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Dipartimento di Ingegneria "Enzo Ferrari"

Diving to deep end - about geopolymers & AAMs

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Lecture contents

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State of the art for construction materials: OPC

Alkali activated materials-AAMs –Definition and Applications

Comparison with cement, glass and zeolites

Reagents and preparation

AAMs properties

Report on published papers from data base (Scopus)

Conclusions

Construction materials: State of the art in OPC

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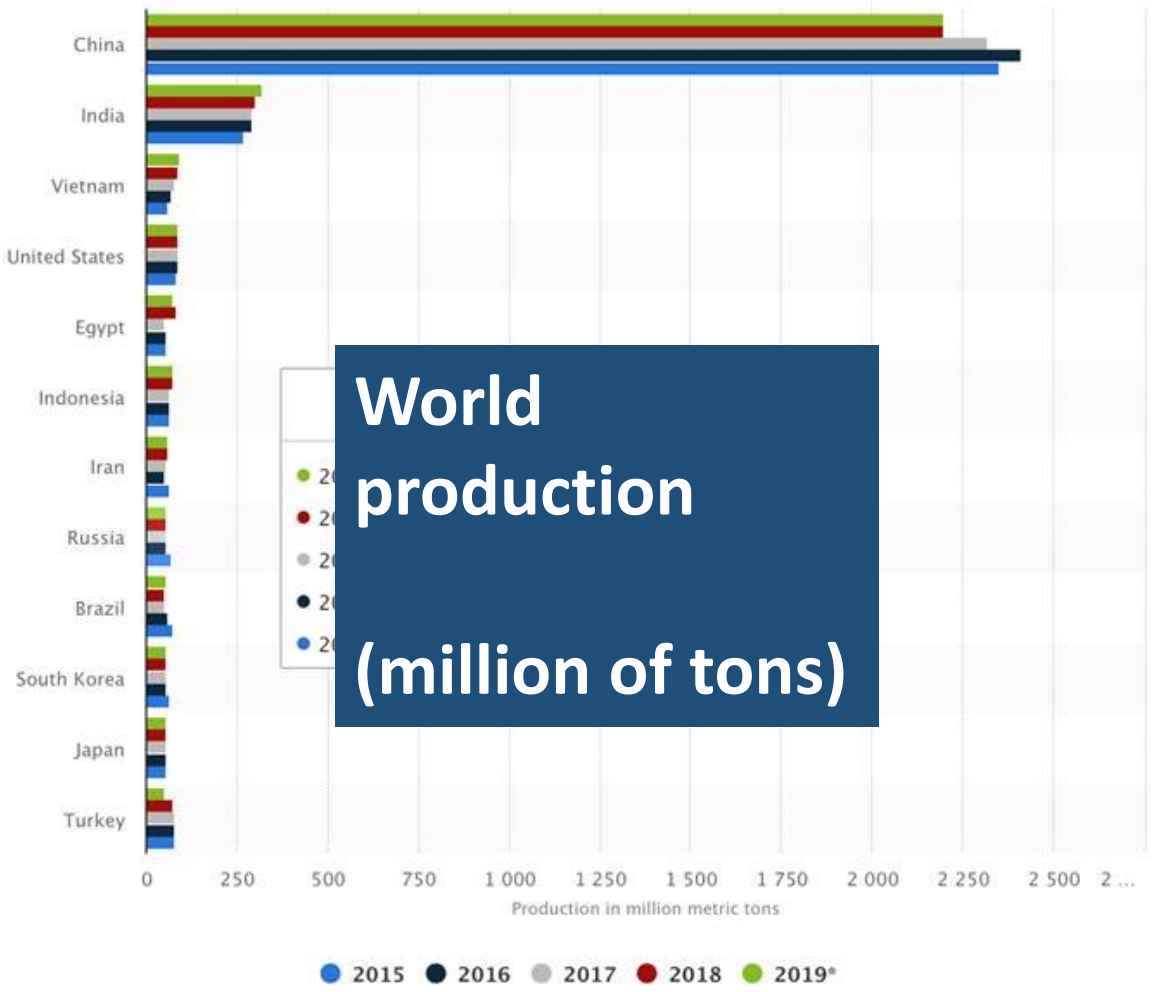
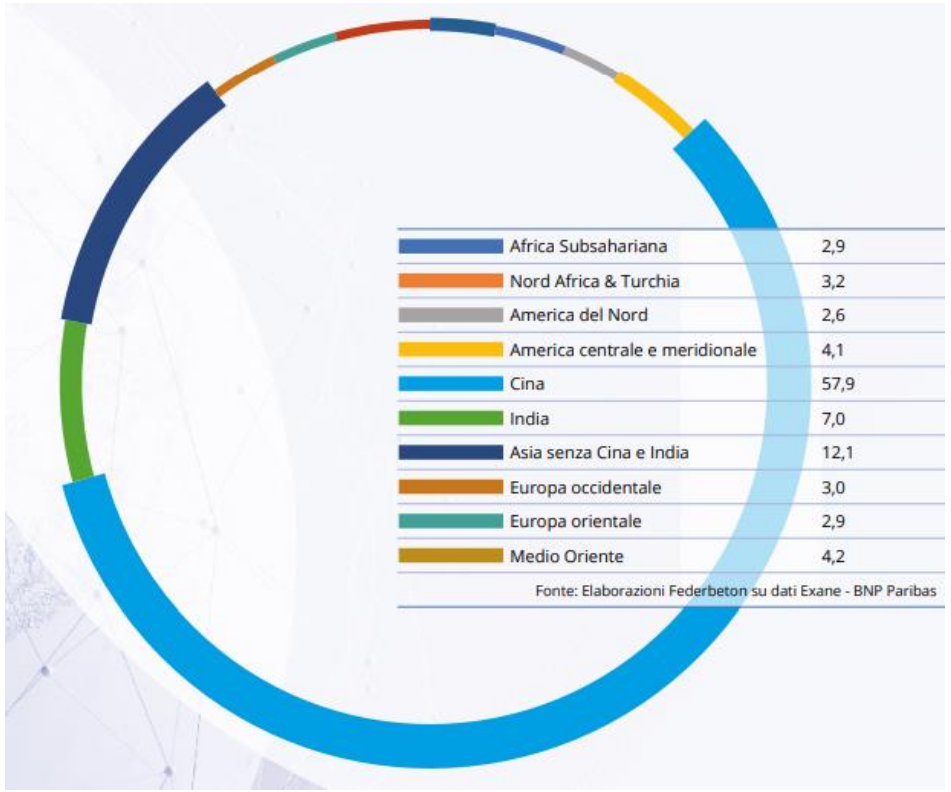


World production

(million of tons)



consumes

Local production=local raw materials?

State of the art in OPC

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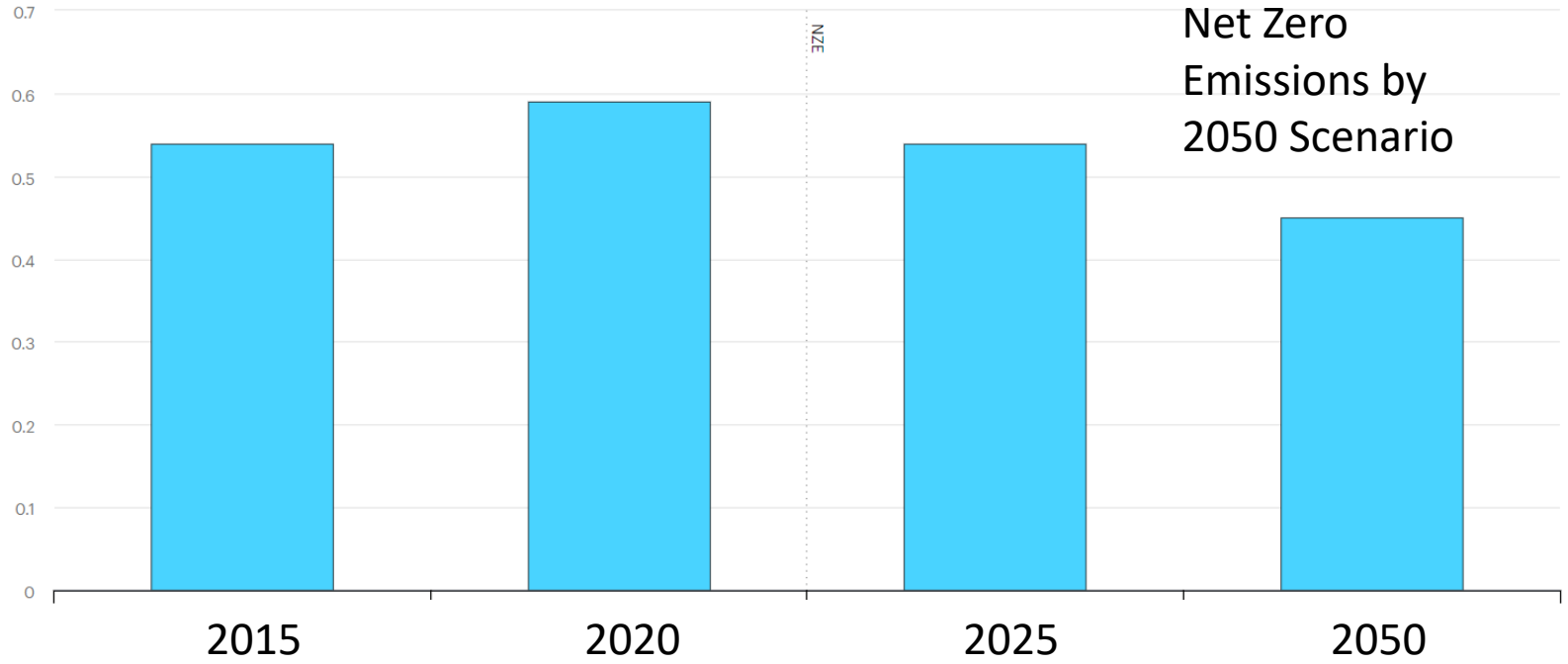
Overall contribution of CO_2 emission from cement industries stands at 7-8% of global anthropogenic CO_2 emissions.

Tons of CO_2 per 1 ton of OPC



https://www.iea.org/reports/cement

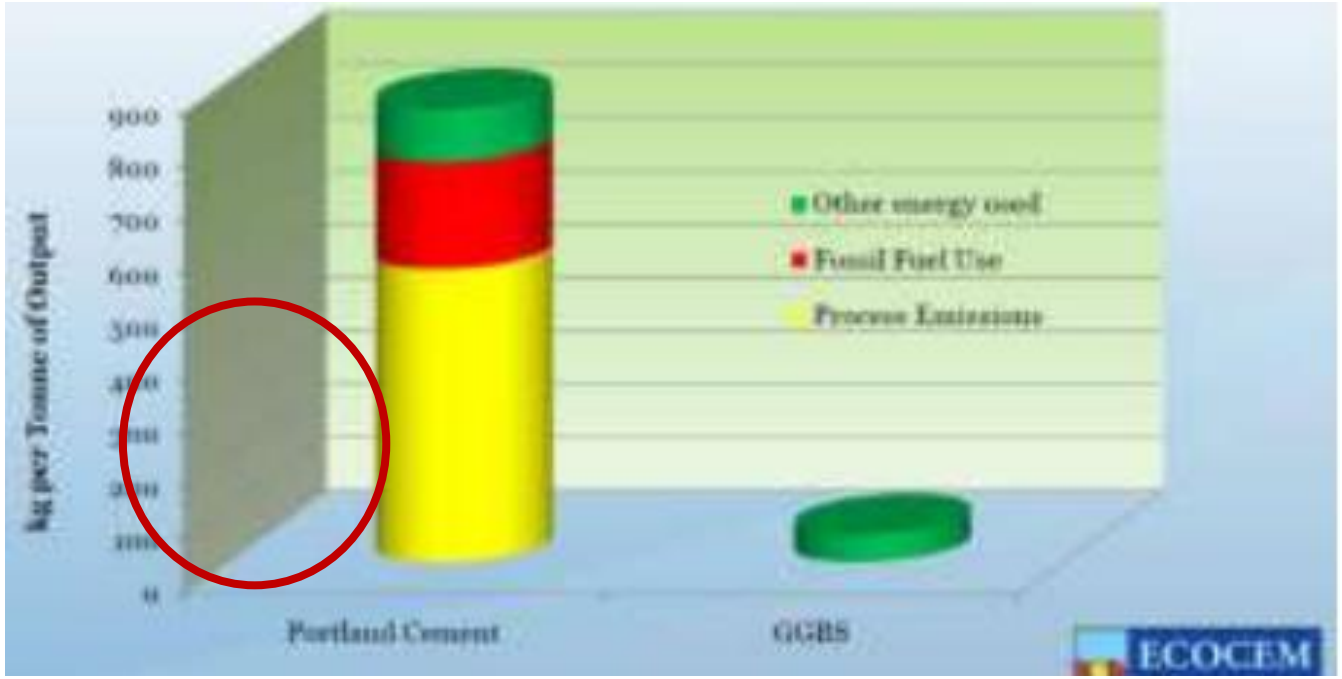
What to do:

- improving energy efficiency
- switching to lower-carbon fuels
- reducing the clinker-to-cement ratio exploiting innovative technologies (including CCS-Carbon Capture and Storage, CCUS-Carbon Capture, Utilization and Storage)

Net Zero is carbon neutrality: balancing of carbon dioxide emissions **put into and taken out of the Earth's atmosphere** to prevent any increases.

CO2 emission from OPC

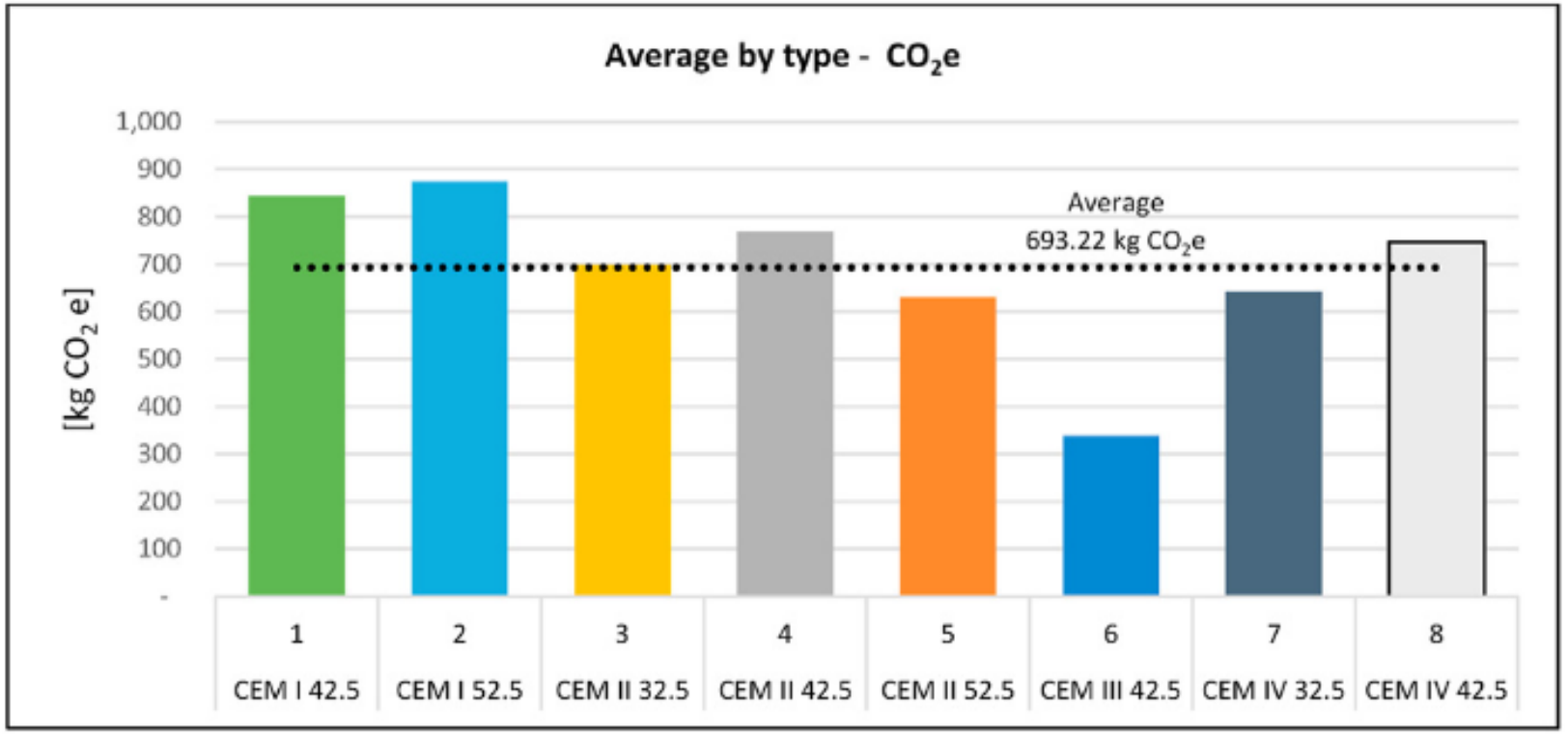
Pradeep U., PurushothamRao S , Markandeya Raio P.
SSRG International Journal of Civil Engineering (SSRG-IJCE) , 3, 12, 2016 ISSN: 2348 – 8352



Two-third of CO2 emissions: from the Portland cement production
One-third: from the combination of combustion of fossil fuels and other energies

The substitution of waste and by-products to clinker is one of possible solutions

Global Warming Potential (GWP) of different mix of cement (kg CO2e)



Clinker content:
CEMI = 95-100
CEM II = 65-94
CEM III= 5-35
CEM IV = 45-89

Cruz Juarez &Finnegan, Cleaner Environmental Systems, 3, 2021

- **CEM I 52.5 MPa is the highest CO_2e emitting mix,**
- **To produce CEM II 42.5 MPa, more CO_2e emissions are released than to produce CEM II 52.5 MPa**

no correlation between strength and the volume of emissions derived from the mix

Possible solution? Geopolymers/AAMs

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Geopolymers are a class of inorganic polymer formed by the reaction between an alkaline solution and an aluminosilicate source.

