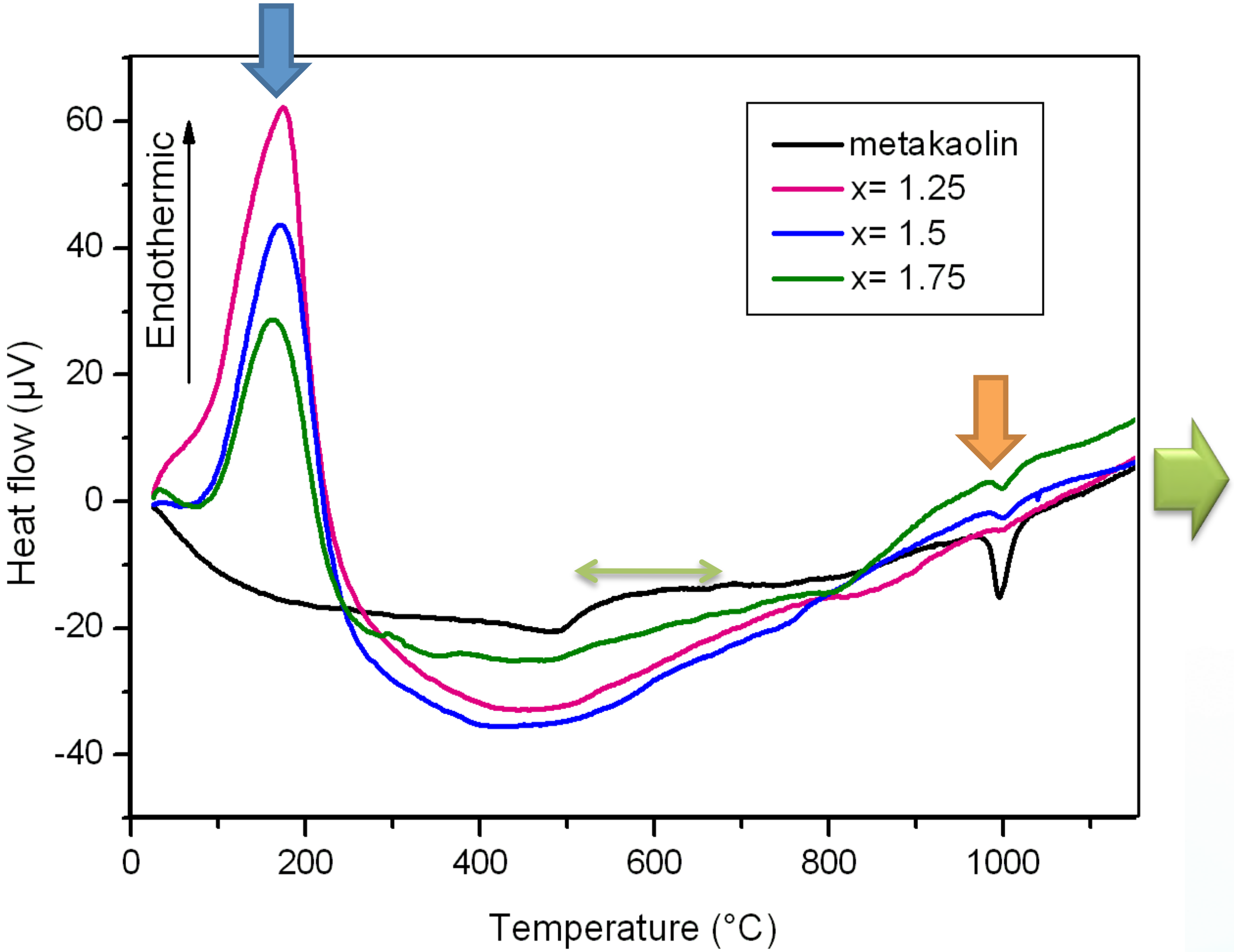
Large endothermic peaks→ dehydration of absorbed water in geopolymer.

DTA curves of metakaolin and phosphoric acid-based geopolymers with different Si/P molar ratio

Thermal and dielectric characterization of the phosphoric acid-based geopolymers

Molar ratio Si/P influence

Thermal Analysis: DTA



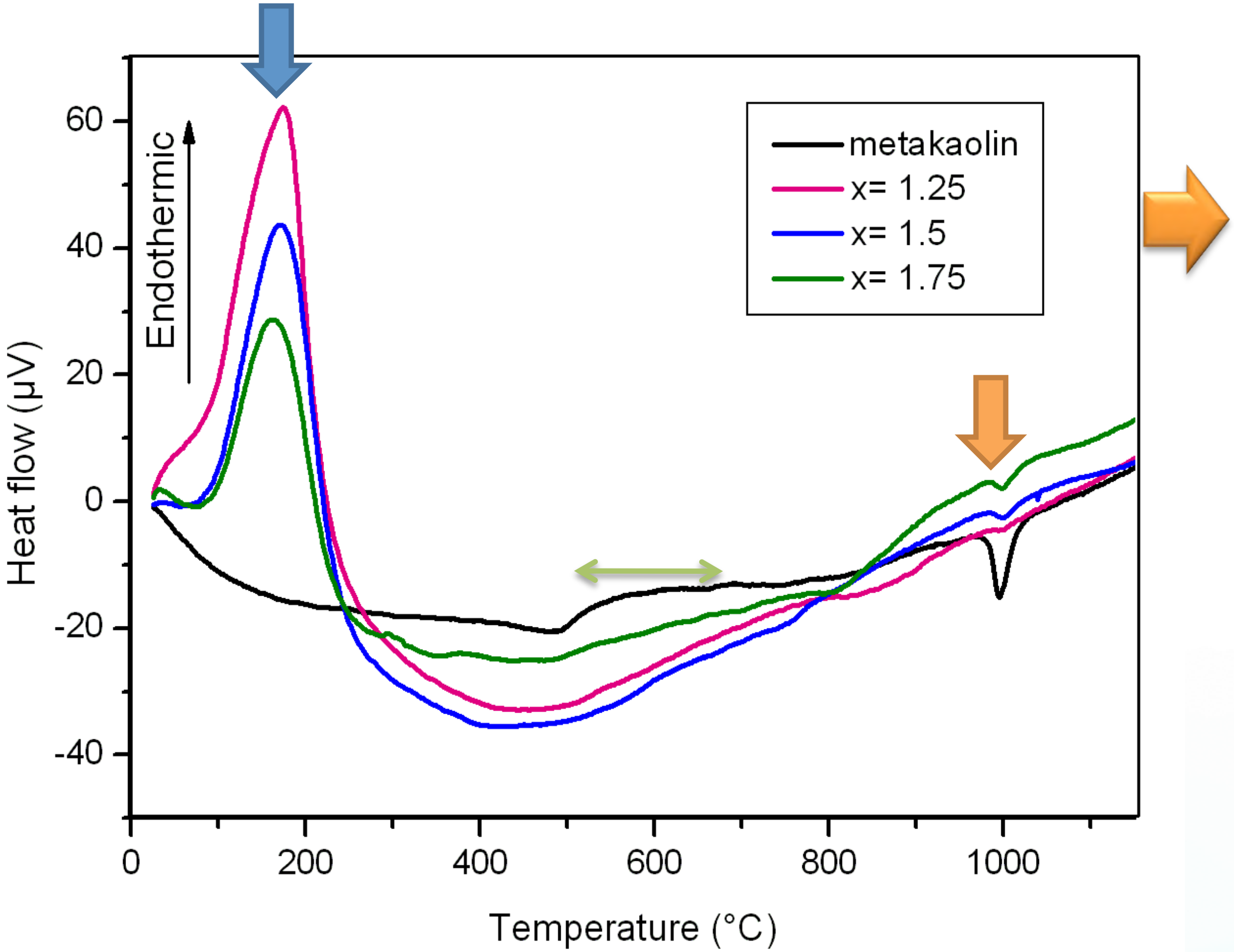
Small endothermic peak (500°C-600°C) in metakaolin → elimination of residual OH groups.

