The Role of Al_2O_3, SiO_2 and Na_2O on the Amorphous → Crystalline Phase Transformation in Geopolymer Systems

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Geopolymers - Chemistry

- **Group of inorganic polymers**

- **Synthesis**

  $(Al_2O_3 + SiO_2)$ + Alkaline activator $\xrightarrow{\text{Amb.} - 100^{o}C}$ geopolymers

- **Mechanism**

  dissolution, orientation, polycondensation → polymeric network)

- **Chemical formula** - $M_n[-(SiO_2)_z-AlO_2]_n.wH_2O$

  (Z = 1,2,3 n= degree of polymerisation)

  $Na_2O.Al_2O_3.3.8\ SiO_2.12\ H_2O$ - (cement composition)

- **Amorphous or semi crystalline**

Geopolymers & Zeolites

Zeolites – a class of aluminosilicate cpds

Similarities

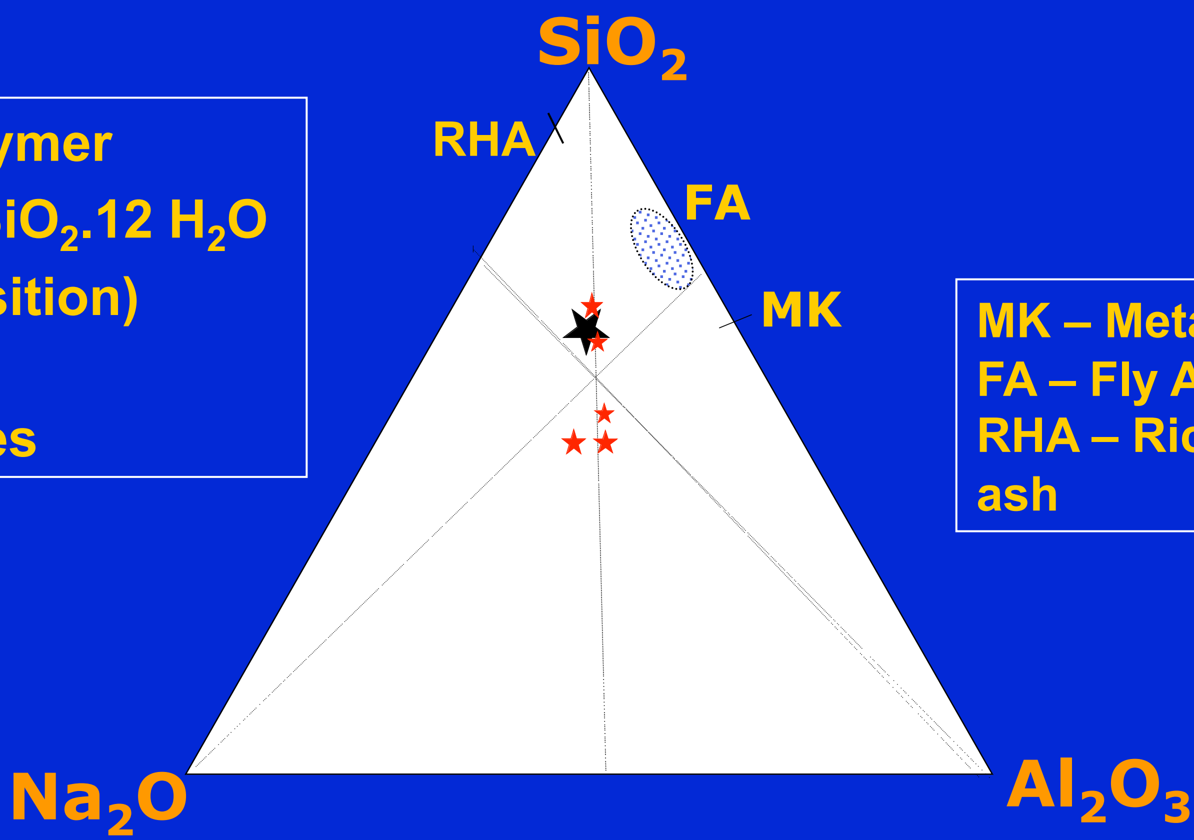
- Raw materials
- Mechanism of reaction
  (dissolution, orientation, condensation
  gel like -> crystalline)
- Chemical composition