Empirical formula :

$R_n[-(SiO_2)_z-AlO_2-]_n . wH_2O$

R = Alkali ions (K+, Na+, …),

n = degree of the polycondensation

w = binding water

z=1,2,3 is indicative of the structural network and it is generally ≤ 3 for three-dimensional structural geopolymer materials

Alkali Activated Materials-AAMs

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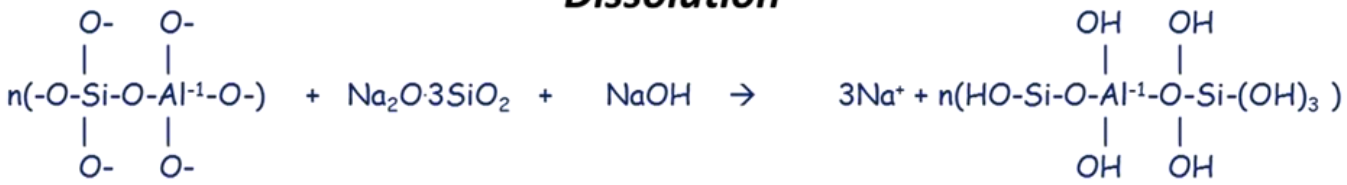
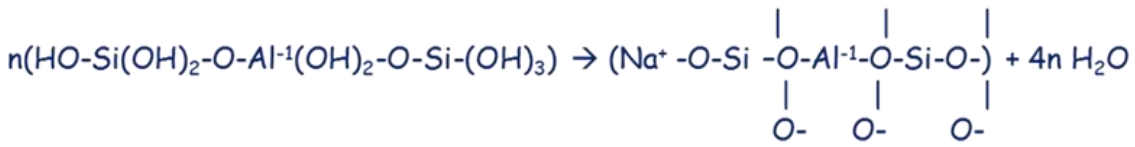
Definition: Inorganic materials **with an amorphous structure**, obtained by the reaction between aluminosilicate materials (such as **metakaolin, fly ash, and blast furnace slag**) with alkaline solutions (generally of sodium or potassium).

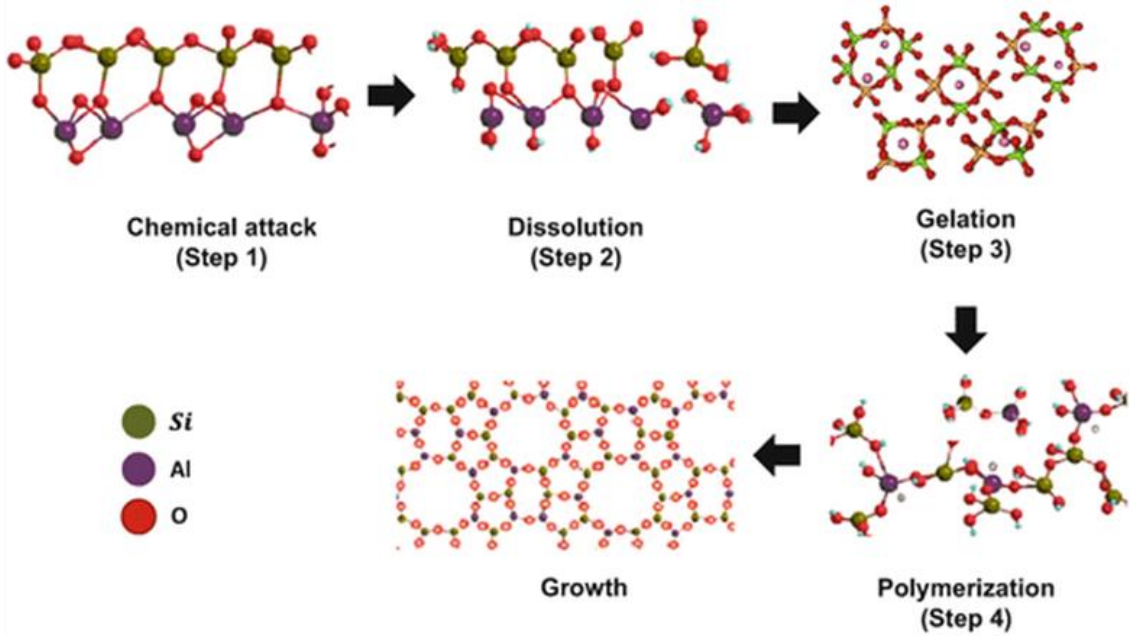
Tetrahedral SiO_4 and AlO_4 are linked alternately by sharing oxygen atom

Dissolution



Condensation and polymerization





Dissolution 1 step

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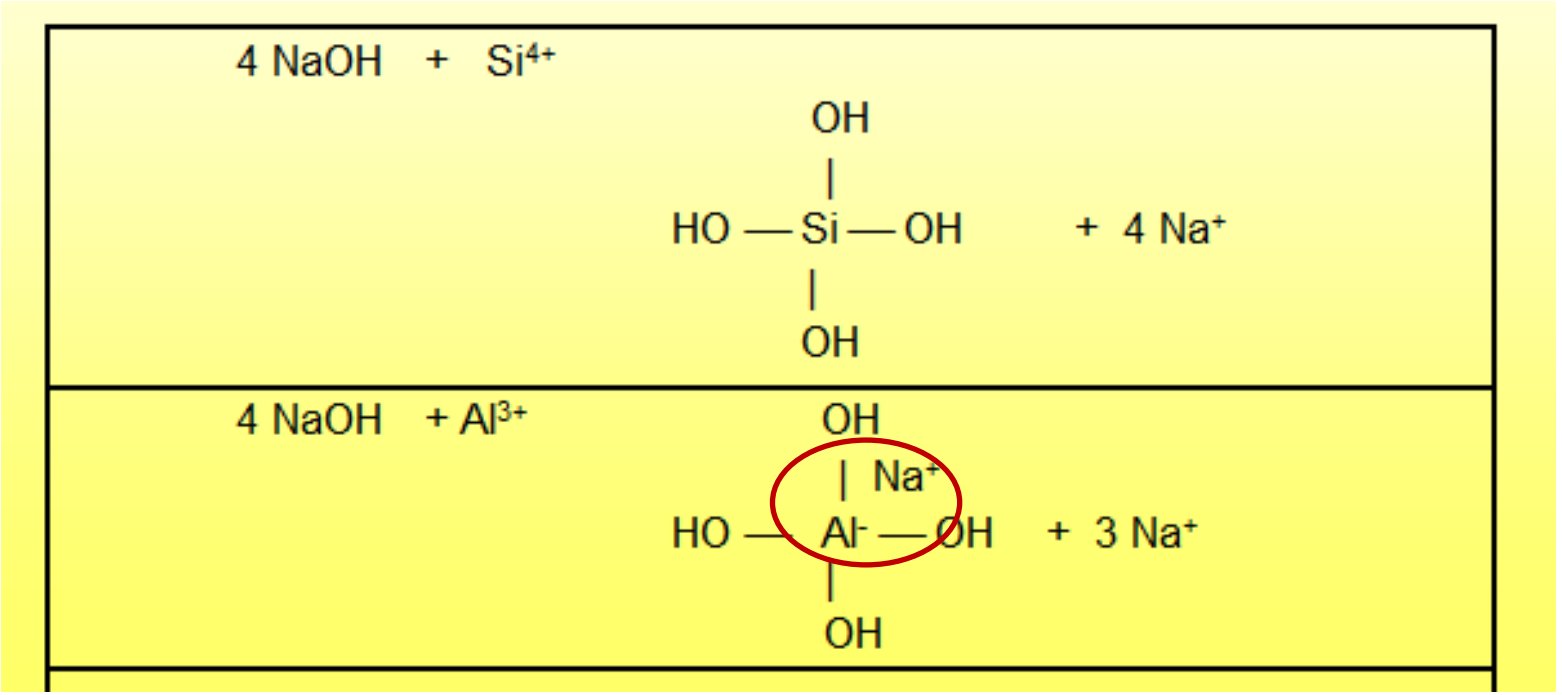
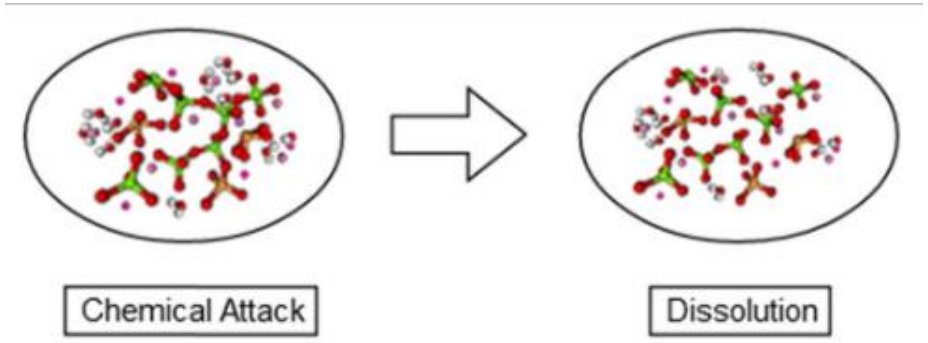


The high amount of OH ions causes the dissolution of the aluminosilicates in the raw material by breaking the bonds that forms these aluminosilicates.

The presence of Al, having an oxidation number of 3+, counterbalance Na+ ions avoiding their release in environment

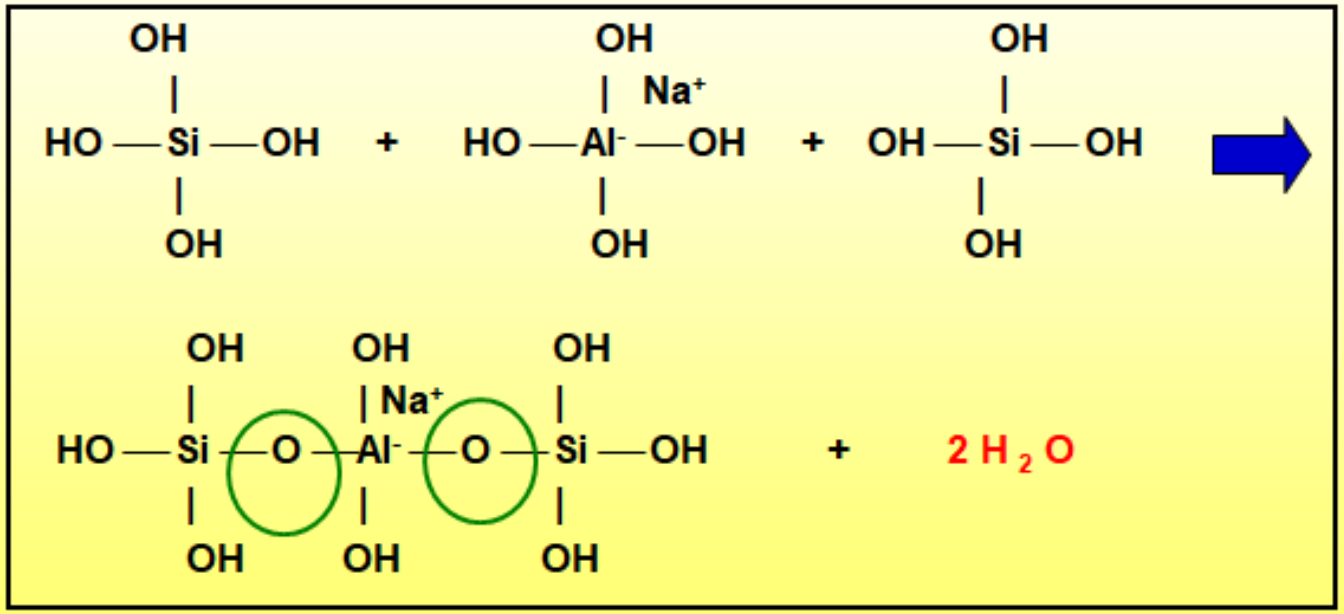


Duxson, Fernández-, iménez, Provis, Lukey, Palomo. van Deventer *Journal of Materials Science* **volume 42**, (2007)

Condensation 2 step

2) - neighbouring silicon or aluminium hydroxide molecules CONDENSE to form an oxygen bond → linking the molecules

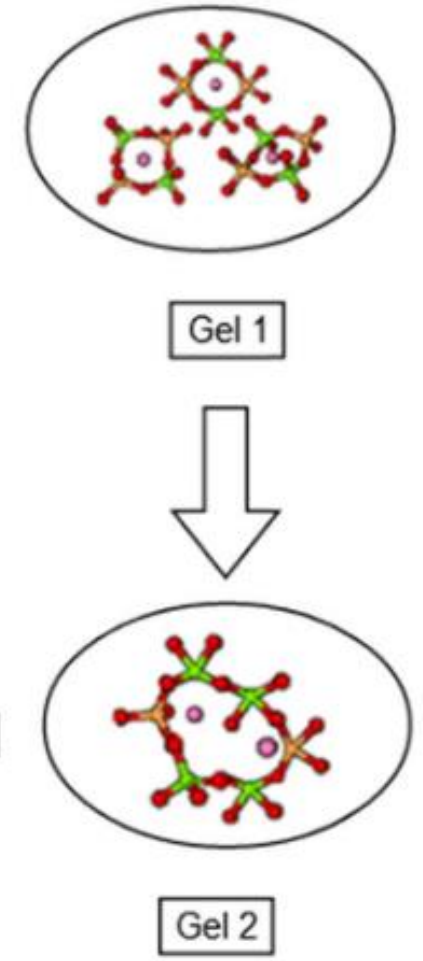
- free molecules of water are formed



(Ref : Hench L L, "Sol-Gel Silica. Properties, Processing and Technology Transfer", Noyes Publications, 1998)

- condensation forms new Si–O–Si bond to generate dimers.
- Dimers interacts with other monomers to create trimers, tetramers etc

These particles grow in many directions, generating colloidal particles, forming a gel.