DTA curves of metakaolin and phosphoric acid-based geopolymers with different Si/P molar ratio

Thermal and dielectric characterization of the phosphoric acid-based geopolymers

Molar ratio Si/P influence

Thermal Analysis: DTA



DTA curves of metakaolin and phosphoric acid-based geopolymers with different Si/P molar ratio

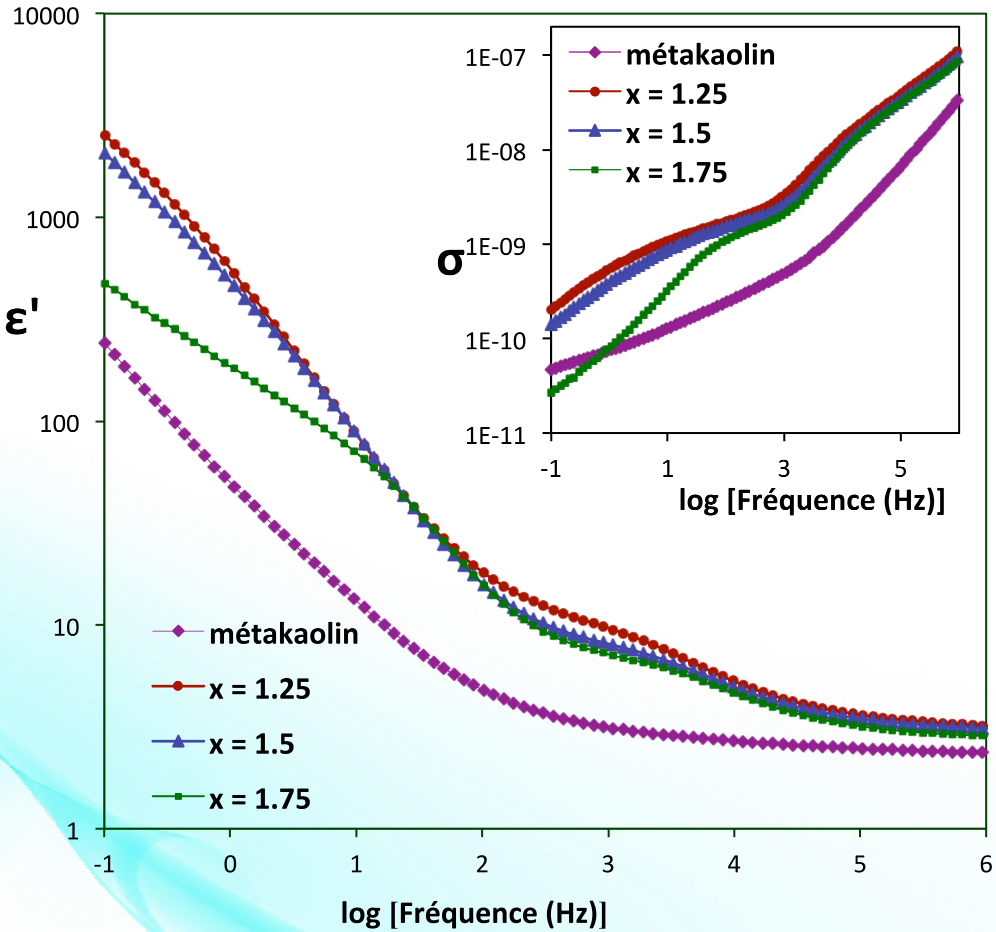
Small exothermic peak at 990°C→ structural reorganization of metakaolin and the residual metakaolin in geopolymers.

With the decreasing of the molar ratio Si/P, the intensity of the exothermic peaks corresponding to the residual metakaolin decreases.

Thermal and dielectric characterization of the phosphoric acid-based geopolymers

Molar ratio Si/P influence

Dielectric properties



Dielectric permittivity ε' and the conductivity σ of metakaolin and phosphoric acid-based geopolymers with different molar ratio Si/P

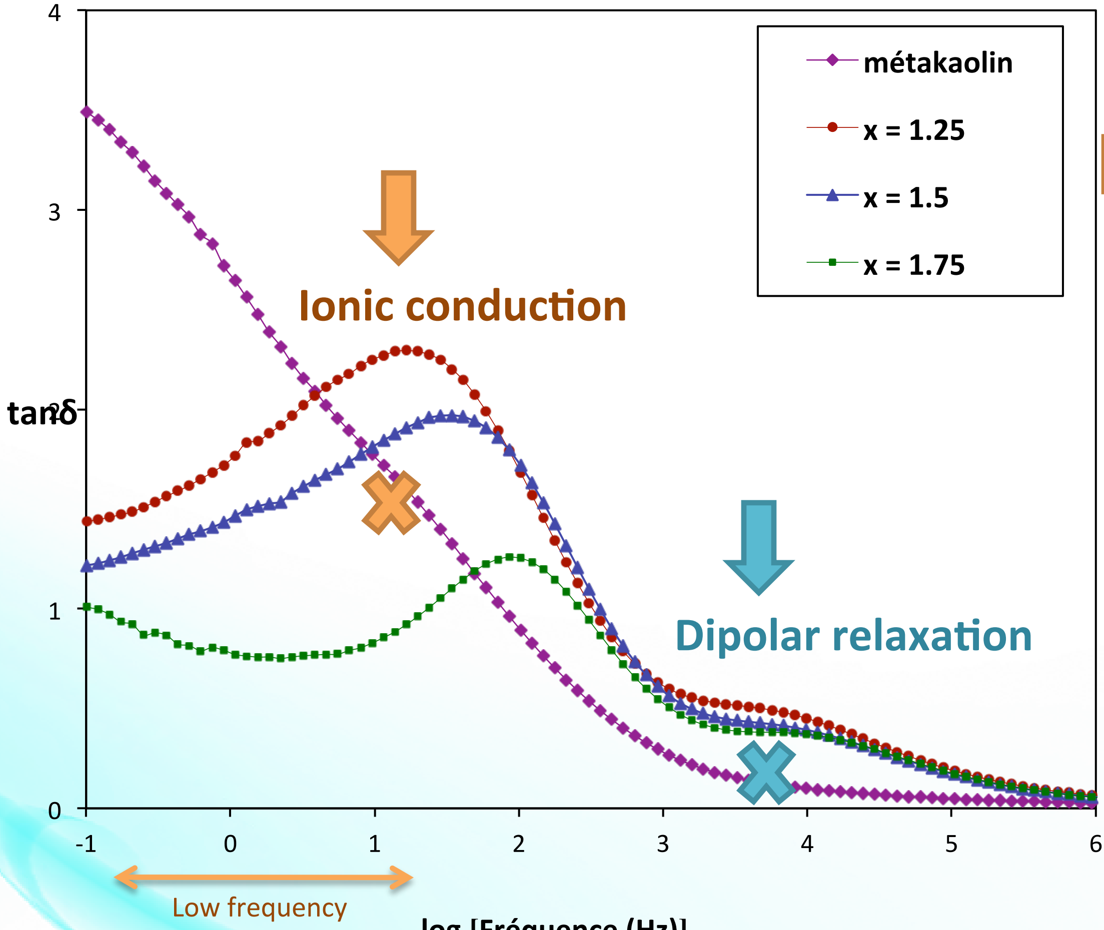
- **These two parameters (ε' and σ) were improved and increased with the decreasing of the molar ratio, i.e. with increasing amount of phosphoric acid.**
- **The ac-conductivity values for phosphoric acid-based geopolymers are higher than the based material (metakaolin)**