Na_2O-Al_2O_3-SiO_2-H_2O compositional diagram

★ - geopolymer

$Na_2O.Al_2O_3.3.8\ SiO_2.12\ H_2O$ (cement composition)

★ – Zeolites



MK – Metakaolin
FA – Fly Ash
RHA – Rice husk ash

Geopolymers & Zeolites

Differences

- **Microstructure**

  geopolymers –amorphous or semi crystalline

  Zeolites - crystalline

- **Different properties → Different Applications**

  (identified in Portland cement – radioactive waste encapsulation)

- **Thermodynamically geopolymers are metastable**
- **Crystalline structures identified in geopolymer matrix**
- **Long term stability of geopolymer phase?**

Geopolymers & Zeolites

Some differences in synthetic conditions

Factors Controlling synthesis

- Curing temperature
- Ageing time
- Reaction rate
- Concentration of Alkaline activator (Na_2O)
- Water content
- SiO_2 & Al_2O_3 content

The degree of crystallinity is largely determined by product formulation and synthesis conditions.

-very important in geopolymer product development

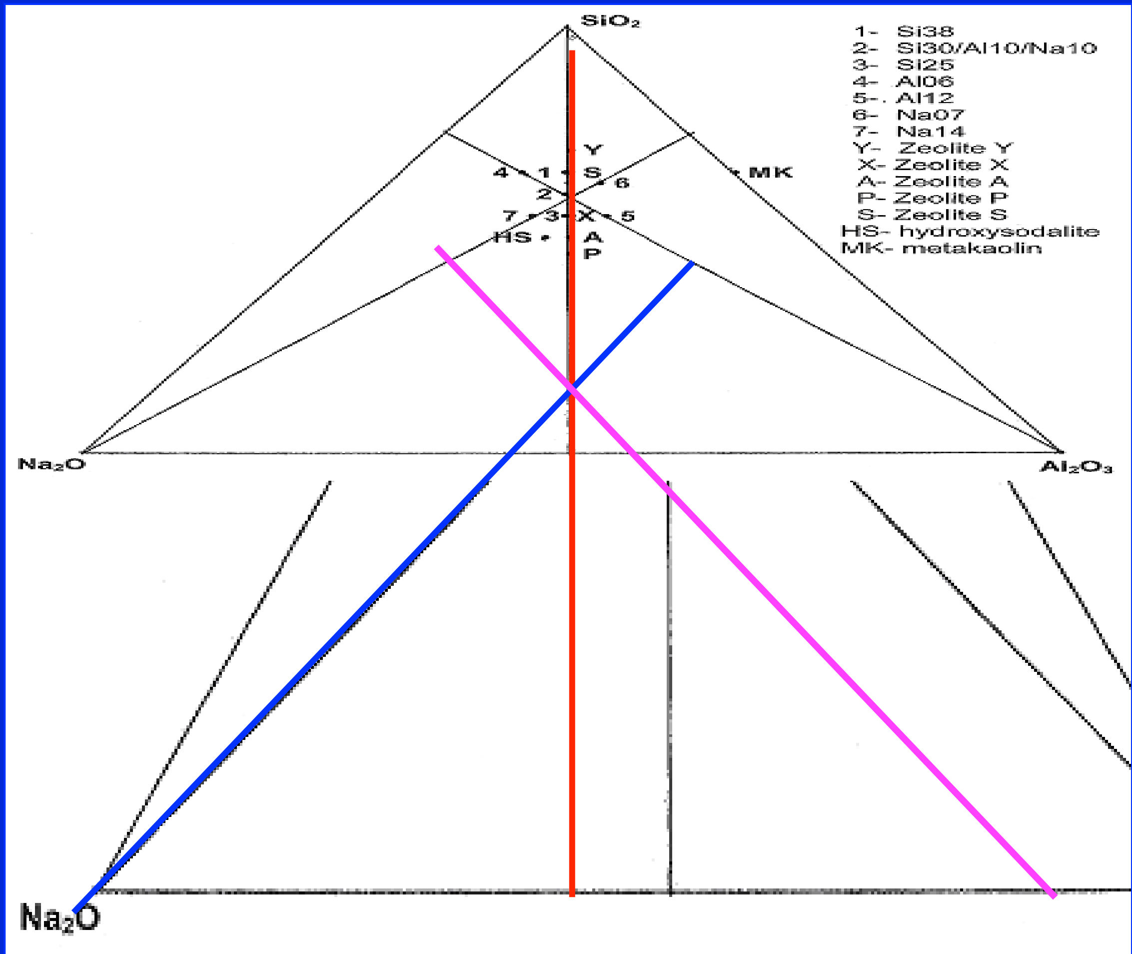
AIM

- Effect of SiO_2 , Al_2O_3 & Alkali oxide on the stability of geopolymer phase with respect to crystallisation
- Low temperature curing regimes
- Long term stability & Impact on the physical properties

Materials & Experimental