Duxson, Fernández-, iménez, Provis, Lukey, Palomo. van Deventer
Journal of Materials Science **volume 42**, (2007)

Polymerization 3 step

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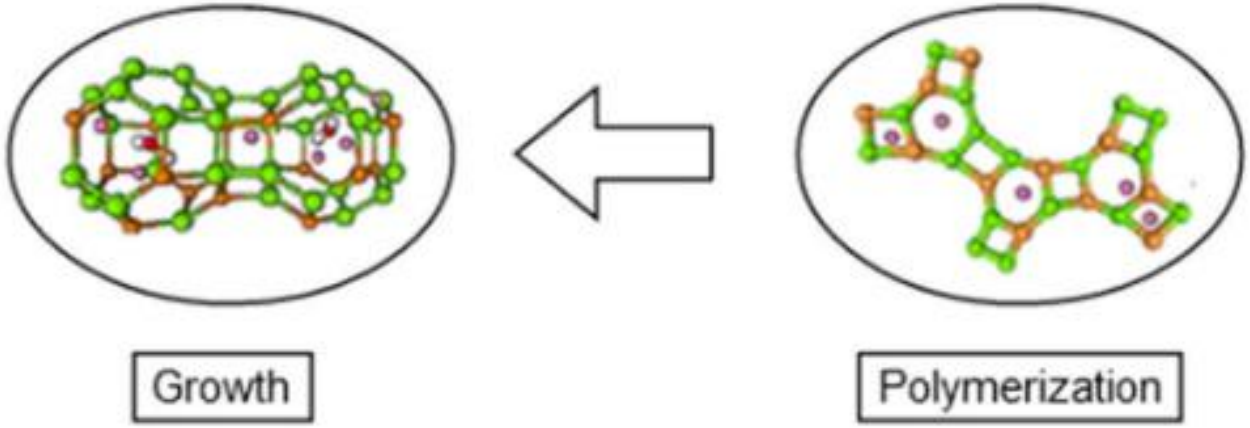
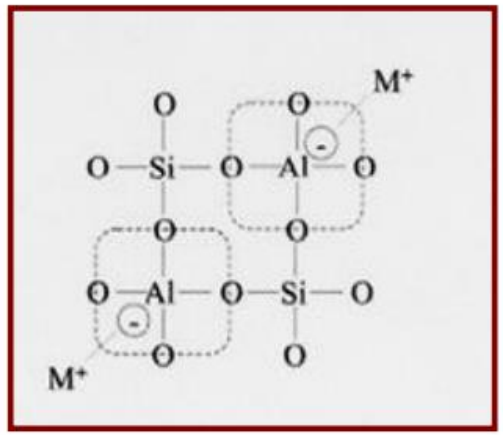


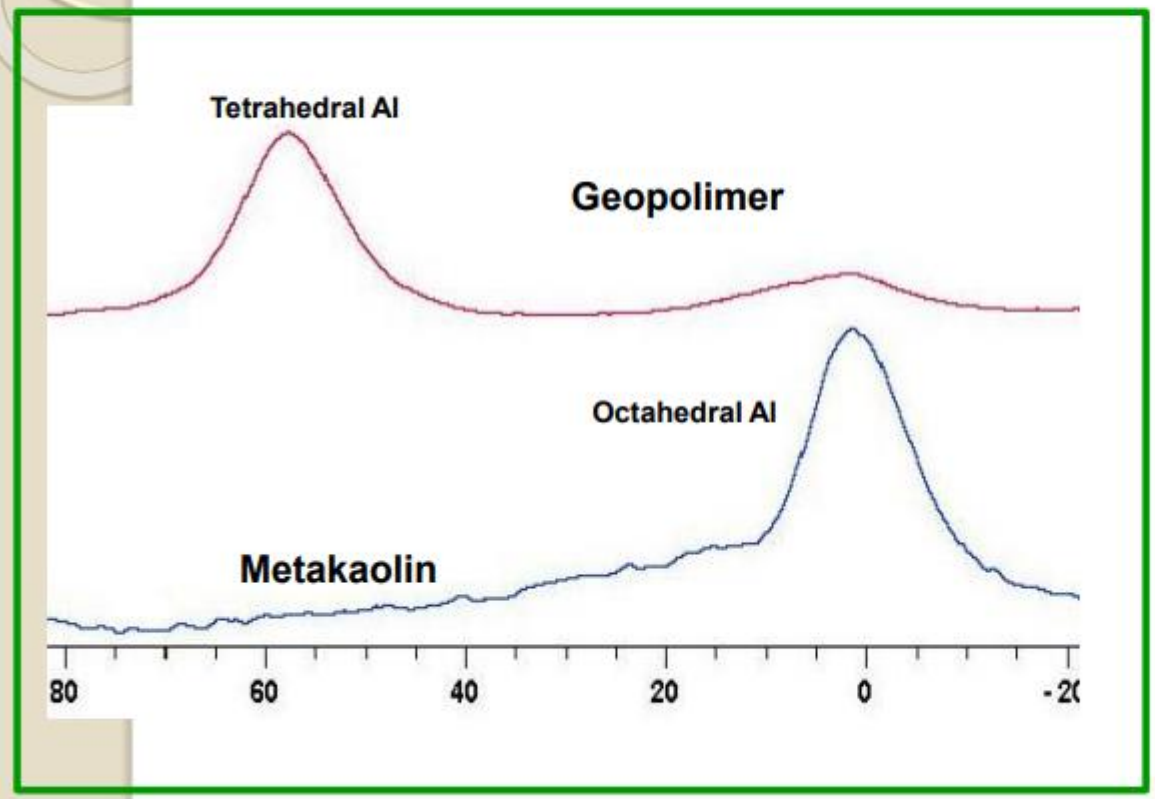
Duxson, Fernández-, iménez, Provis, Lukey, Palomo. van Deventer
Journal of Materials Science **volume 42**, (2007)

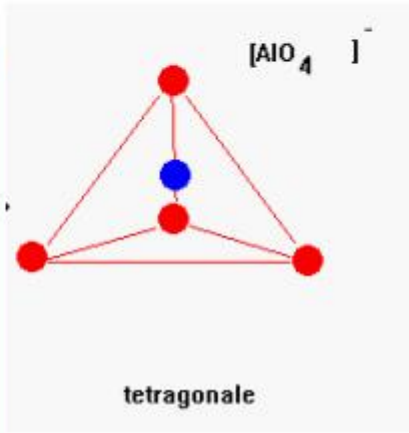
- connectivity of the gel network **increases**
- formation of a **3D network** of aluminosilicates

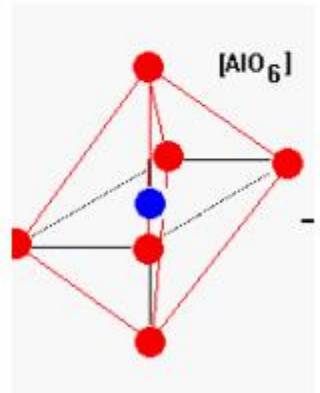
polymerization and hardening determines the microstructure and pore distribution of the final material (physical properties)

^{29}Al MAS NMR


M+
O
Si
Al
M+


Tetrahedral Al
Geopolimer
Octahedral Al
Metakaolin
80
60
40
20
0
-20

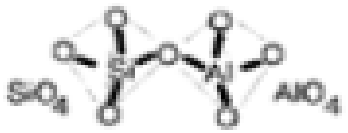

[AlO4]-
tetragonale

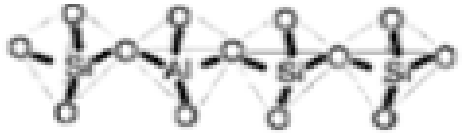

[AlO6]

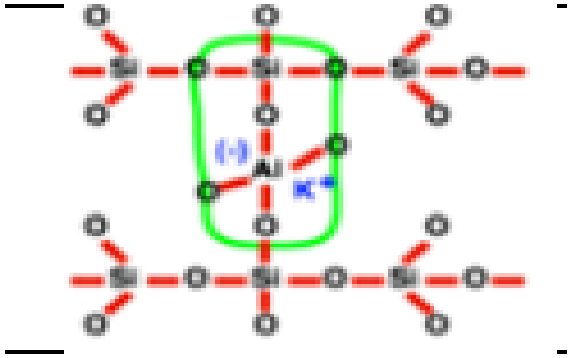
Geopolymers/Alkali activated materials (AAMs)

$Rn[-(SiO_2)_z-AlO_2-]_n \cdot wH_2O$

Si-O-Si-O- siloxo, poly(siloxo) Si:Al = 0,
-Si-O-Al-O- sialate, poly(sialate) Si:Al = 1, sialate (acronym for silicon-oxo-aluminate of Na, K, Ca, Li)
-Si-O-Al-O-Si-O- sialate-siloxo, poly(sialate-siloxo) Si:Al = 2, sialate-siloxo
-Si-O-Al-O-Si-O-Si-O- sialate-disiloxo, poly(sialate-disiloxo) Si:Al = 3, sialate-disiloxo
Si:Al > 3, sialate link







Poly(sialate) -Si-O-Al-O-	Poly(sialate-siloxo) -Si-O-Al-O-SI-O-	Poly(sialate-disiloxo) -Si-O-Al-O-Si-O-Si-O-	Sialate link
Z= Si:Al = 1	Si:Al = 2	Si:Al = 3	Si:Al > 3

Important ratios

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- Si/Al ratio influences the physical properties

•Si/Al ratio < 3:1, the resultant 3D networks are rigid, suitable as a concrete, cement or waste encapsulating medium.

Si/Al ratio > 3, the resultant geopolymer becomes less rigid and more flexible or "polymer-like".

Si/Al ratios up to 35:1, the resultant cross linked 2D chains are more suitable as adhesive or sealant, (Davidovits 1999).

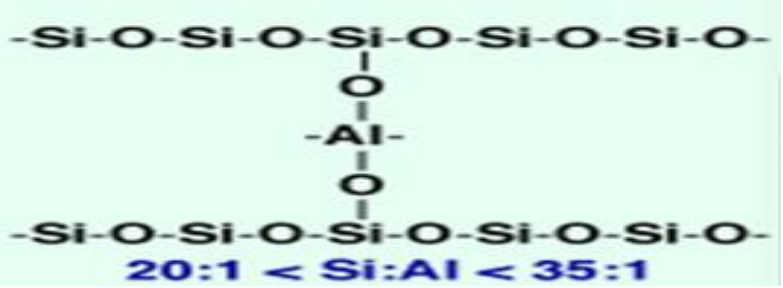
- **Na/Al ratio**

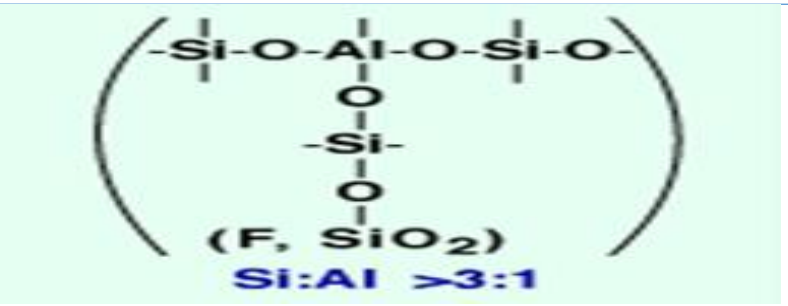
Na+ ion contributes to the polymerization, OH- ion contributes towards the dissolution step of Si4+ and Al3+

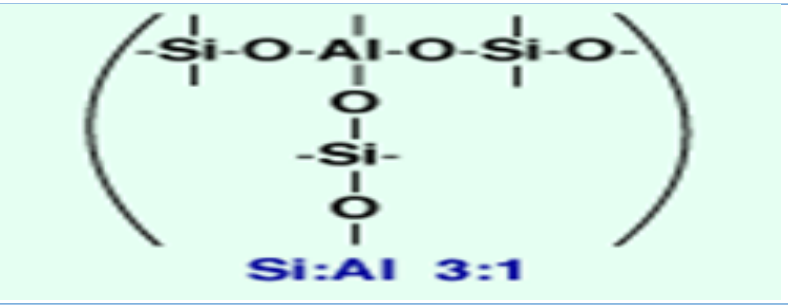
low sodium content, there would be both insufficient OH- to completely dissolve Si4+ and Al3+ from the metakaolin, and insufficient Na+ to allow for complete polymerization of the network.

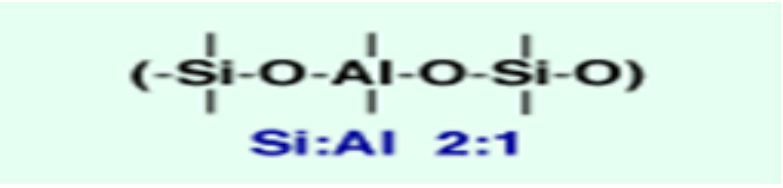
high sodium content, there would be excess OH-, allowing for a complete dissolution of Si4+ and Al3+ from the metakaolin, but excess sodium would be left in the sample, weakening the structure (Murayama et al. (2002))

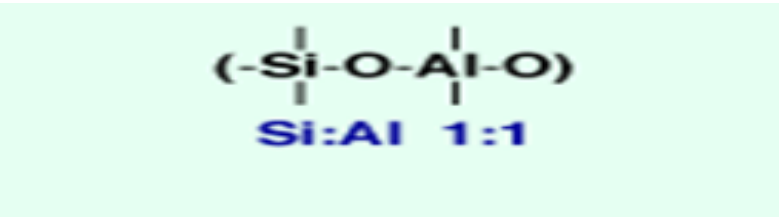
Proper Na/Al ratio for waste encapsulating medium = 1

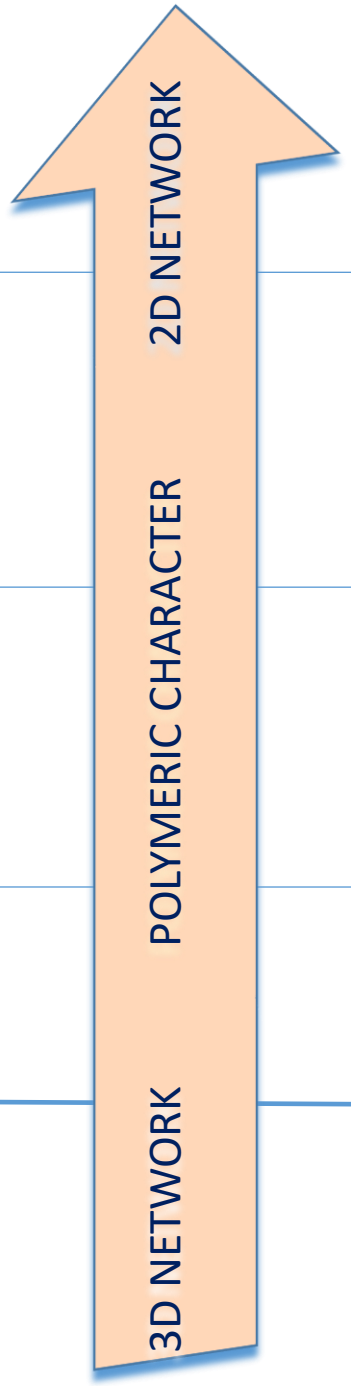












Heat resistant fiber composites

Sealants for Industry up to 1000°C
Toolings for SPF aluminum

Foundry Equipments
Toolings Titanium Proc.

