



GEOPOLYMERCAMP

5-6th July 2011 - Saint Quentin



AlPO₄- Geopolymer

Synthesis routes

Potential applications

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Aluminum phosphate materials

- Low density (2,56 g/cm³)
- Chemically inert and stable at high temperature
- Chemically compatible with many metals and ceramic materials (silicon carbide, alumina, silica)

Useful for many applications :

- Catalysts
- Refractories
- Composites
- Phosphate bonded ceramics
- Coatings

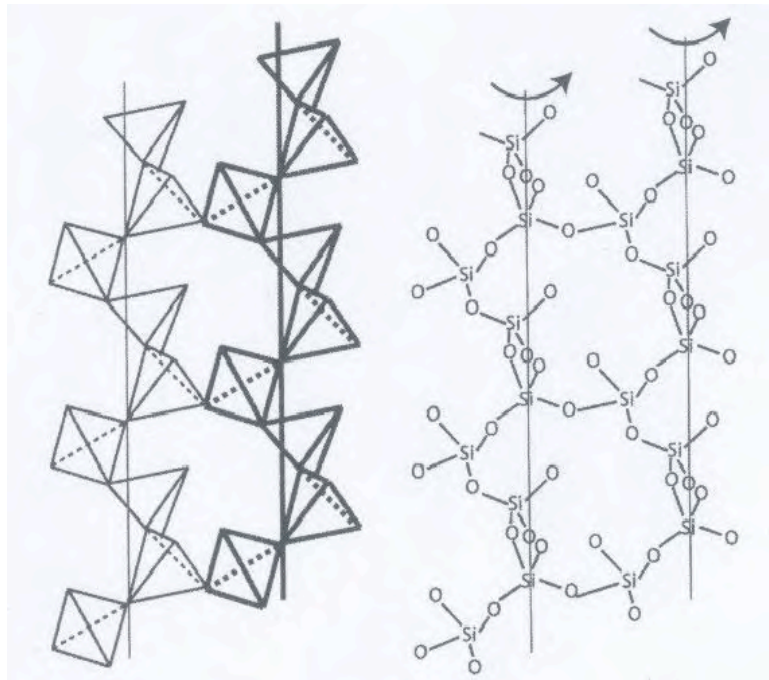
Conventional AlPO_4 ceramics are unsuitable for high temperature applications