Enhancement in the dielectric ε' as well as the σ of geopolymers → presence of the additional charge centers caused by the donation of an extra proton by the H_3PO_4 molecule

Thermal and dielectric characterization of the phosphoric acid-based geopolymers

Molar ratio Si/P influence

Dielectric properties



Dielectric loss tanδ of metakaolin and geopolymers with different molar ratio Si/P measured at room temperature

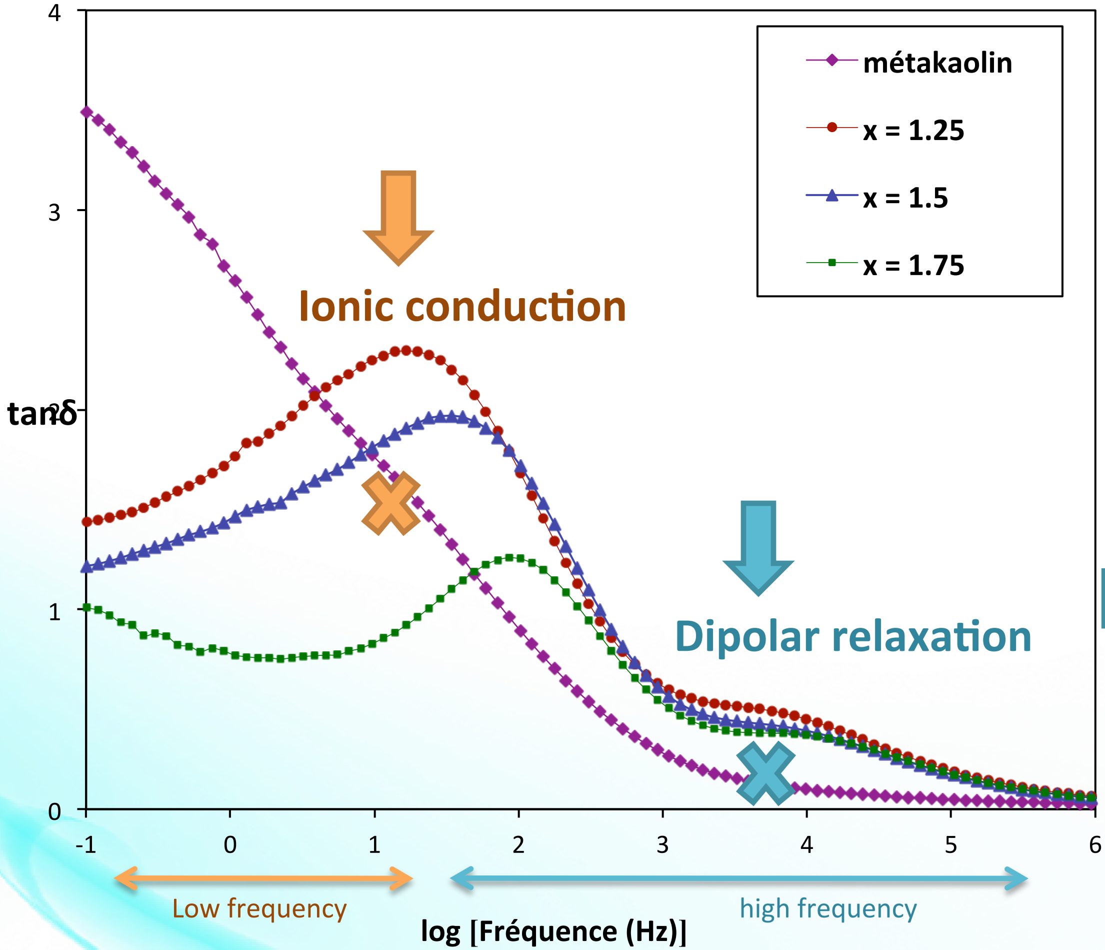
The first one –> located in the low frequency range → Related to Conduction phenomenon

In fact, phosphoric acid is a good proton conductor because of its extensive self-ionization.

Thermal and dielectric characterization of the phosphoric acid-based geopolymers

Molar ratio Si/P influence

Dielectric properties



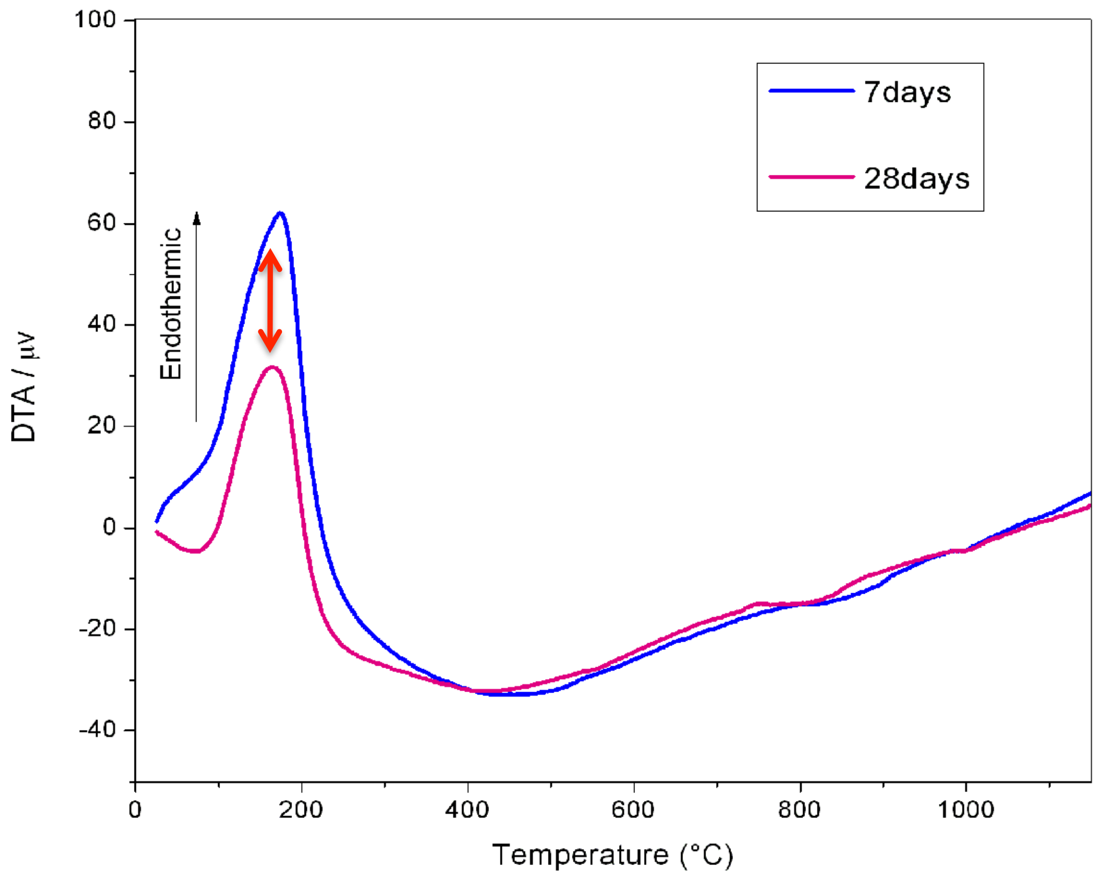
Dielectric loss tanδ **of metakaolin and geopolymers with different molar ratio Si/P measured at room temperature**