- Metakaolin (complete reactivity)
- Sodium silicate / sodium hydroxide
- Curing temperature – 40^{o}C
- Curing time - 7 months
- Compressive strength
- Phase development (XRD, SEM, EDAX)

Mix Formulations



Changing SiO_2 content

Mix 1, 2, 3 (Si38, Si30, Si25)

Changing Al_2O_3 content

Mix 4, 2, 5 (Al06, Al10, Al12)

Changing Na_2O content

Mix 6, 2, 7 (Na07, Na10, Na14)

(Y, X, A, P, S, HS)

Zeolite compositions

Geopolymers - metastable

Mix Formulations

Sample	Initial composition	SiO_2 (moles)	Al_2O_3 (moles)	Na_2O (moles)	SiO_2/Al_2O_3 (molar ratio)	Al_2O_3/Na_2O (molar ratio)	SiO_2/Na_2O (molar ratio)
Si-38	$1.0Na_2O.1.0Al_2O_3.3.8SiO_2.13.6H_2O$	3.81	1.0	1.0	3.81	1.00	3.80
Si-30	$1.0Na_2O.1.0Al_2O_3.3.0SiO_2.13.6H_2O$	3.00	1.0	1.0	3.00	1.00	3.00
Si-25	$1.0Na_2O.1.0Al_2O_3.2.5SiO_2.13.6H_2O$	2.50	1.0	1.0	2.50	1.00	2.50
Al-06	$1.0Na_2O.0.6Al_2O_3.3.0SiO_2.13.6H_2O$	3.00	0.6	1.0	5.01	0.60	3.00
Al-10	$1.0Na_2O.1.0Al_2O_3.3.0SiO_2.13.6H_2O$	3.00	1.0	1.0	3.00	1.00	3.00
Al-12	$1.0Na_2O.1.2Al_2O_3.3.0SiO_2.13.6H_2O$	3.00	1.2	1.0	2.50	1.20	3.00
Na-07	$0.7Na_2O.1.0Al_2O_3.3.0SiO_2.16.3H_2O$	3.00	1.0	0.7	3.00	1.70	4.28
Na-10	$1.0Na_2O.1.0Al_2O_3.3.0SiO_2.13.6H_2O$	3.00	1.0	1.0	3.00	1.20	3.00
Na-14	$1.4Na_2O.1.0Al_2O_3.3.0SiO_2.13.6H_2O$	3.00	1.0	1.4	3.00	0.86	2.14