⇒ Polymorphic transformations

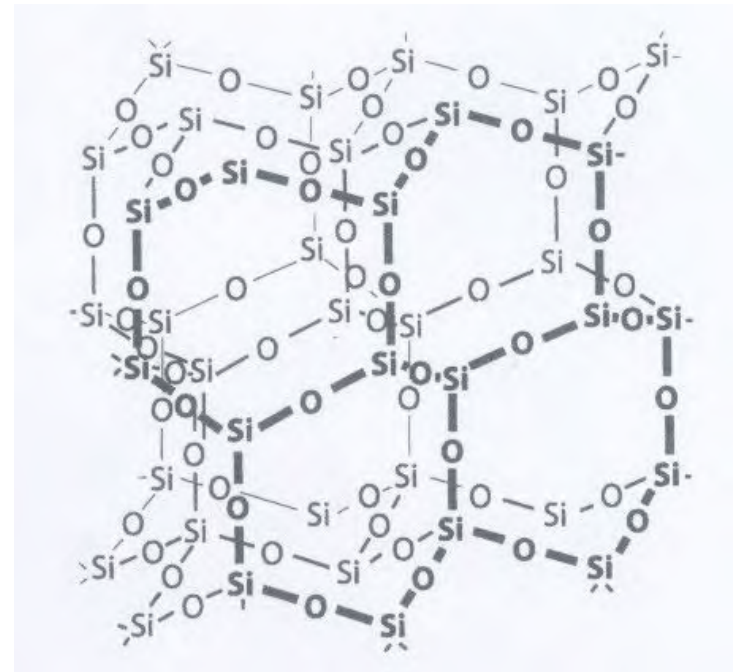
AlPO₄ structures

- isostructural with SiO₂
- isomorphous with the three crystalline forms of SiO₂

Quartz ⇔ **Berlinite**



Tridymite ⇔ **Phosphotridymite**



Cristobalite ⇔ **Phosphocristobalite**

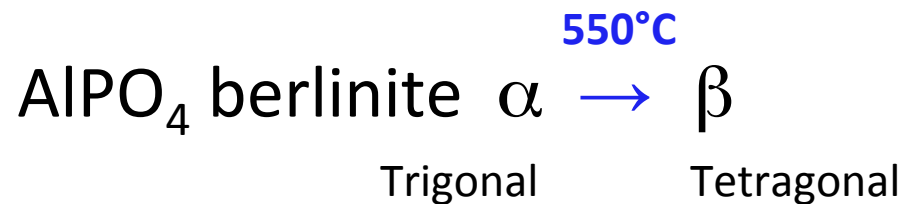
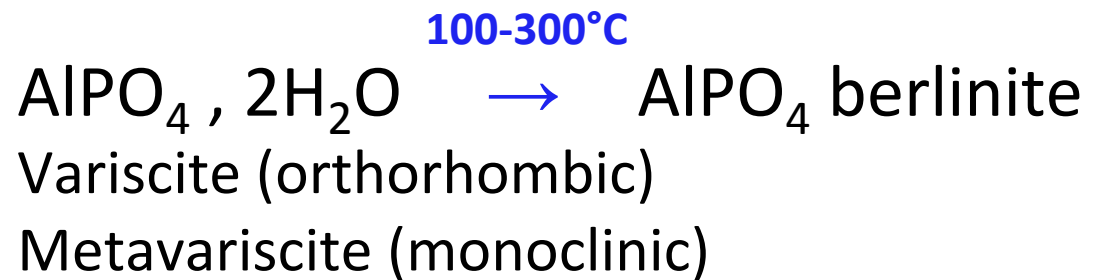
Berlinite AlPO_4



Thermal treatment of Aluminum phosphate hydrates



Natural variscite



Generalized geopolymerization structures

Comprise molecular units (or chemical groups):

-Si-O-Si-O- siloxo, poly(siloxo)

-Si-O-Al-O- sialate, poly(sialate) $\text{Si/Al} = 1$

-Si-O-Al-O-Si-O- sialate-siloxo, poly(sialate-siloxo) $\text{Si/Al} = 2$

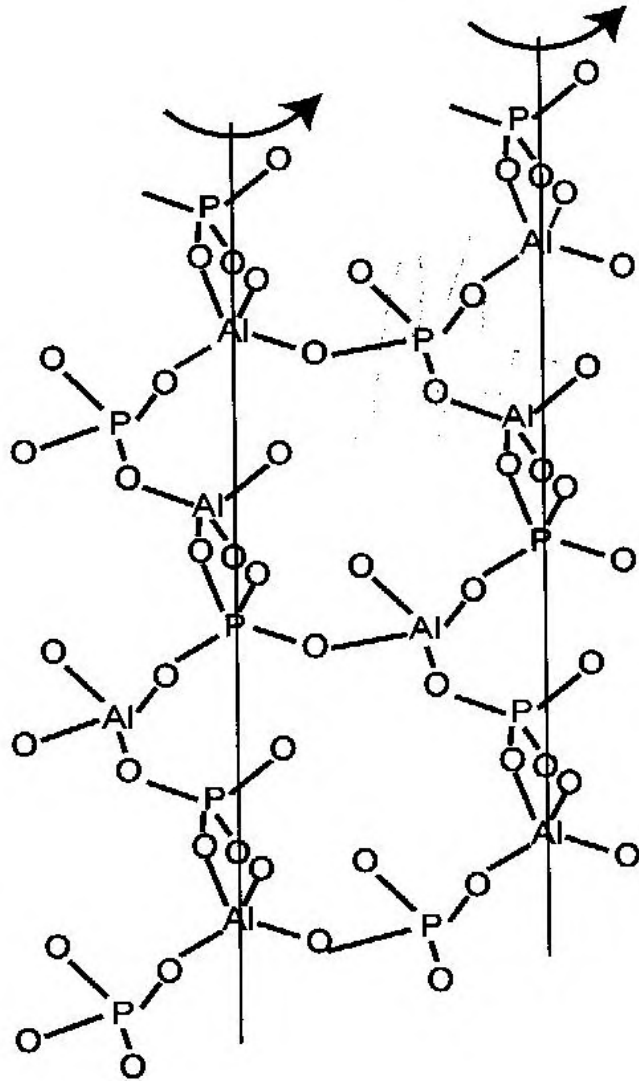
-Si-O-Al-O-Si-O-Si-O- sialate-disiloxo, poly(sialate-disiloxo)
 $\text{Si/Al} = 3$