The second one –> located in the high frequency range → indicate the presence of relaxing dipoles in the specimens (water dipoles)

Thermal and dielectric characterization of the phosphoric acid-based geopolymers

Curing age influence

Thermal Analysis: DTA



DTA curves of phosphoric acid-based geopolymers (Si/P=1.25) with curing age

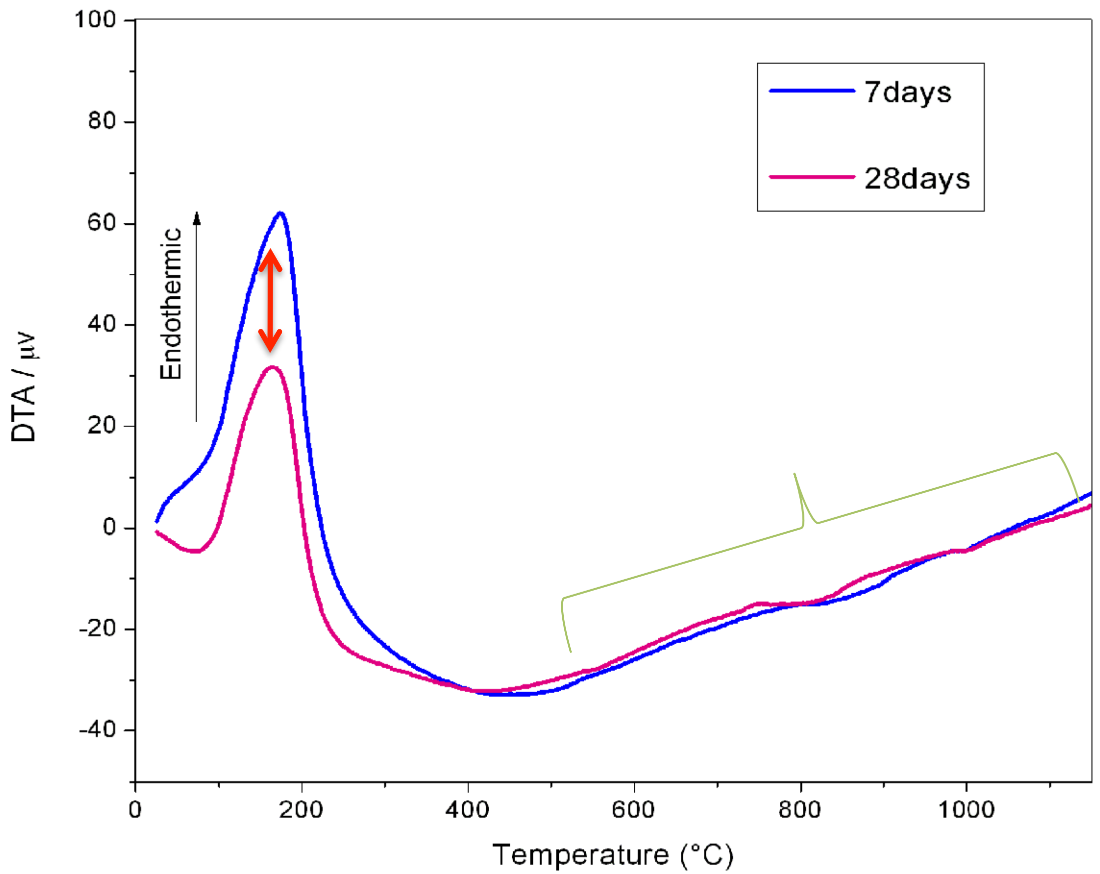
A decreasing in the intensity of the endothermic peak for 28 days

geopolymerization reaction evolves over time resulting in a higher consumption of water into geopolymers.

Thermal and dielectric characterization of the phosphoric acid-based geopolymers

Curing age influence

Thermal Analysis: DTA



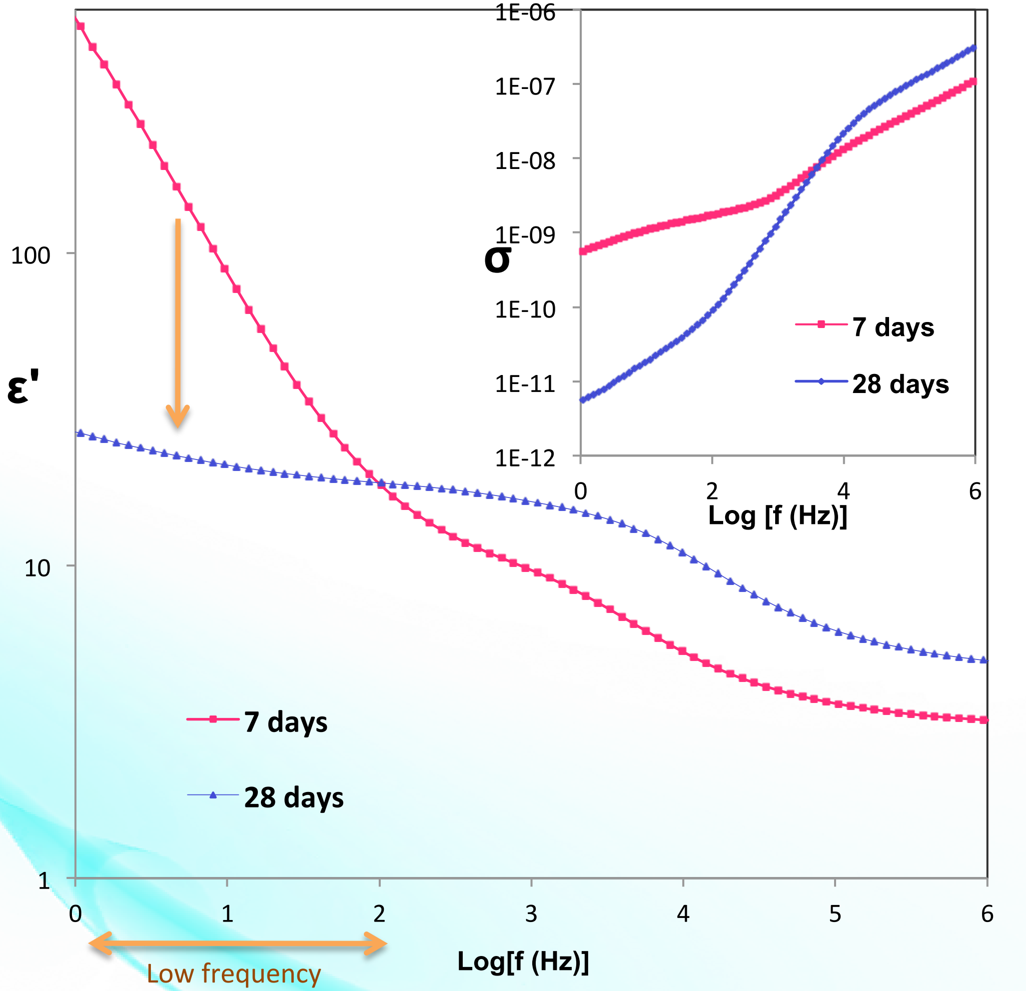
DTA curves of phosphoric acid-based geopolymers (Si/P=1.25) with curing age

No change on the thermal behaviors for both geopolymers at high temperatures.