Ceramic and structural materials
Cements and wastes inertization

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AAMs applications

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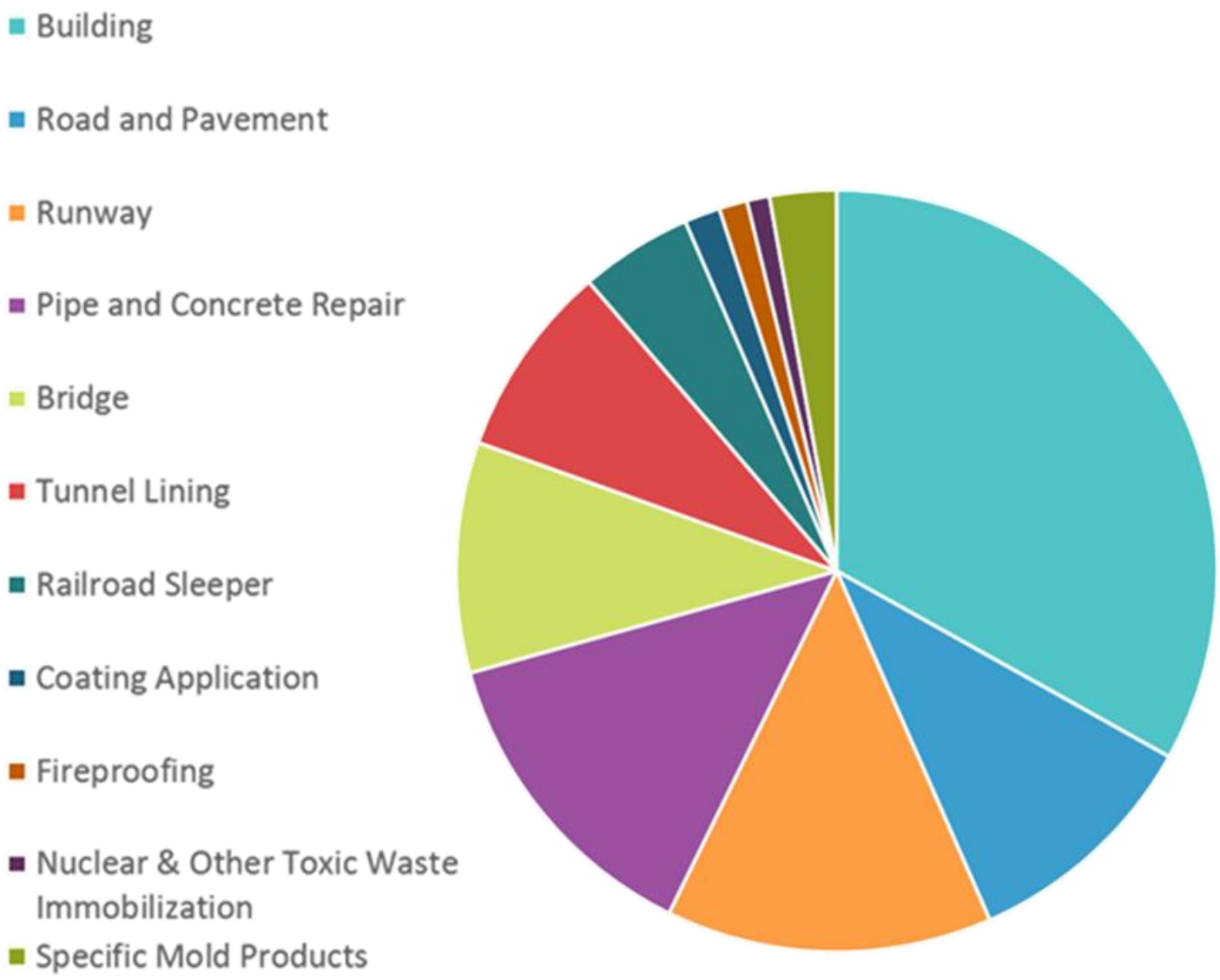

The University of Queensland's Global Change Institute (GCI) is the world's first building to successfully use geopolymer concrete

Airport of Toowoomba Wellcamp

Comparison geopolymer-cement

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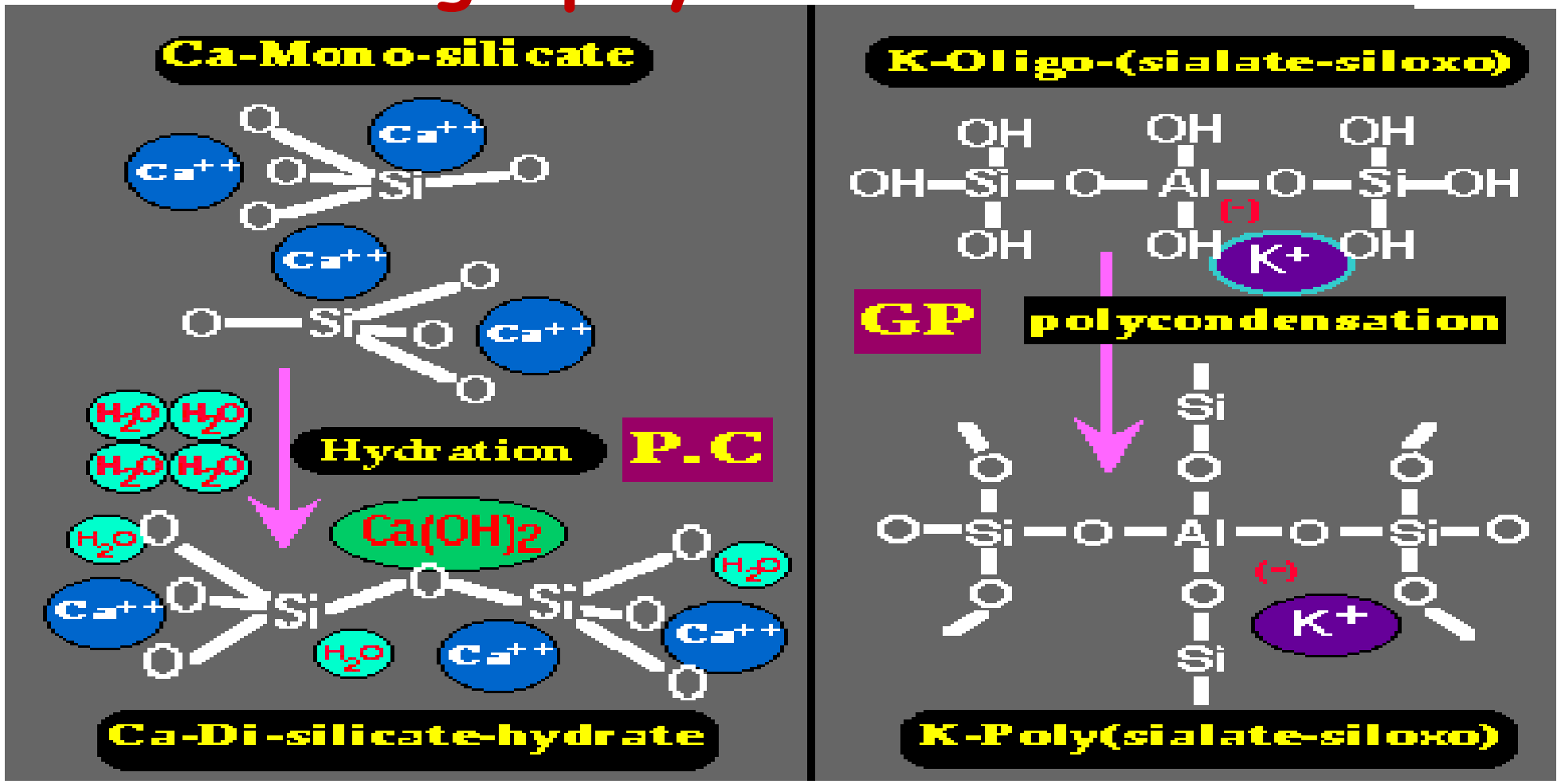


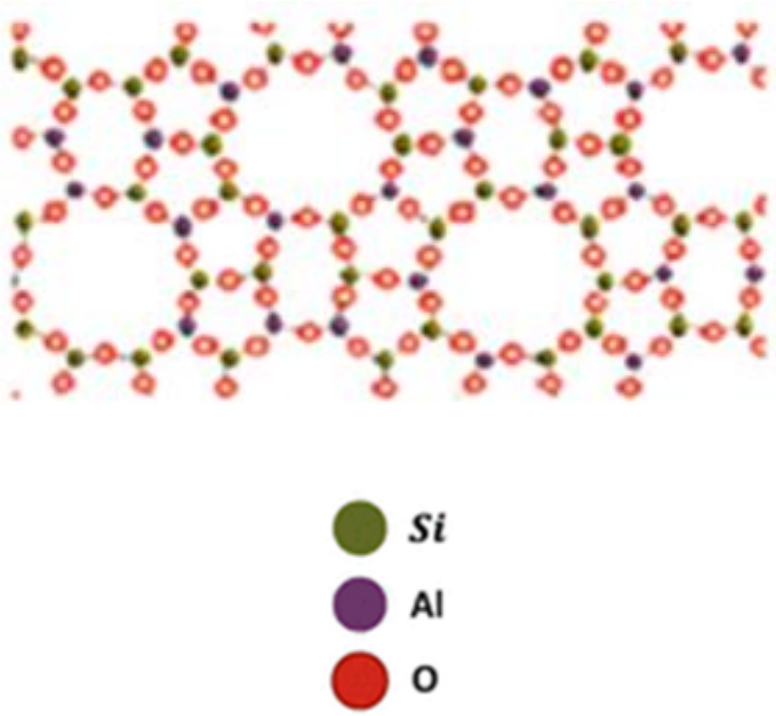
Differently from Portland cement, geopolymers do not contains hydratate phases in high amount which subjected to heat might produce undesired explosions.

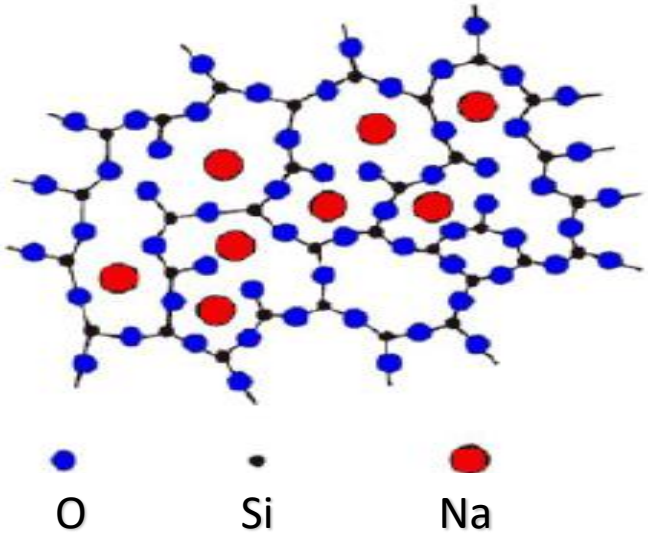
Comparison geopolymer-glass

After consolidation geopolymers presents a 3D structure similar to aluminosilicate glasses

BUT

They are produced at room T





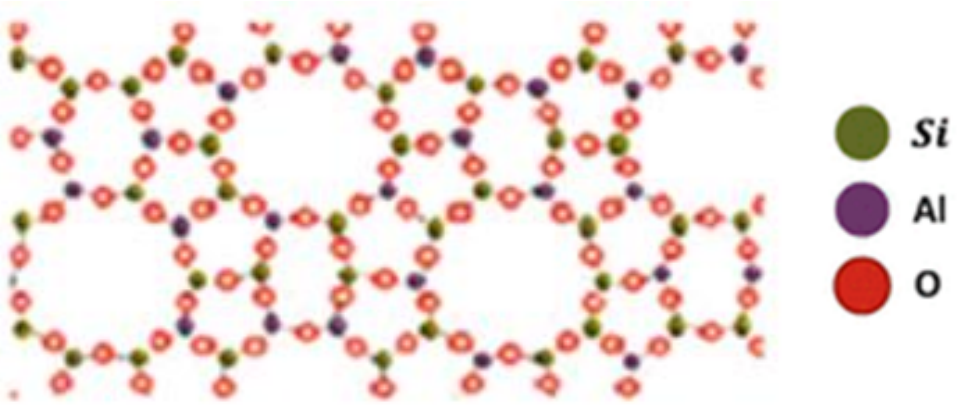
Comparison geopolymer-zeolite

Geopolymers are similar to zeolite, but being the reaction fast the structure is amorphous/semicrystalline, while zeolites are highly crystalline

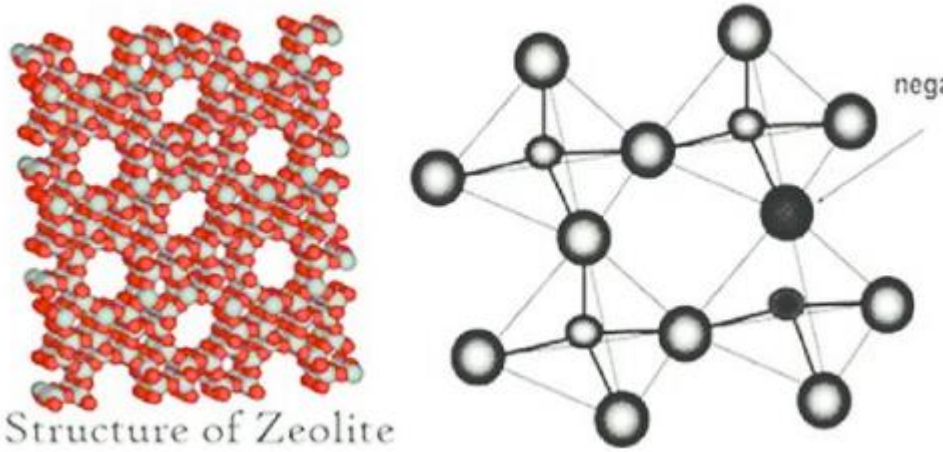
$$(Na, K, Ca_{0,5})_x\,[AlxSi_n\text{-}xO_{2n}]\cdot mH_2O$$

Rn[-(SiO2)z-AlO2-]n. wH2O geopolymer

Geopolymer



Zeolite



Golomeova & Zendelska, 2016, In book: Microporous and Mesoporous Materials

Geopolymers Reactants

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1. alkali metal hydroxide/silicate (chemical activator)

Activators: sodium and potassium hydroxide and silicate, carbonate, alluminate, sulphate

any **waste source of concentrated alkali (Olive oil biomass ash,etc)**.

To avoid the risks associated with handling alkaline solutions, the one-part geopolymer approach ("just add water") can be used to favor the practical application

2. aluminosilicate fine PRECURSOR

The precursor needs to have a significant proportion of the silicon and aluminium ions (SiO_2 + Al_2O_3 > 80%wt), held in amorphous phases.

Precursors include:
Metakaolin
Class F coal fly ash,
Granulated slags
... **any fine amorphous aluminosilicate material can be used ALSO wastes**

From industrial point of view…

Geopolymerization needs chemical ingredients that may be dangerous and therefore requires some safety procedures.

Material Safety rules classify the alkaline products in two categories:

- **corrosive** products
- **irritant** products

hostile	friendly
CaO (quick lime) NaOH, KOH	$Ca(OH)_2$ Portland cement, Iron slag
Sodium metasilicate $SiO_2:Na_2O = 1.0$	Slurry soluble silicate/kaolin $1.25<SiO_2:Na_2O<1.45$
Any soluble silicate $SiO_2:Na_2O<1.45$	Any soluble silicate $SiO_2:Na_2O >1.45$

The corrosive products must be handled with gloves, glasses and masks. They are User-hostile and cannot be implemented in mass applications without the appropriate safety procedures.

In User friendly: Portland cement or hydrated lime, typical mass products. Geopolymeric mixes belonging to this class may also be termed as User-friendly.