SiO_2 series – Si38, Si30, Si25

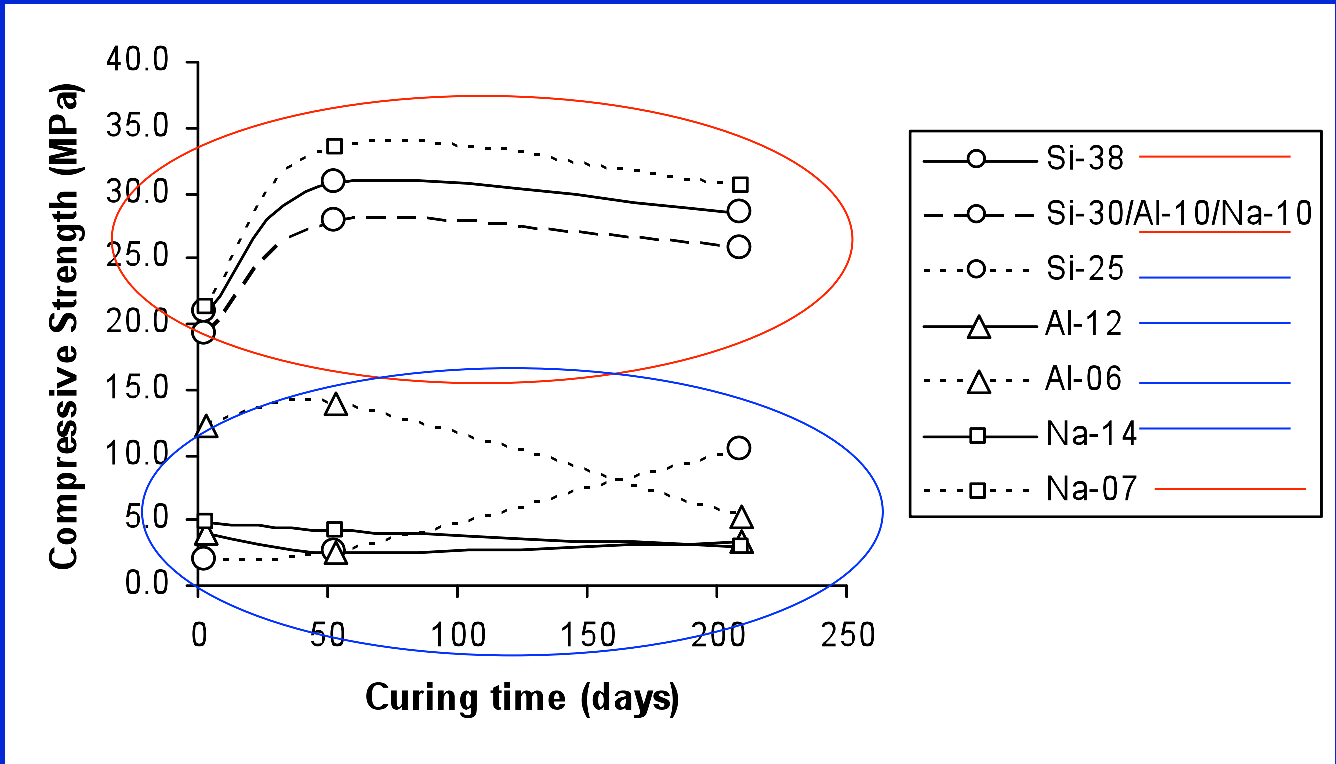
Na_2O series – Na07, Na10, Na14

Al_2O_3 series – Al06, Al10, Al12

H_2O - CONSTANT

Compressive Strength Development

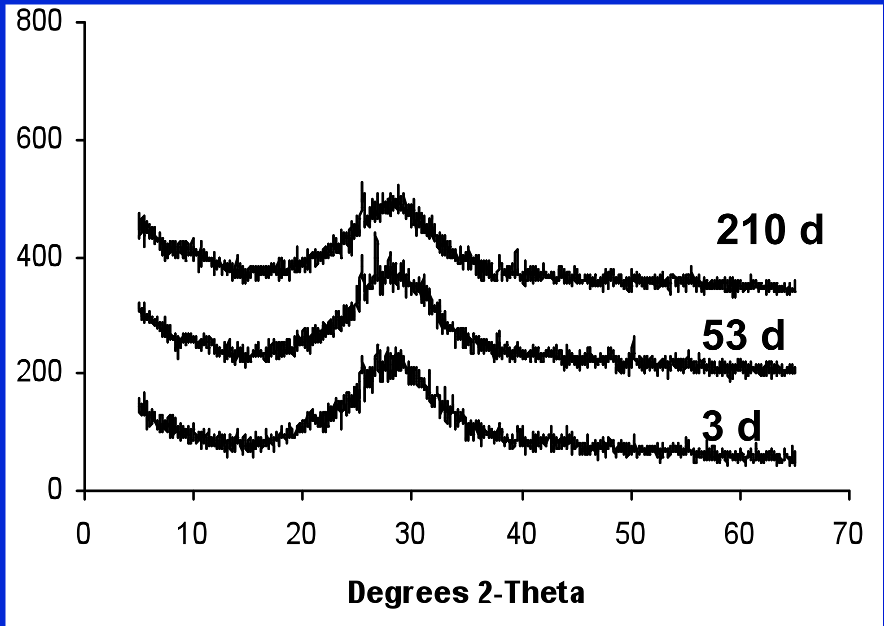
Si-38 > Si-30 > Si-25
Al-10 > Al-06 > Al-12.
Na-07 > Na-10 > Na-14