Thermal and dielectric characterization of the phosphoric acid-based geopolymers

Curing age influence

Dielectric properties



Dielectric permittivity **ε′ and the conductivity σ of metakaolin and phosphoric acid-based geopolymers with curing ages**

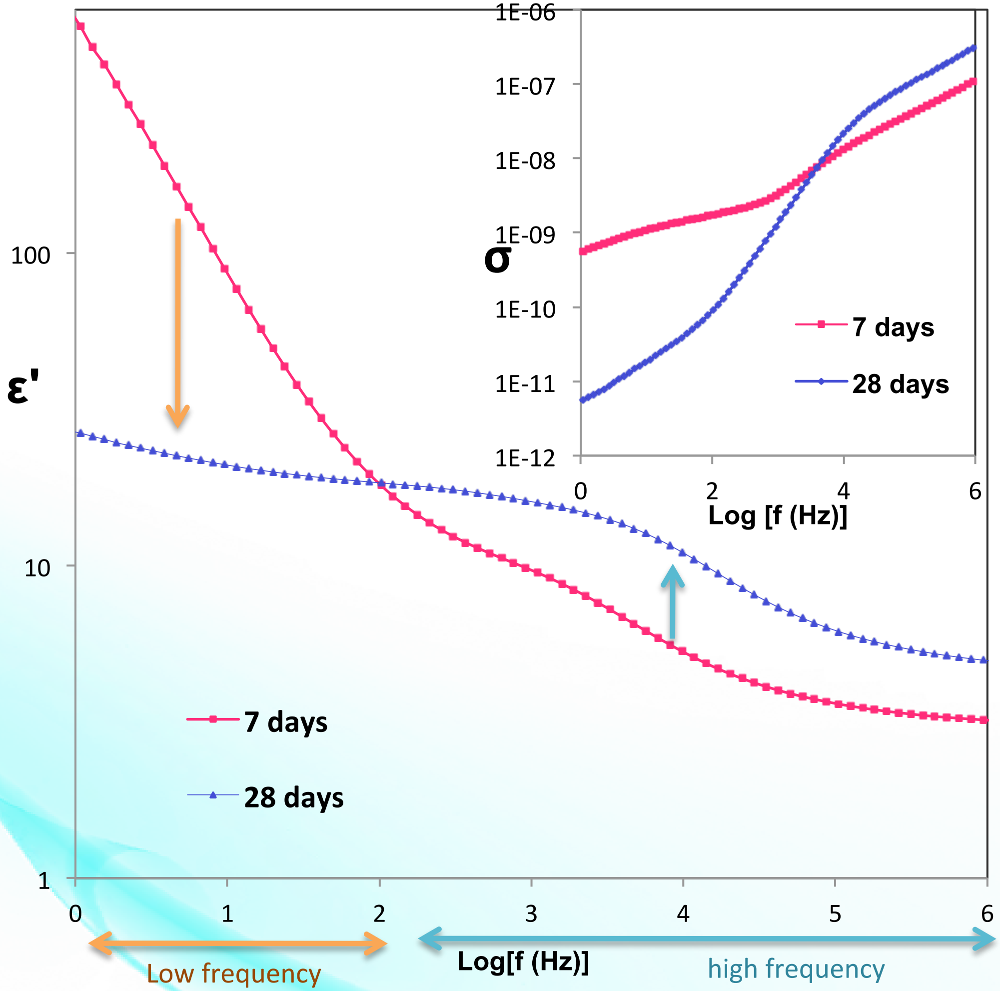
➢ **F(Hz) < 10^2 : ε' and σ decreased for geopolymer aged of 28 days.**

This ↘ resulted from the reduction in the number of free charges provided by phosphoric acid whose consumption was more important for geopolymerization reaction during 28days

Thermal and dielectric characterization of the phosphoric acid-based geopolymers

Curing age influence

Dielectric properties



***Dielectric permittivity* ε' and the conductivity σ of metakaolin and phosphoric acid-based geopolymers with curing ages**

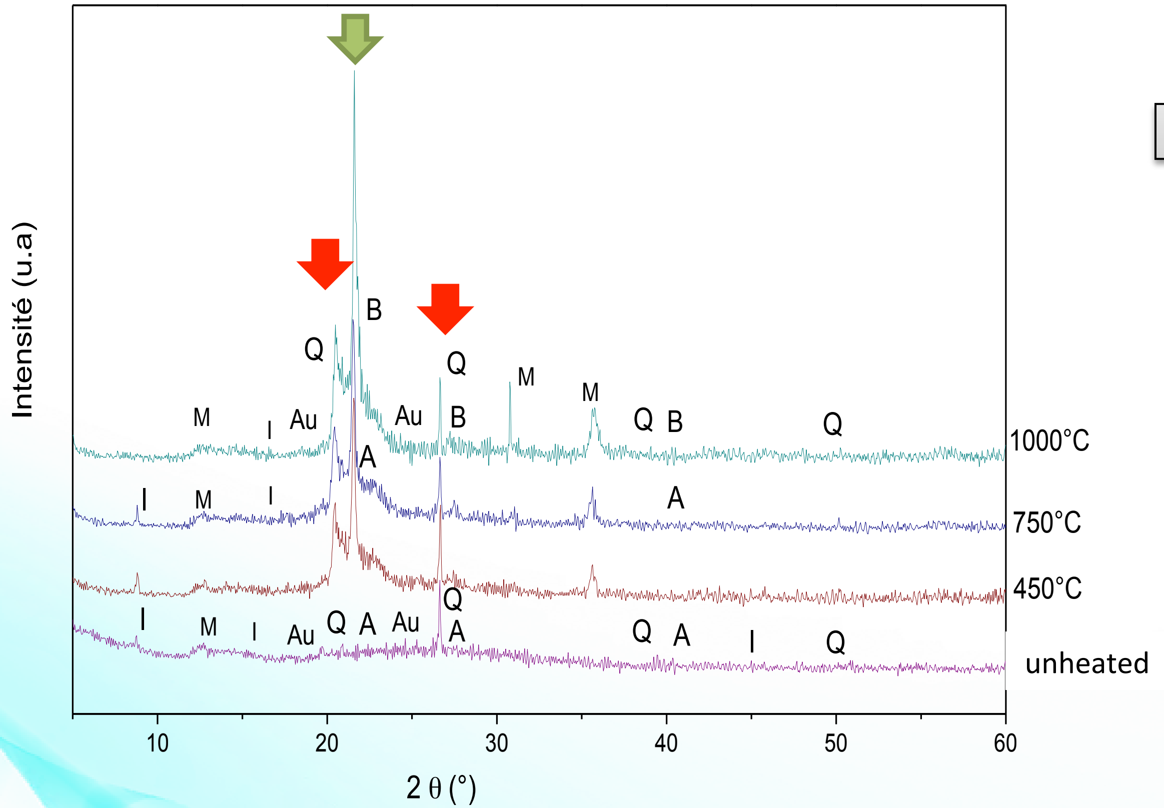
➢ **Higher (f(Hz)): ε' and σ increased.**

This ↑ could be a result of the decrease in the porosity into geopolymers. Indeed, it was found in previous studies that adding phosphoric acid to the kaolin leads significantly to the emergence of a glassy phase that fills the majority of the pores.