Typical solutions for geopolymers = $SiO_2/Na_2O = 3$

Summarizing preparation procedures

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Also wastes and end of wastes

Aluminosilicate source ($SiO_2 - Al_2O_3$):

- Fly Ash and/or
- Metakaolin and/or
- Mine Tailing

Low CO_2 emission

Alkaline activador solution:

- Hidroxides (e.g., NaOH) and /or
- Silicates (SiO_2) + Water

Mixed

Curing stage (25-90°C)

Low temperature technology, no thermal cycle

$Na\text{-}Al\text{-}Si\text{-}H_2O$ Gel

Hardening

Geopolymer

Three pillars of sustainability

Geopolymers preparation

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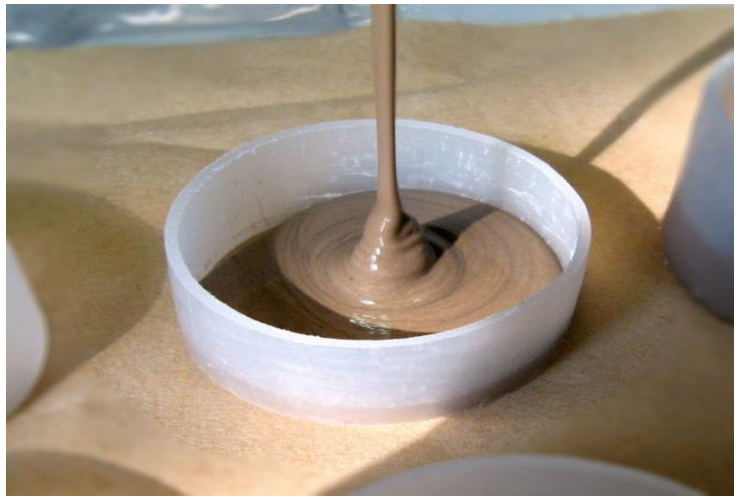
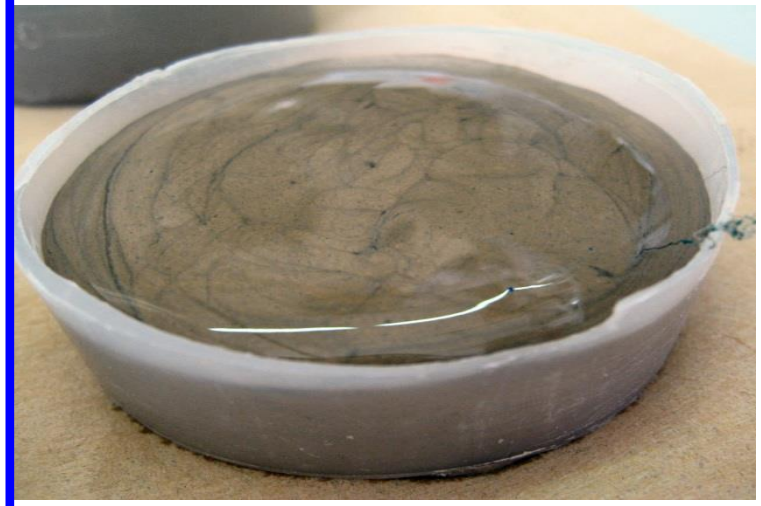
Mixing

Casting

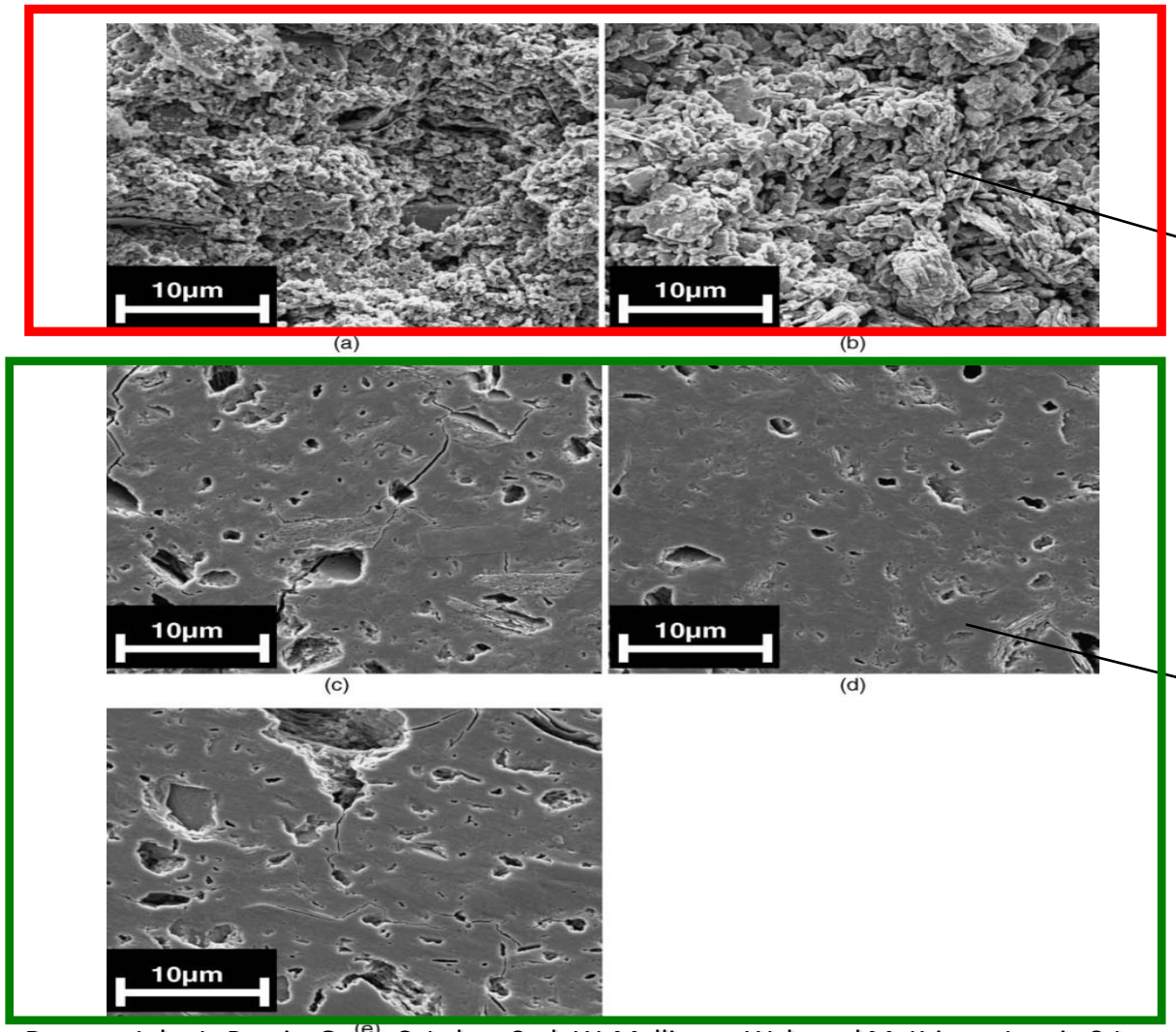


setting and curing



AAMs properties: Microstructure vs Si/Al ratio

SEM micrographs of Na-geopolymers



Large interconnected pores

Not completely reacted structure

Si/Al ratio of (a) 1.15, (b) 1.40

homogeneous structure with isolates pores

Si/Al ratio of (c) 1.65, (d) 1.90 and (e) 2.15.

Peter Duxson, John L. Provis, Grant C. Lukey, Seth W. Mallicoat, Waltraud M. Kriven, Jannie S.J. van Deventer, Understanding the relationship between geopolymer composition, microstructure and mechanical properties *Colloids and Surfaces A: Physicochemical and Engineering Aspects, Volume 269, Issues 1-3, 1 November 2005, Pages 47-58*

Mechanical properties vs Si/Al ratio

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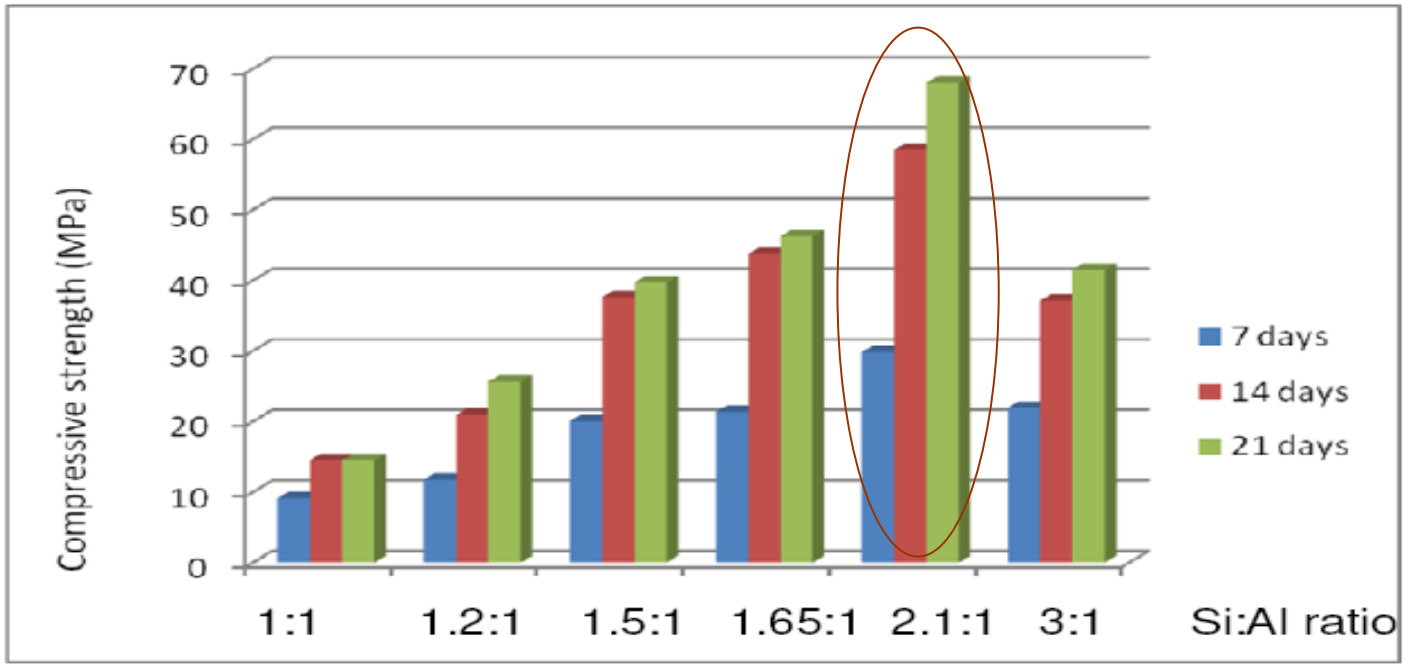

Compressive test Norm:
ASTM C-62
Used for ceramics

AAMs properties

IOP Conf. Series: Matls Sci. Engineering 613 (2019) 012048

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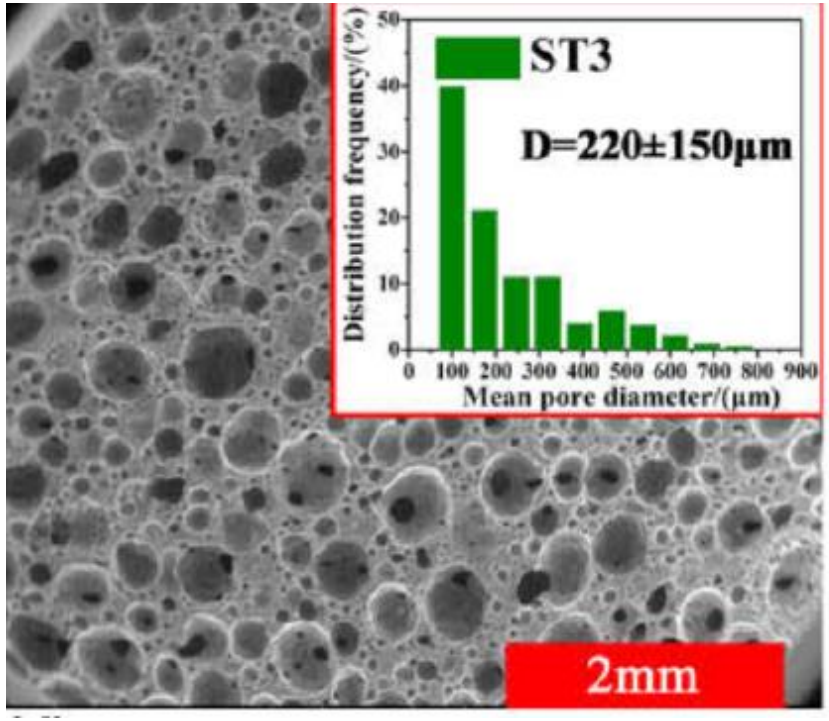
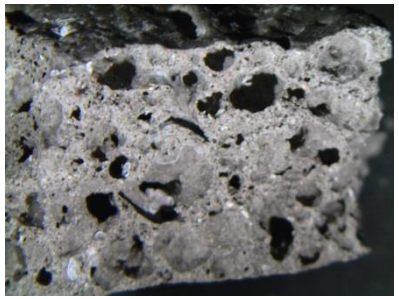
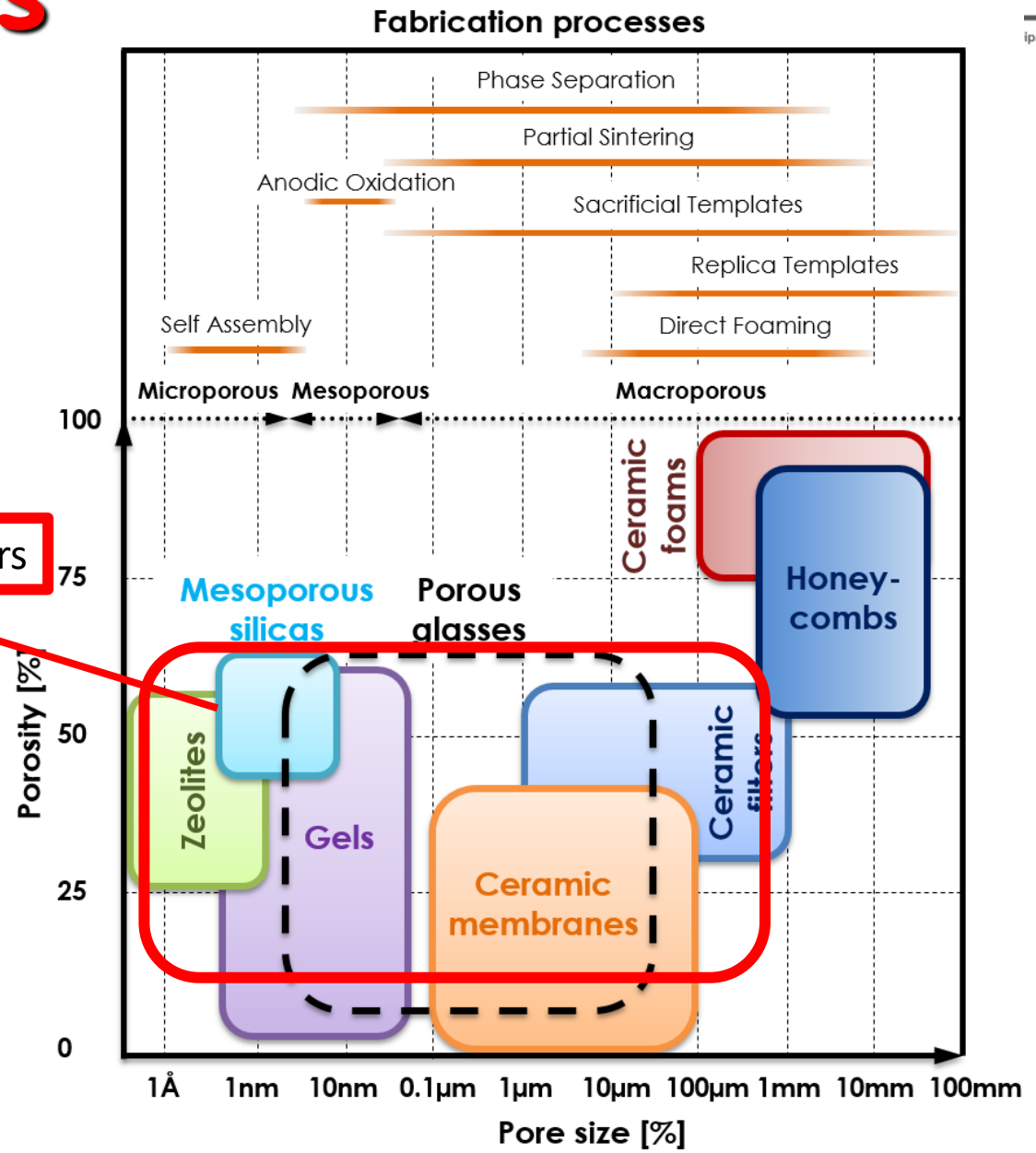
Natural hierarchical porosity