-P-O-P-O- phosphate, poly(phosphate)

-P-O-Si-O-P-O- phospho-siloxo, poly(phospho-siloxo)

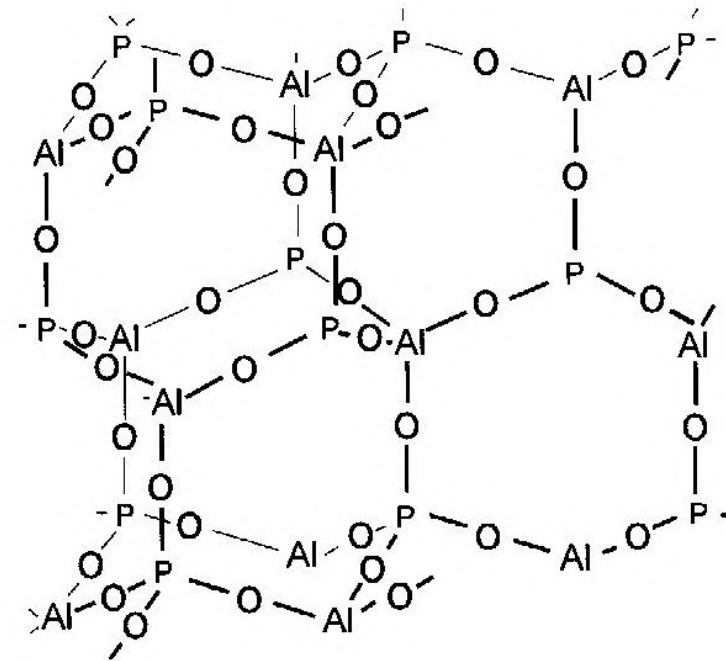
-P-O-Si-O-Al-O-P-O- phospho-sialate, poly(phospho-sialate)

Polymeric structures of AlPO_4 -Geopolymers



AlPO_4 -berlinite (isostructural to quartz)

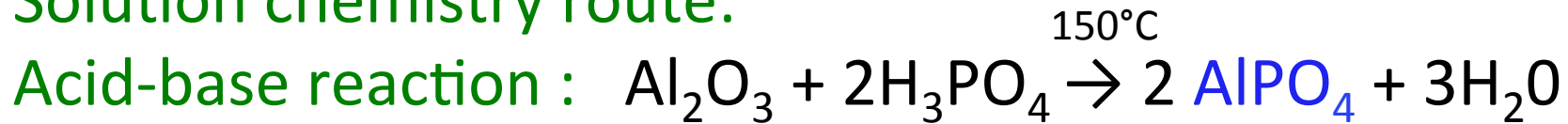
⇒ Cross-linked (P-O-Al-O)_n
poly(alumino-phospho) chains