Thermal and dielectric characterization of the phosphoric acid-based geopolymers

Heat Treatment influence

XRD



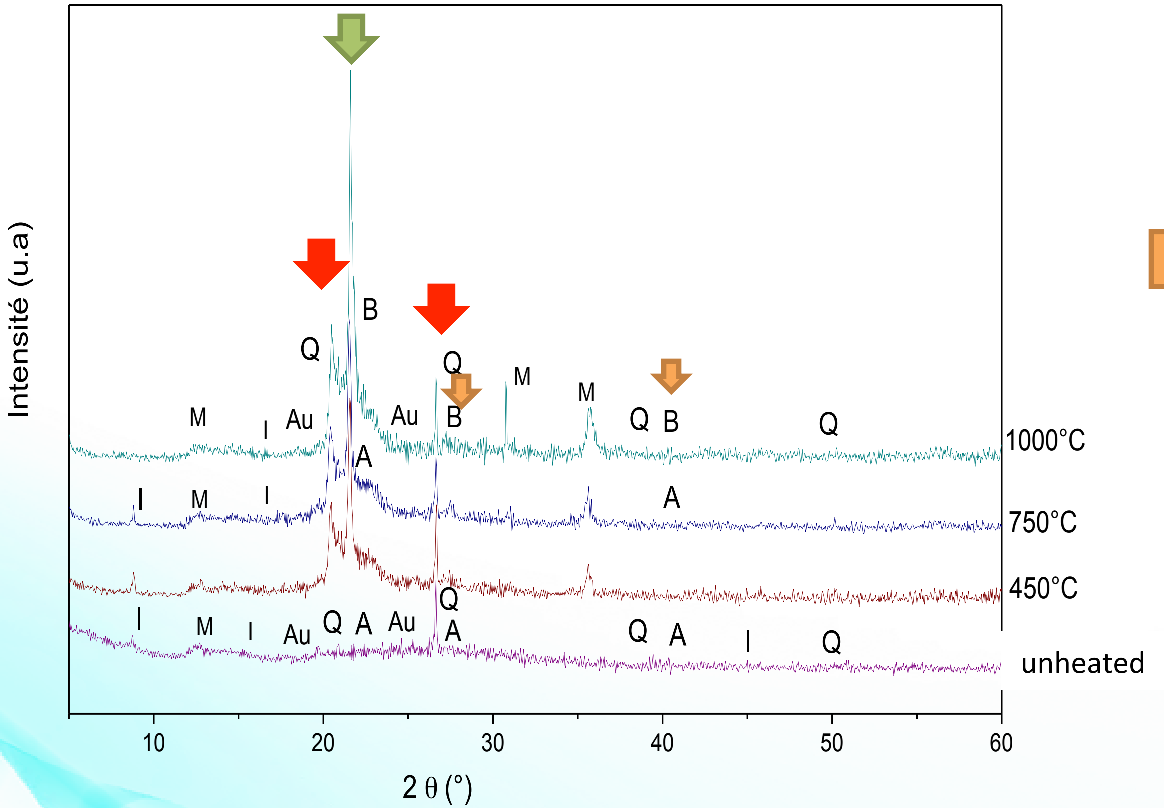
XRD patterns of phosphoric acid-based geopolymers unheated and heated for 1hour at different temperatures

Intensities of peaks→
aluminum phosphate, quartz
↑ with the ↑ of heating T°C

Thermal and dielectric characterization of the phosphoric acid-based geopolymers

Heat Treatment influence

XRD



XRD patterns of phosphoric acid-based geopolymers unheated and heated for 1hour at different temperatures

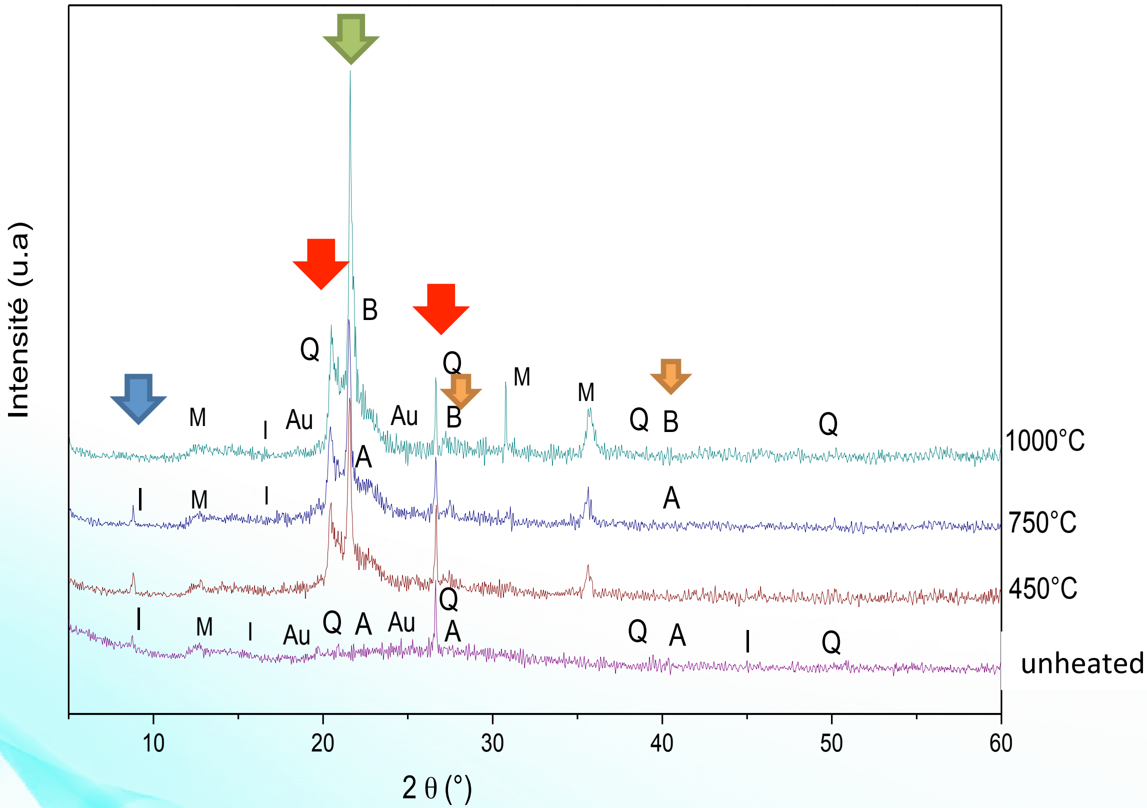
At 1000°C: new phase of $AlPO_4$ → berlinite ($AlPO_4$ with α-quartz structure) appeared

This phase results from the crystallization of aluminum phosphate which generally takes place at 900°C.

Thermal and dielectric characterization of the phosphoric acid-based geopolymers

Heat Treatment influence

XRD



XRD patterns of phosphoric acid-based geopolymers unheated and heated for 1hour at different temperatures