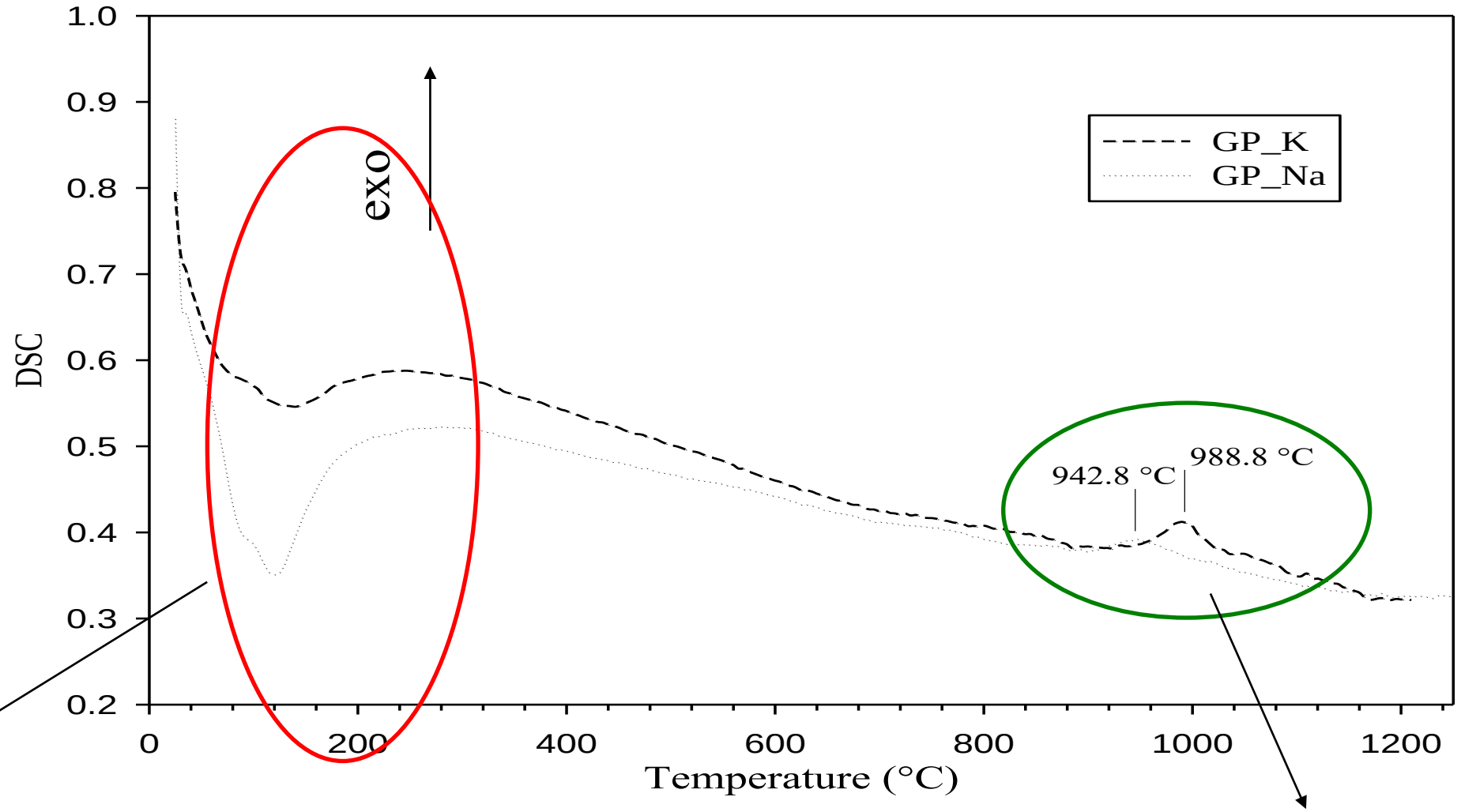
J. Mater. Res., Vol. 32, No. 17, Sep 14, 2017



geopolymers



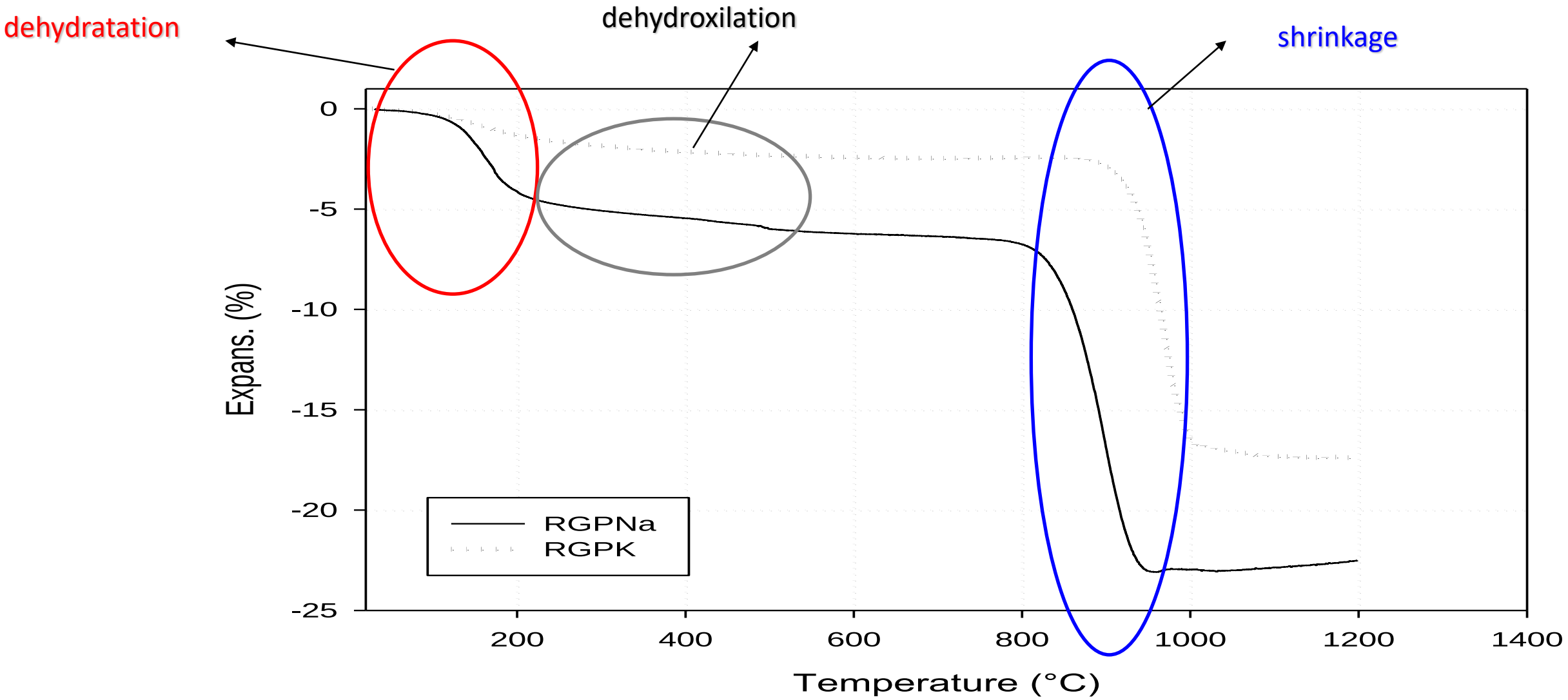
Thermal properties (DTA)



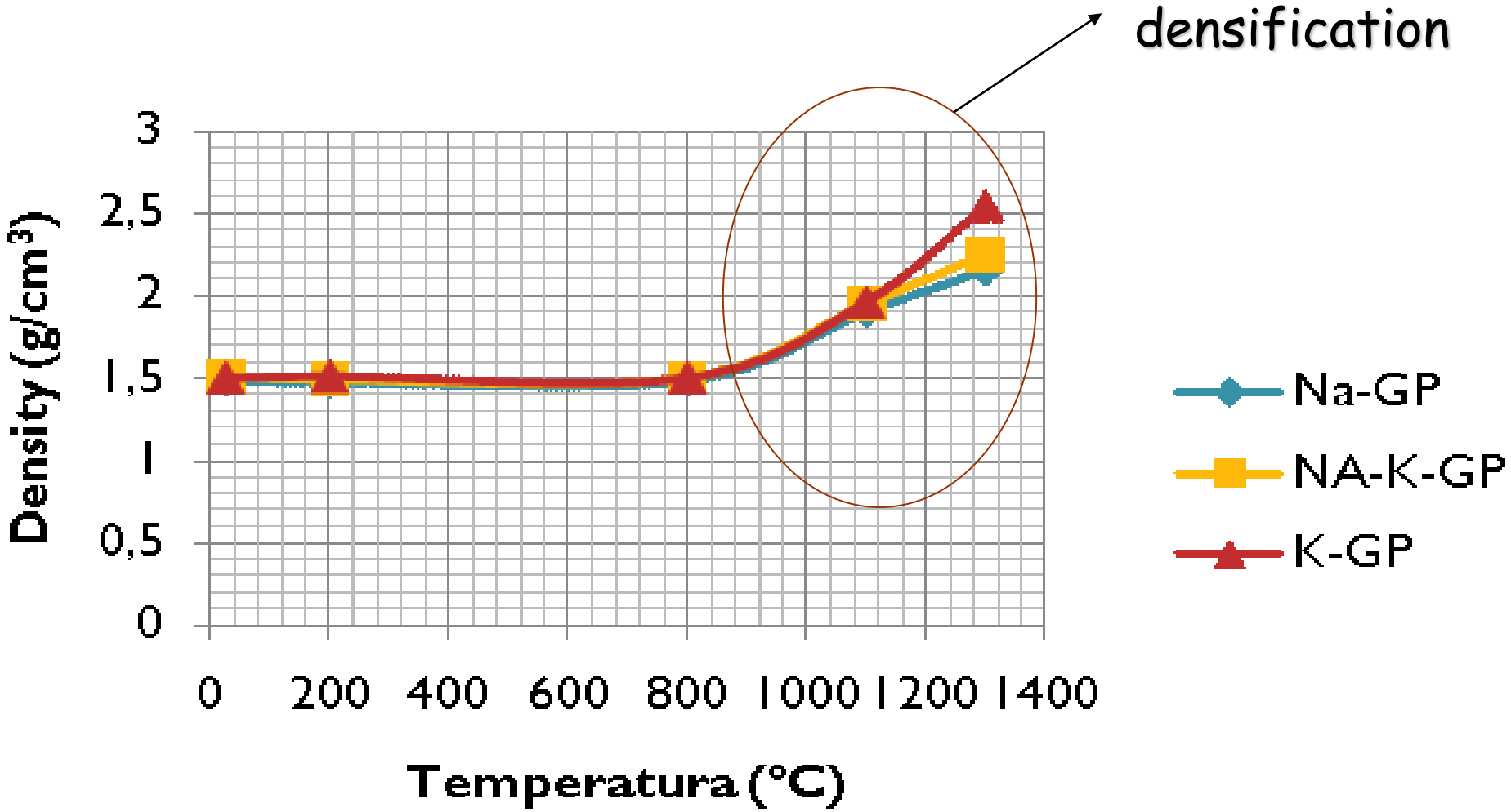
Dehydratation and dehydroxilation

Structural reorganization

Thermal properties (dilatometry)



Thermal properties



Fire resistance

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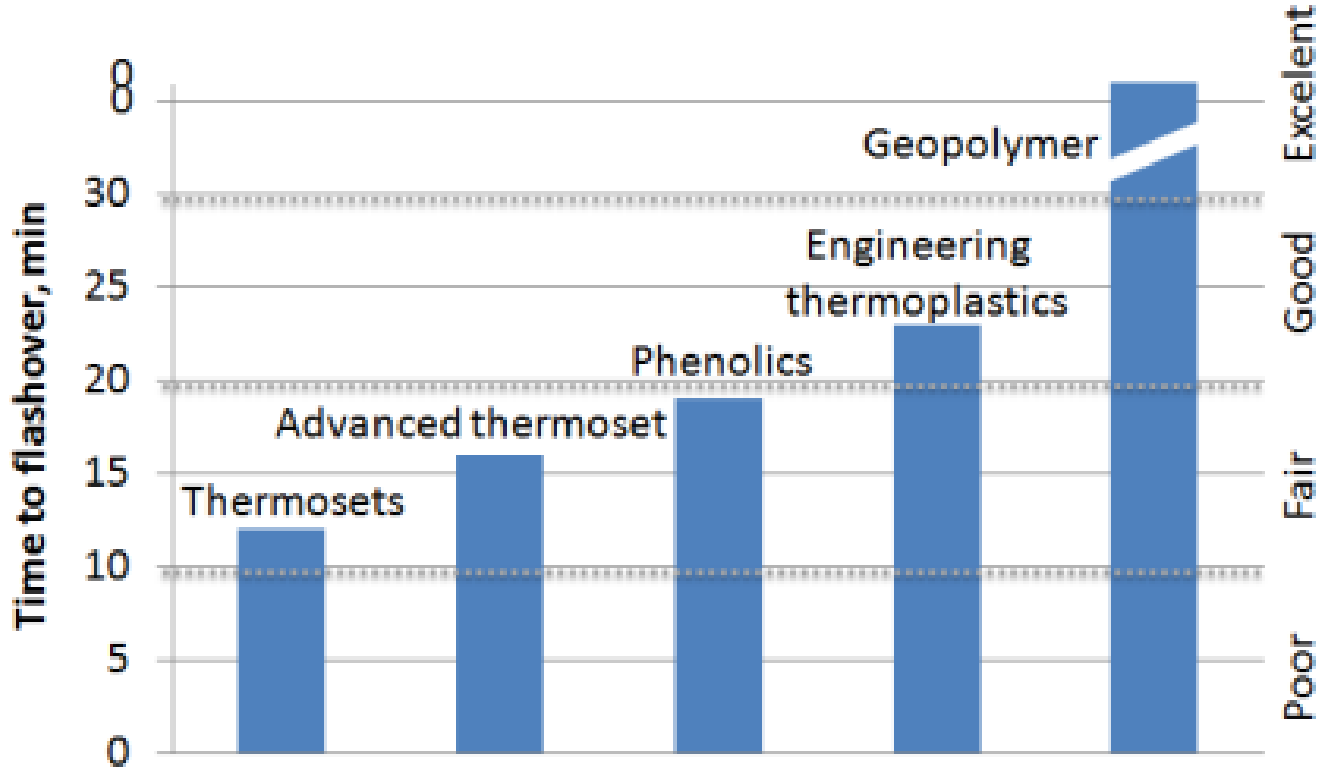

Time to flashover (minutes) for various organic resins compared to geopolymer resin

D D Burduhos Nergis et al 2018 IOP Conf. Ser.: Mater. Sci. Eng. 374 012019

AAMs properties (mineralogy)

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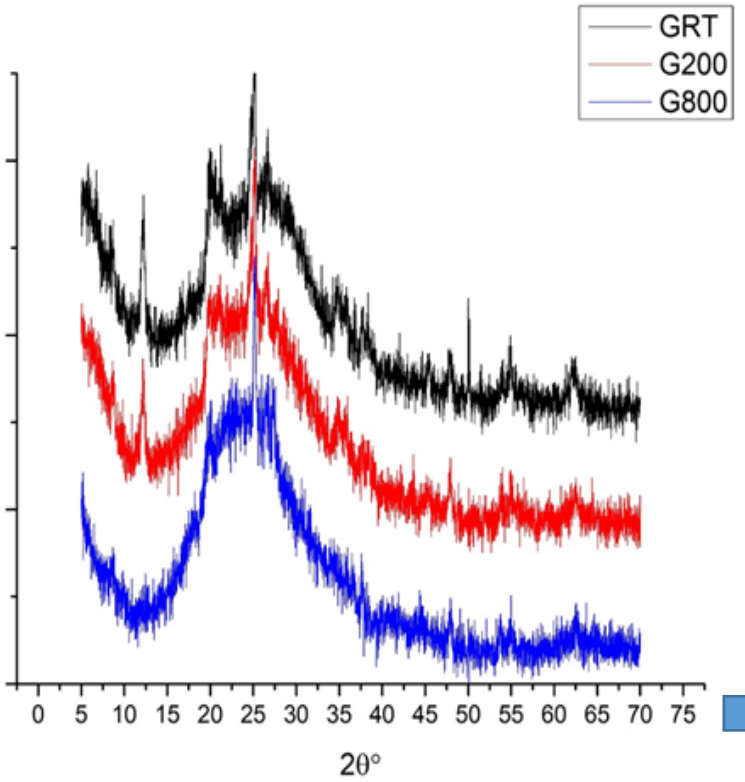
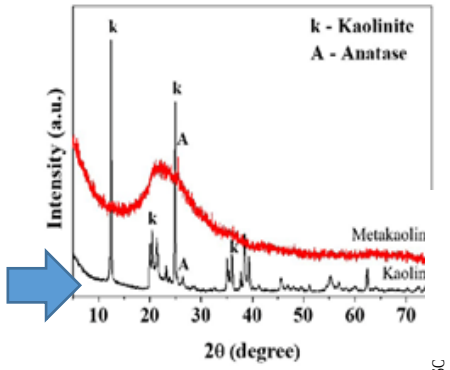
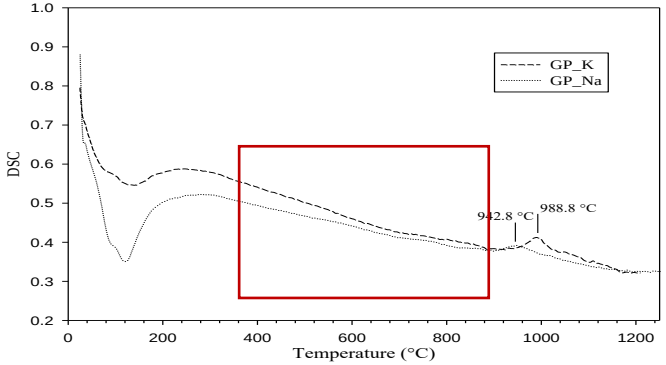
Amorphous XRD characteristic of metakaolin