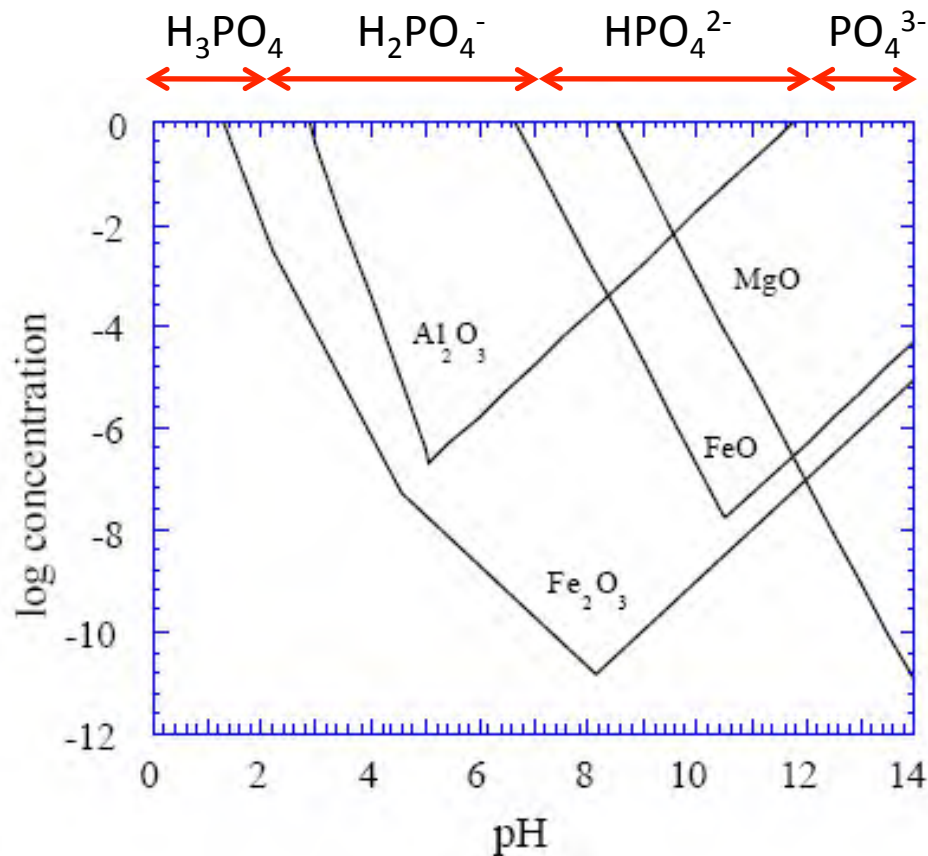
AlPO_4 -tridymite/cristobalite

Synthesis routes of AlPO_4

Solution chemistry route:



"Ceramic bonding reaction" \Rightarrow phosphate based
geopolymer



Synthesis in the pH range 7-9
(\neq alkaline environment for
silicate based geopolymers)

The modified Al_2O_3 routes

- Al_2O_3 with low specific surface area
high crystallinity ($\alpha\text{-Al}_2\text{O}_3$)
 \Rightarrow Long reaction times to form AlPO_4
- Al_2O_3 with high specific surface area
low crystallinity
 \Rightarrow faster reactions
 \Rightarrow produce more AlPO_4

1993, Bothe and Brown

Synthesis routes of AlPO_4

- Fibres, coatings, binders or fine particles
- High temperature application
- Porosity

Ceramic / Composite

⇒ Synthetic form of AlPO_4 meta-stable by remaining amorphous at increasing temperatures or during heating and cooling cycles

Coating

⇒ composition having a low oxygen diffusivity at high temperature to provide thermal, oxidation and corrosion protection for metal and ceramics

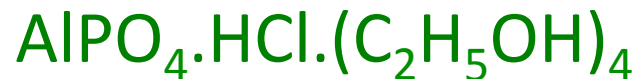
Solution chemistry route : Sol-gel processes

- Aqueous sol-gel route
- Polymerized organic-inorganic complex route

Polymerized organic-inorganic complex route

1977, Birchall et al.

New precursors : complex phosphate of aluminium



100 - 150°C



H₂O

Viscous AlPO₄ solution

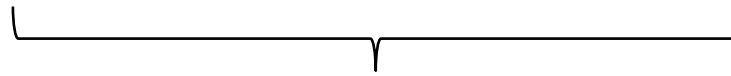
⇒ Elaboration of thin coating

⇒ fibers

⇒ Chain molecular structures
of AlPO₄-geopolymer

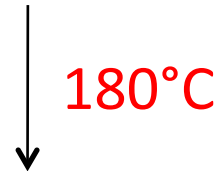
Sol-gel route

1989, Coury et al.



Gel

Precipitated AlPO_4



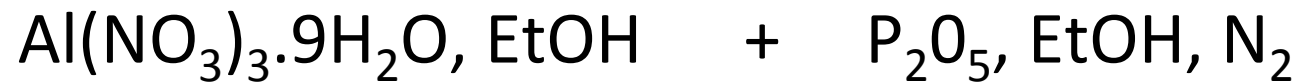
AlPO_4 -cristobalite

AlPO_4 -berlinite

AlPO_4 -tridymite

Solution chemical route

2000, Sambasivan et al.



Precursor solution

↓ Dip-coating

304 stainless steel

↓ 1000°C

Dense amorphous aluminum phosphate coating

Conclusion

Several synthesis routes for AlPO_4 -geopolymer

- Acid-base reaction

Low temperature curing method

Presence of hydrated form of aluminum phosphate

⇒ Unsuitable for the elaboration of hard and dense coating

⇒ Unsuitable for high-temperature application

- Sol-gel

Preparation of amorphous aluminum phosphate materials

Fibers, coatings, particles...

Low cost ?

environmentally friendly process?

MK-750 metakaolin-based AlPO_4 -geopolymer

Inclusion of PO_4 units into silicate and silicate-siloxo sequences