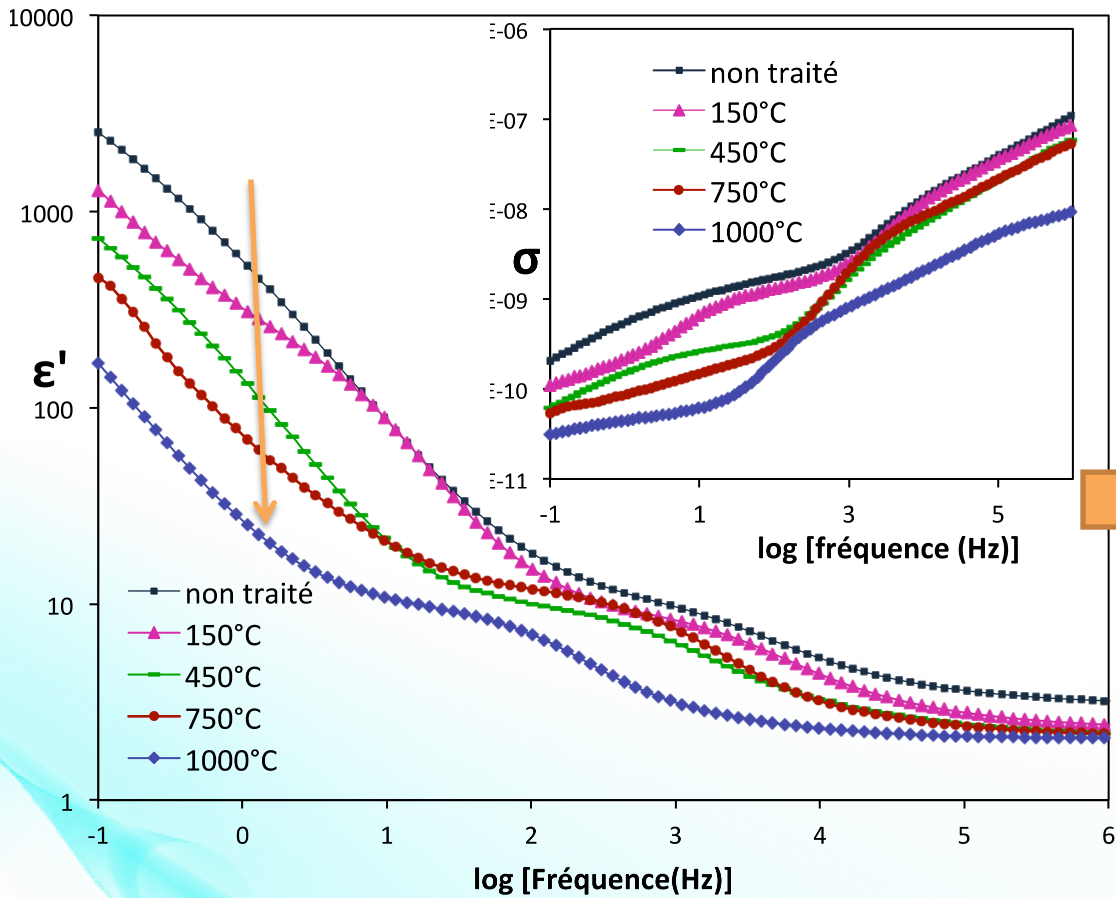
Furthermore, the illite existing in the geopolymer changed to another new phase

In fact, between 900°C and 1000°C, the gibbsite-layer starts forming spinal/γ-Al_2O_3 and some aluminum-rich mullite.

Thermal and dielectric characterization of the phosphoric acid-based geopolymers

Heat Treatment influence

Dielectric properties



***Dielectric permittivity* ε' and the conductivity σ of phosphoric acid-based geopolymers heated at different temperature (150°C, 450°C 750°C and 1000°C)**

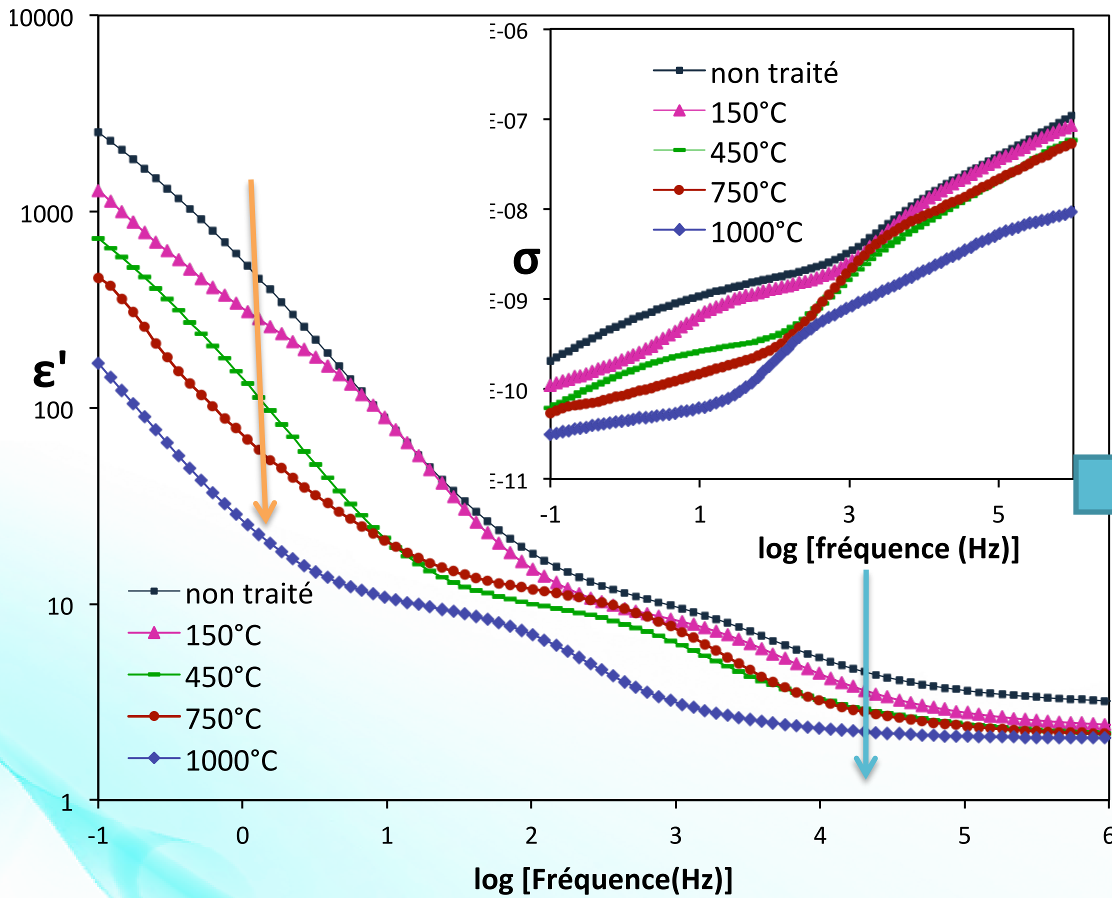
➢The ε' and σ ↘ with the ↗ in the draying T° at fixed f(Hz)→ the ↘ observed for geopolymer heated at (150°C, 450°C and 750°C)

the decrease was related to the elimination of free water and bound water

Thermal and dielectric characterization of the phosphoric acid-based geopolymers

Heat Treatment influence

Dielectric properties



***Dielectric permittivity* ε′ and the conductivity σ of phosphoric acid-based geopolymers heated at different temperature (150°C, 450°C 750°C and 1000°C)**

➢At high T°C →the ↓ in ε' and σ

Related to the rearrangement in the structure of geopolymers such as formation (aluminum-rich mullite) known by its low dielectric constant

Conclusions

The main finding of this study can be summarized as follows:

→ ***Structural characterization of phosphoric acid based geopolymers:***

- The mechanical strength of geopolymers increases with age and with the amount of phosphoric acid. It reaches a maximum value when Si/P molar ratio equal 1. Beyond these molar ratio Si / P the resistance tends to decrease.
- The SEM micrographs of the phosphoric acid-based geopolymers show that the age and the increasing with the amount of phosphoric acid promote the densification of geopolymers

Conclusions

- The obtained phosphoric acid-based geopolymers are essentially amorphous with the presence of some crystalline phases such as Aluminum phosphate..
- The Infrared Spectrum of the sample (Si/P=1) shows that the product of the geopolymerization has a polymeric Si-O-Al-O-P.
- The MAS-NMR analysis show a tetrahedral P environments, hex-coordinated Al environment and the Si exists in three different environments

Conclusions

→ ***Thermal and dielectric characterization of phosphoric acid based geopolymers:***

- Unlike alkali-based geopolymers used as fast ionic conductors, acid -based geopolymers can be used as insulators.
- The molar ratio (Si/P) as well as the curing age have a great influence on acid based geopolymers.

Conclusions

Heat treating of geopolymer material at high temperature decreases the dielectric properties. Therefore, to ensure the best dielectric performance, an appropriate heat treatment is required for geopolymer based on phosphoric acid.