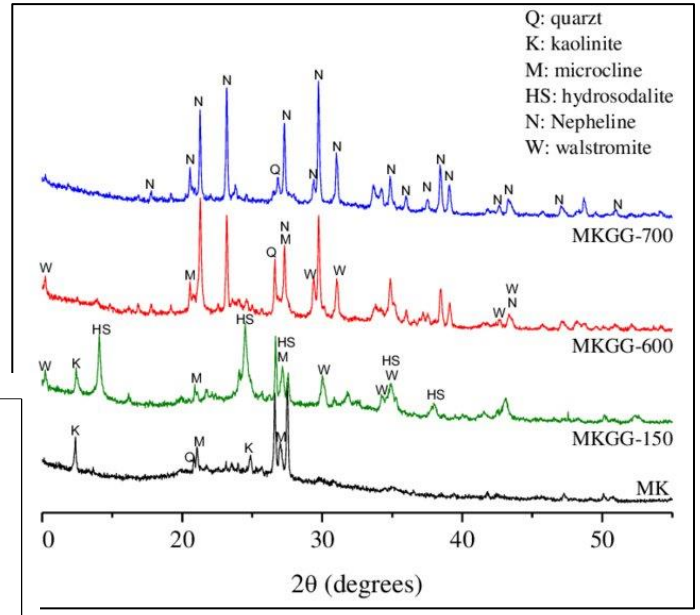


With the increment of temperature the XRD patterns remained predominately amorphous, indicating the non-crystallization of matrix.





Starting from partially crystalline precursors:



Determination of reactive fraction and reformulation

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Basic attack : 5hs in NaOH 8M at 80°C.

Si and Al analyzed by ICP to determine Si/Al reactive

•Ruiz-Santaquiteria, C., Fernández-Jiménez, A., Palomo, A., 2011. Quantitative determination of reactive SiO2 and Al2O3 in aluminosilicate materials. In:Proceedings of XIII International Congress on the Chemistry of Cement, Madrid,Spain.

Sample	Bottom ash (BA)	Metakaolin (MK)	NaOH 8M	Na-Silicate	H_2O	Si/Al	Na/Al	Si/Al_R	Na/Al_R
50_50MK_BAR	25 g	25 g	8 ml	20 ml	-	2.5	1.09	2.03	1.11
40_60MK_BAR	30 g	20 g	5 ml	18 ml	1 ml	2.63	1.10	2.14	1.13
30_70MK_BAR	35 g	15 g	5 ml	12 ml	3 ml	3.26	1.09	2.06	1.24

Obtained taking into account the reactive fraction of precursor

Reactive fraction of aluminosilicate precursor

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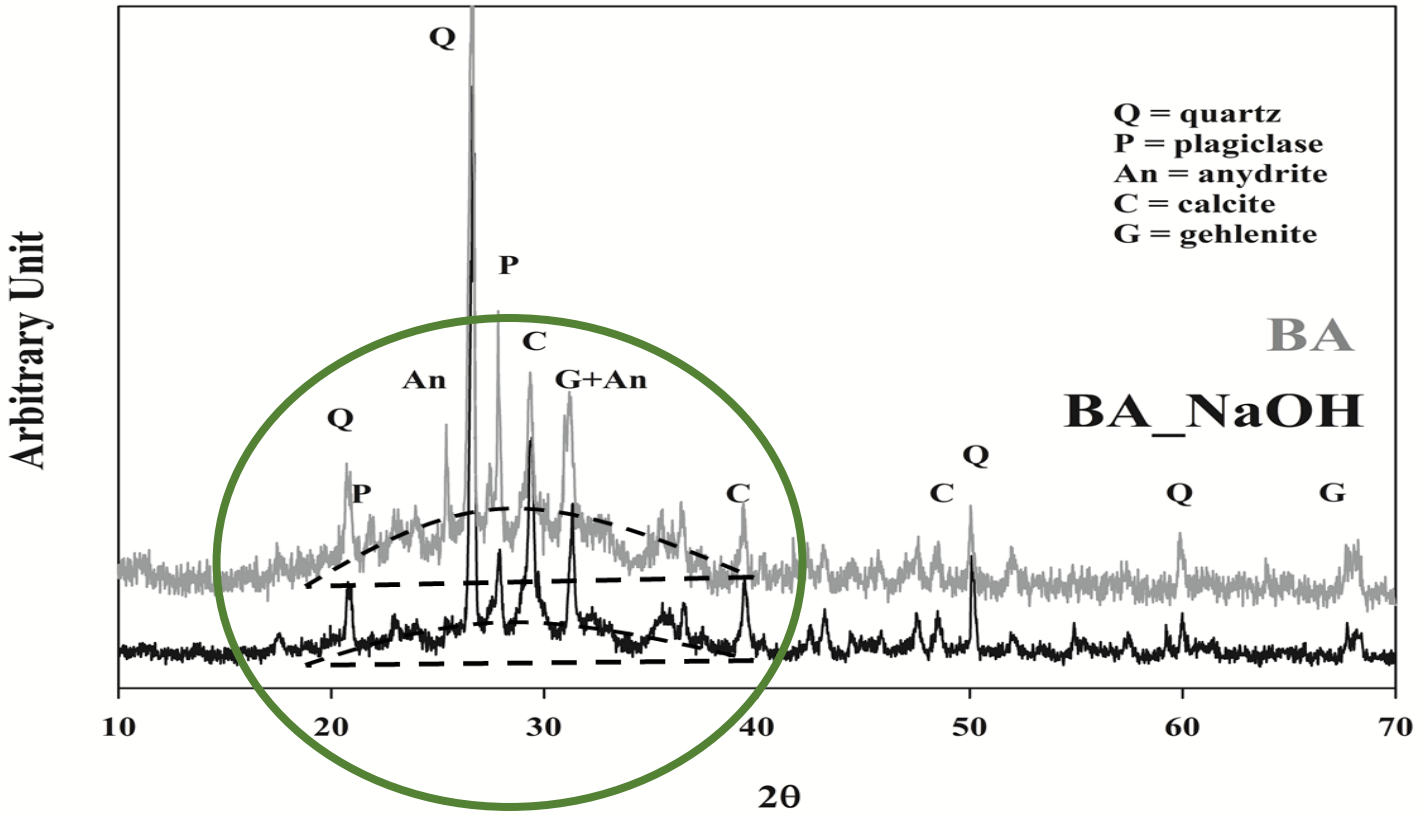


Bottom ash before and after treatment in NaOH 8M

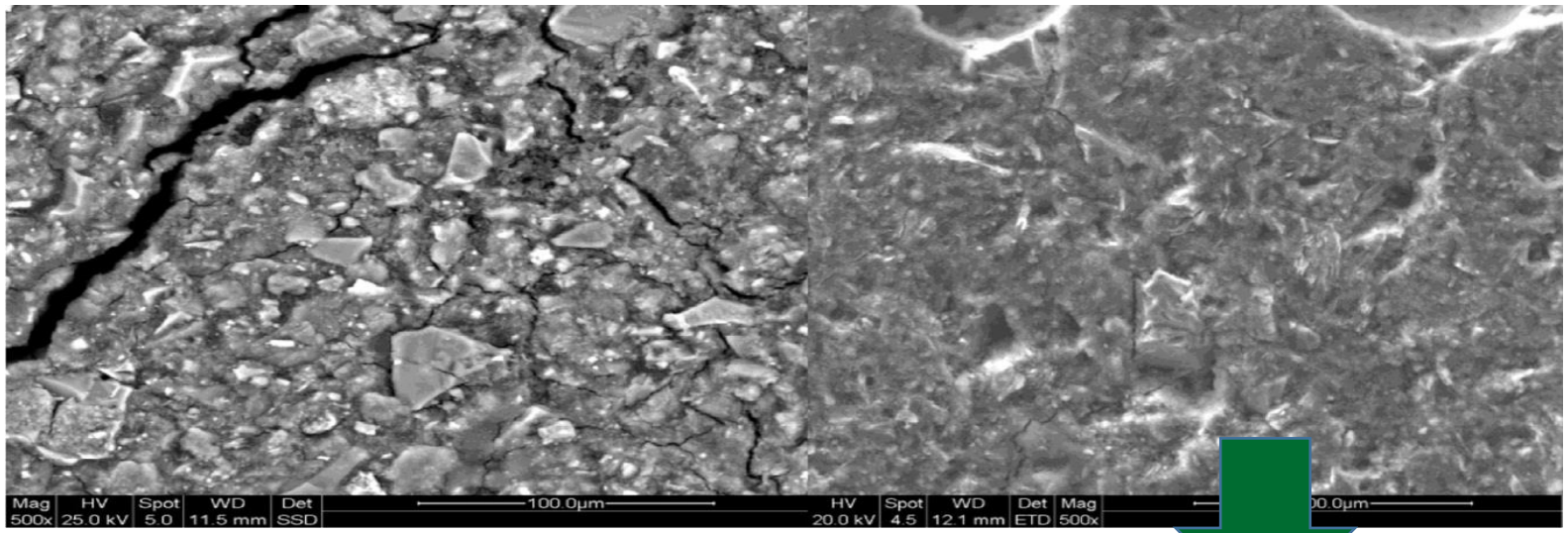
Amorphous fraction decreases

reacts

Microstructural modification

50-50 MK_BA

50-50 MK_BA after reformulation.



Samples cured for 15 days

Sample after reformulation is more homogeneous and dense

Concluding

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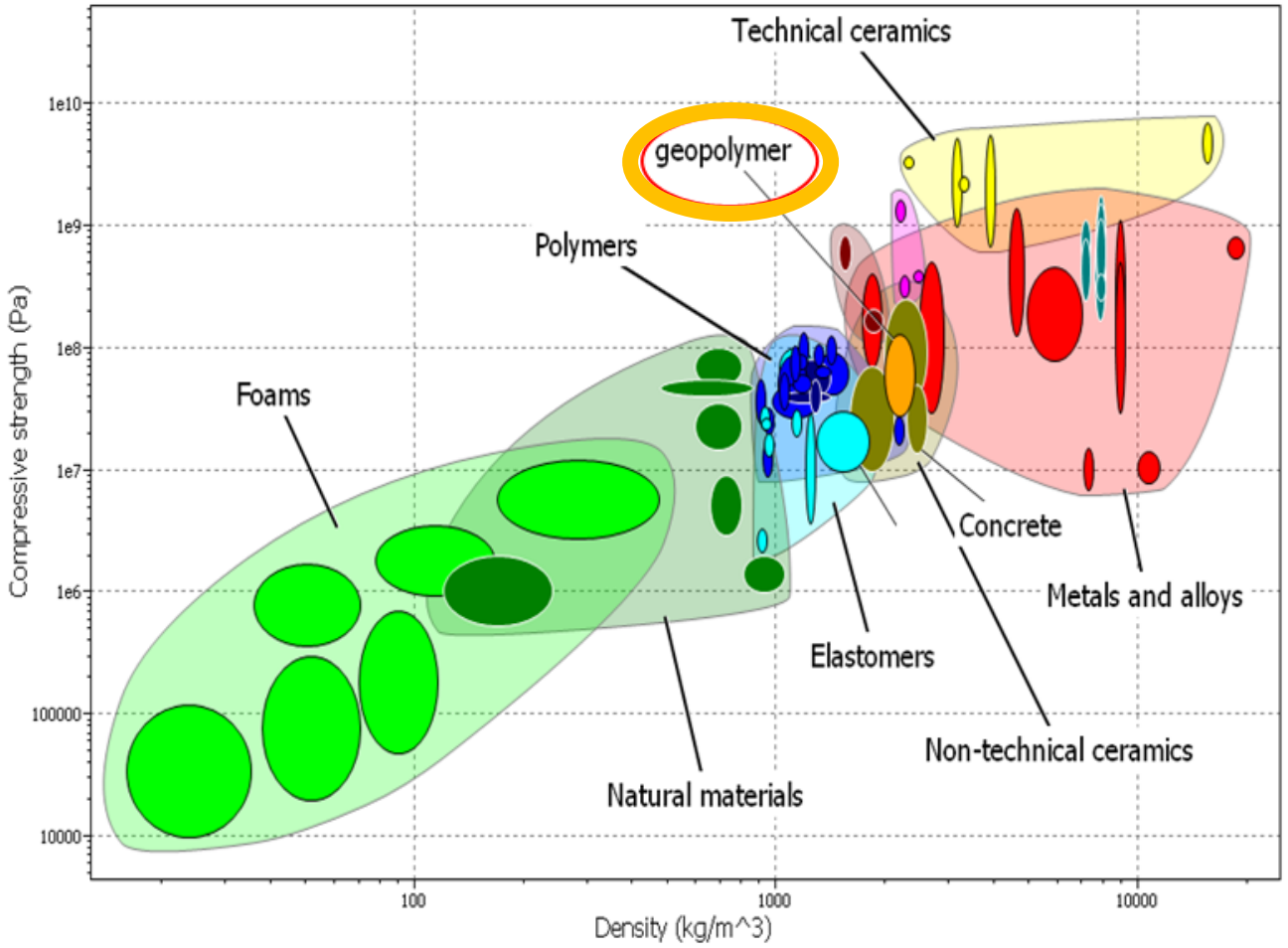


100 MPa

10 MPa

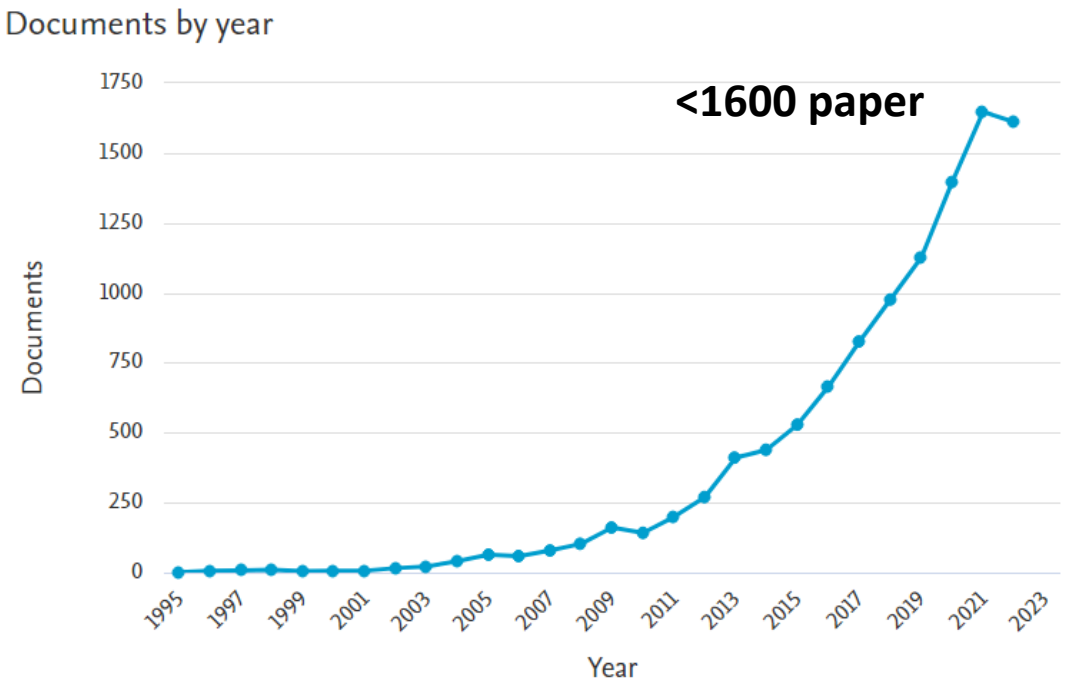
1 MPa

- **Easy processing,**
- **low density,**
- **fire and acid resistance,**
- **lower embodied CO2 content**
- **good thermal properties**