High strengths —— Si38, Si30, Na07 (High SiO_2, Low Na_2O)

Low strengths —— Si25, Al 12, Na14 (Low SiO_2, High Al_2O_3, High Na_2O)

Phase Development – XRD (High Strength Category)



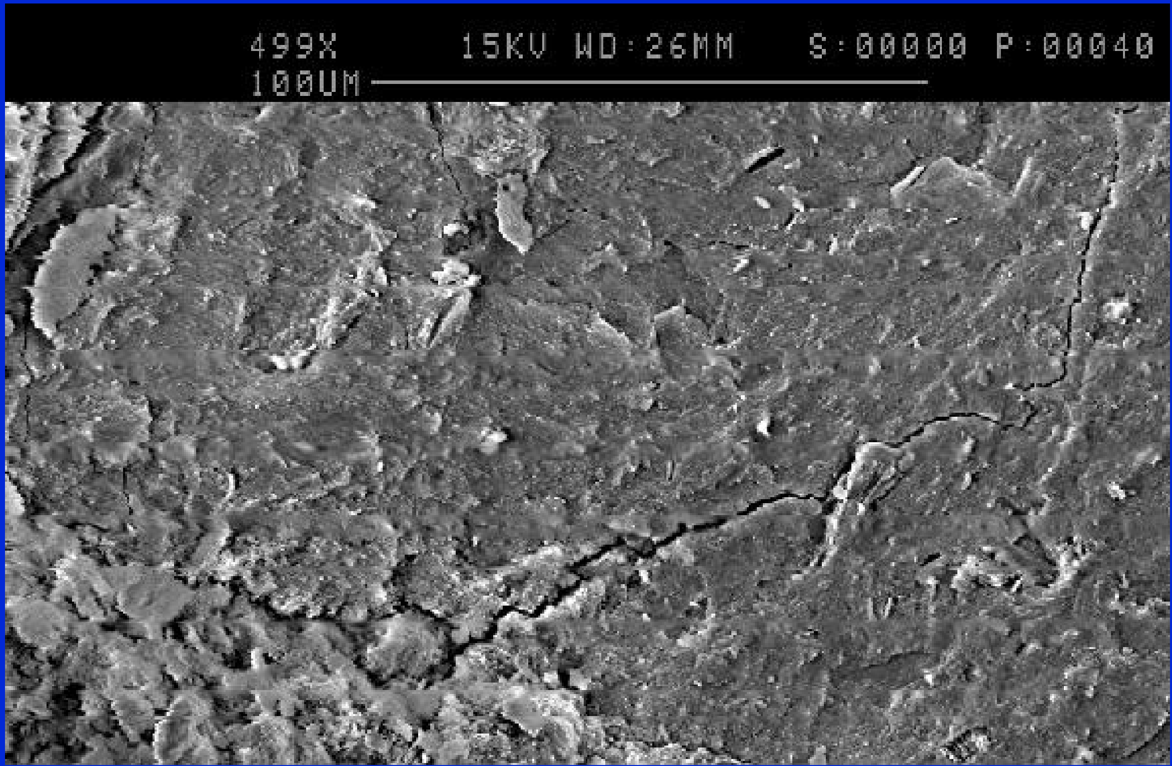
Amorphous phase throughout

(broad band around 28° 2-theta)