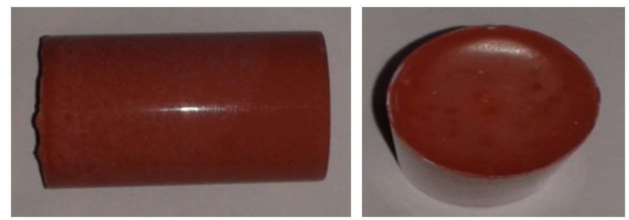
Perspective

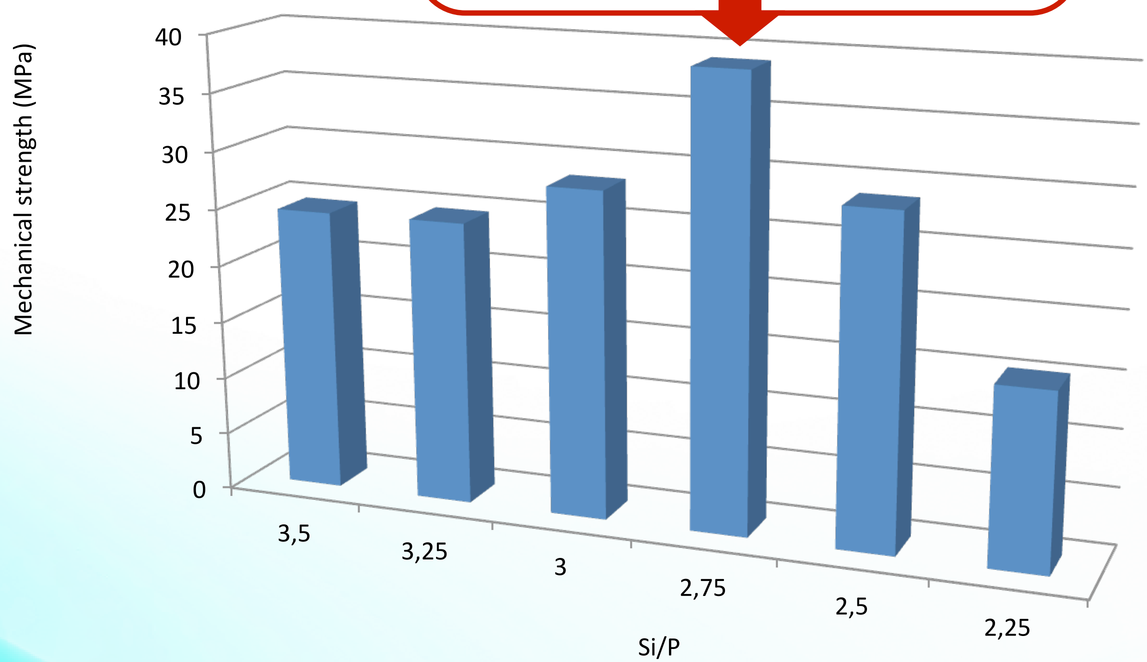
- Synthesis of geopolymers from local (Tunisian) calcined clay
- Synthesis of geopolymers while varying other parameters such as the particle size of the clay, calcinated temperature ...
- Performance comparison geopolymers with those materials conventionally used in civil engineering
- Numerical modeling

Thank you for your attention

Structural characterization of the phosphoric acid-based geopolymers from Medenine calcined clay

Mechanical properties: compressive strength

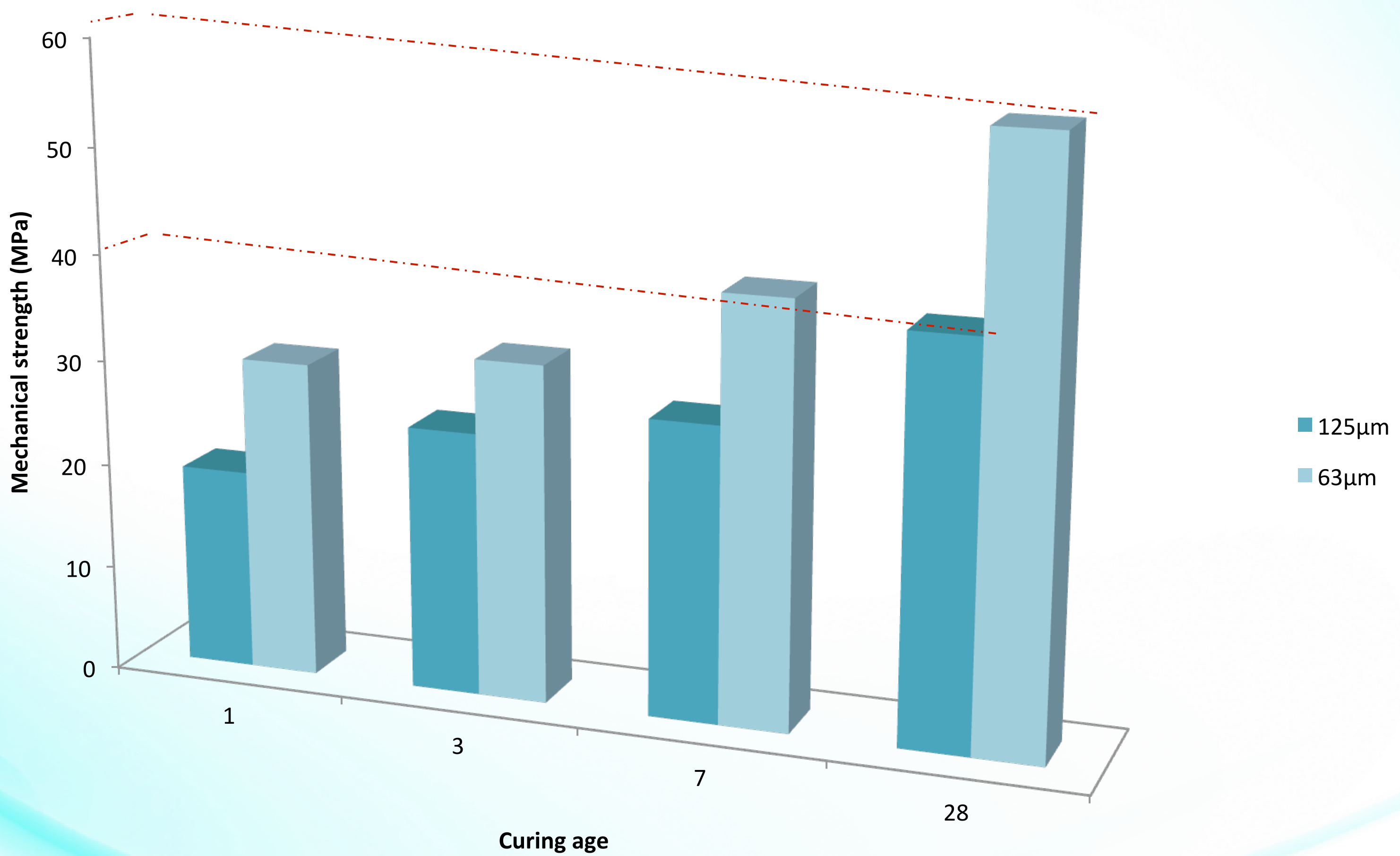




Mechanical strength evolution of the product acid-based geopolymers synthesized from Medenine with the different Si/P molar ratio

Characterization of acid-based geopolymers from raw Tunisian clay (Medenine)

Mechanical properties: compressive strength



Mechanical strength evolution of the product acid-based geopolymers synthesized from Medenine with the particle size and the curing days

Conclusion

→ ***acid-based geopolymers obtained from Tunisia clay:***

- The compressive strength is equal 39MPa (Si/P=2,75)
- The compressive strength increases (60MPa) as the particle size of clay decreases

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