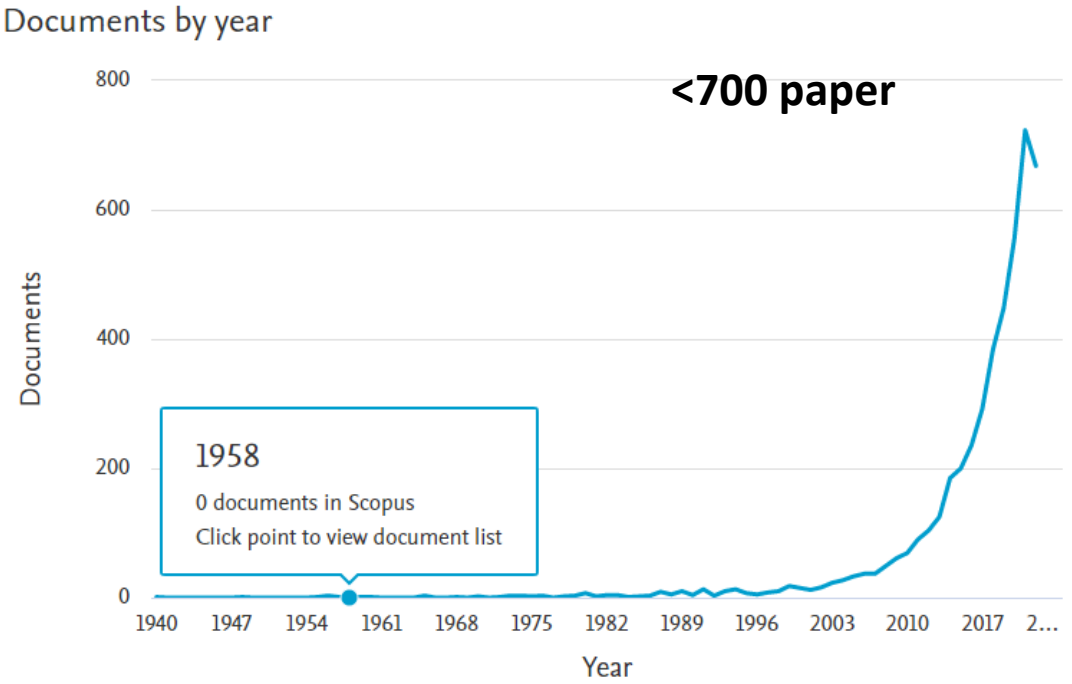
interesting materials for several applications

Properties and performance depend on their composition or mix design and synthesis procedure.

Geopolymers



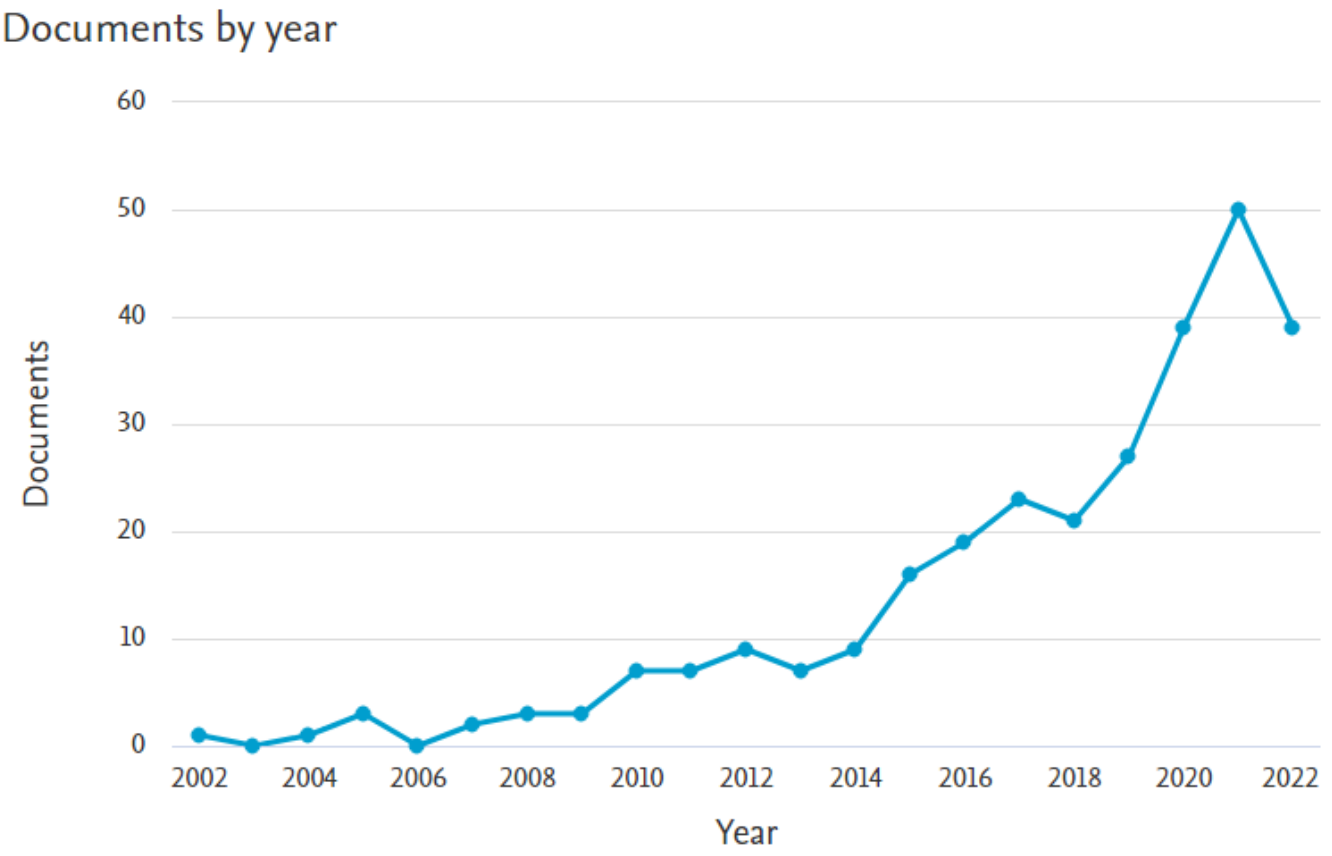
Alkali activated materials



From 2003

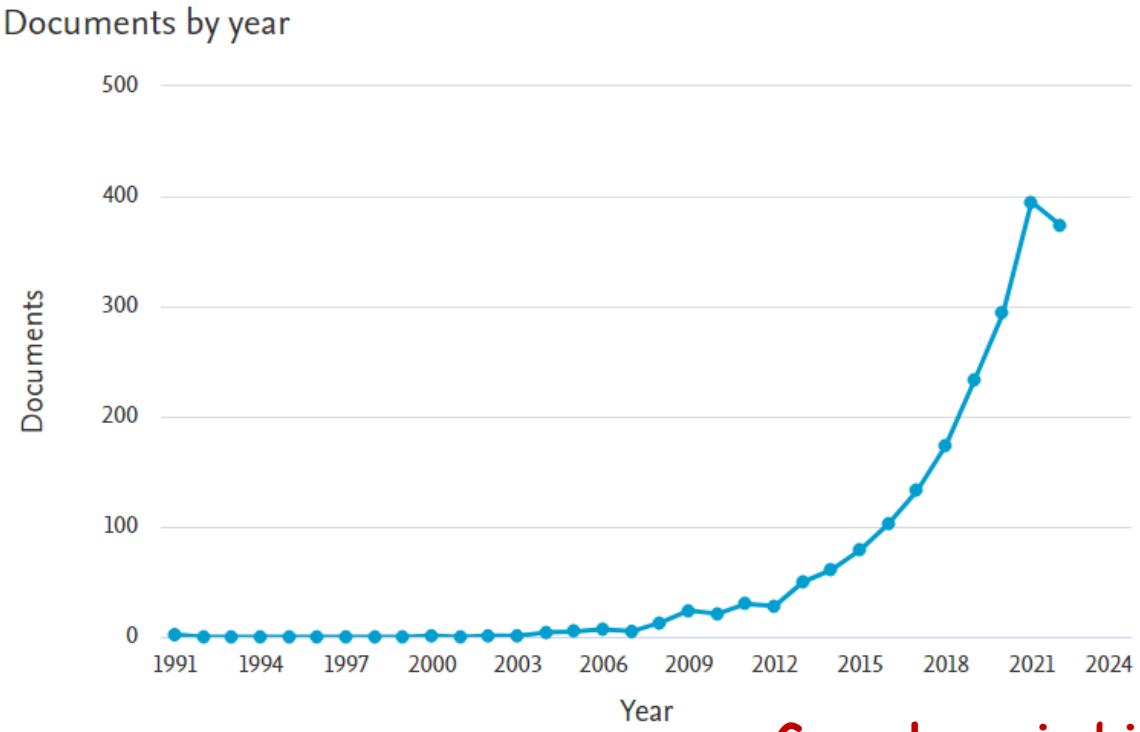
Database SCOPUS

Raw materials for geopolymers: Aluminosilicate precursors

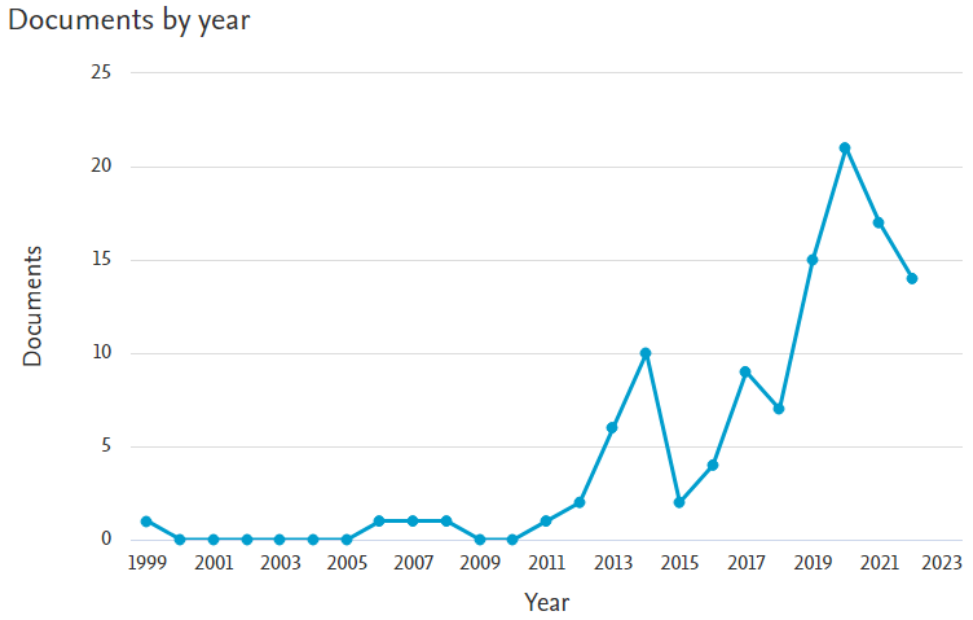


Database SCOPUS

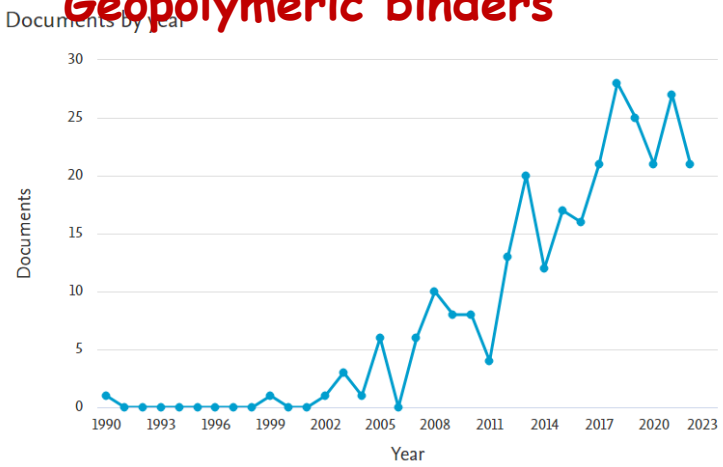
Geopolymers:Construction materials



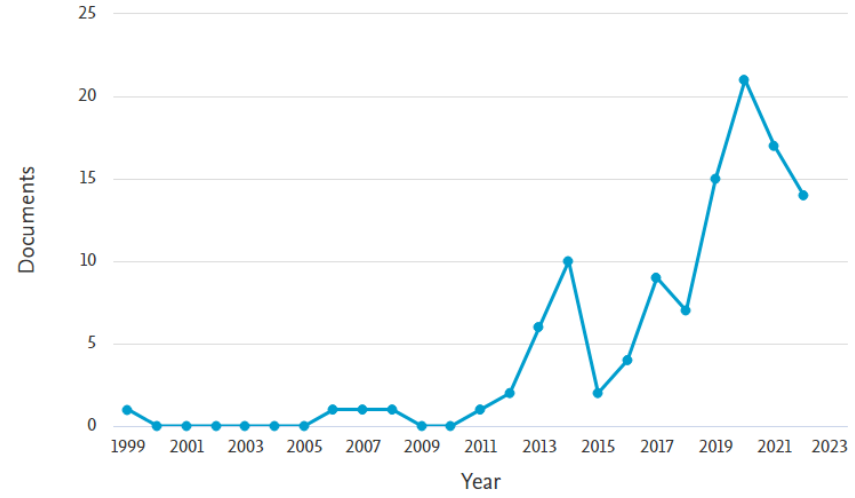
Geopolymers as insulating materials



Geopolymeric binders



Geopolymers as membrane



Database SCOPUS

Come To Modena and Work with US

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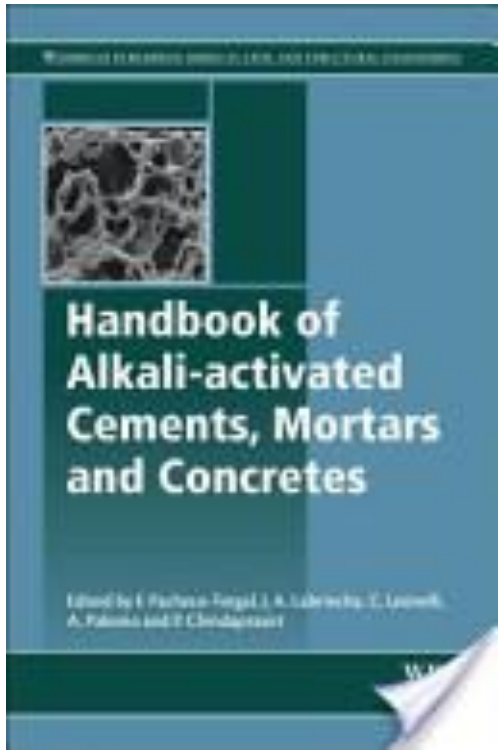

Department "Enzo Ferrari"

- Geopolymer Formulation
- Mechanical Properties
- ICP-MS
- XRD
- FT-IR
- Rheological Properties
- SEM
- TEM

Handbook of Alkali-Activated Cements, Mortars and Concretes

Edited by: Fernando Pacheco-Torgal, João Labrincha, C Leonelli, A Palomo, P Chindaprasit, **Elsevier**

Thanks for listening!!!!!

Acknowledgement