Similar pattern for Na-07 & Si-30

Mix Formulation – Si-38 High Strength Category

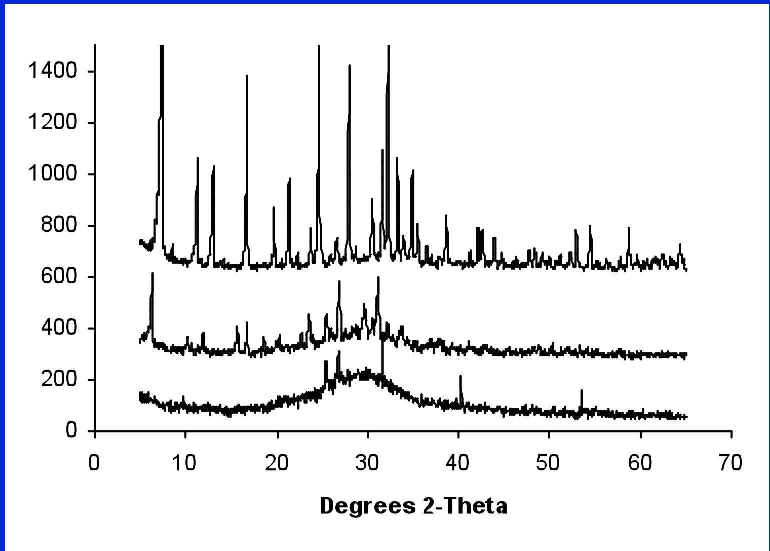
Microstructure - SEM
(High Strength Category)



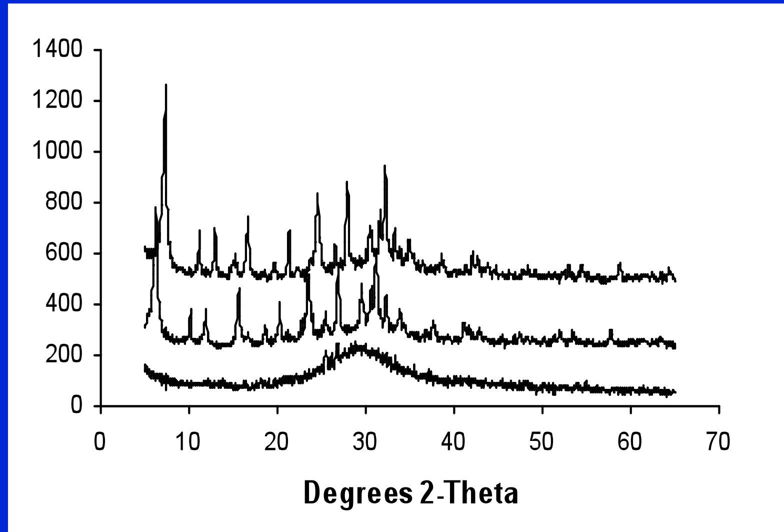
Na-07, Si-38 and Si-30

Dense, homogeneous phases

Phase Development – XRD
(Low Strength Category)



Si 25

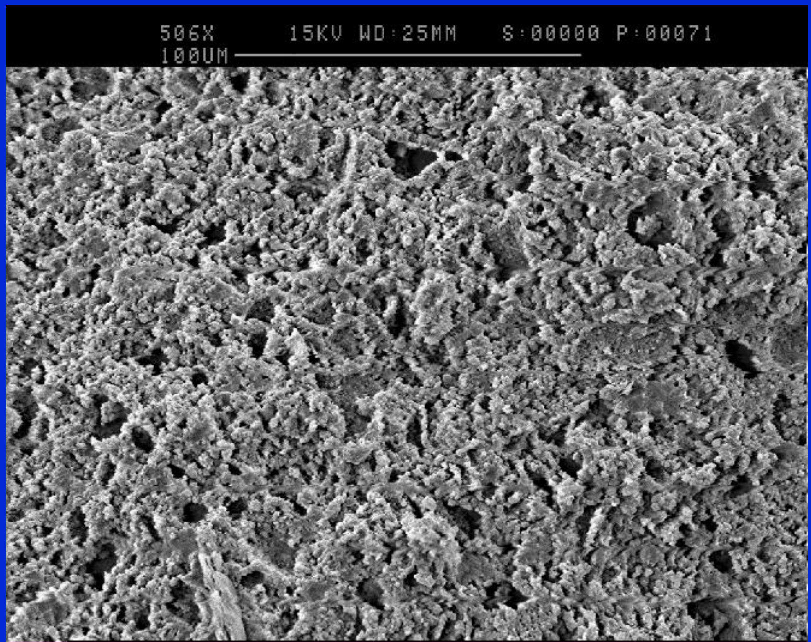


Na14

- Transition of amorphous to crystalline **(mainly Zeolite A & Zeolite P)**
- Associated with low strengths

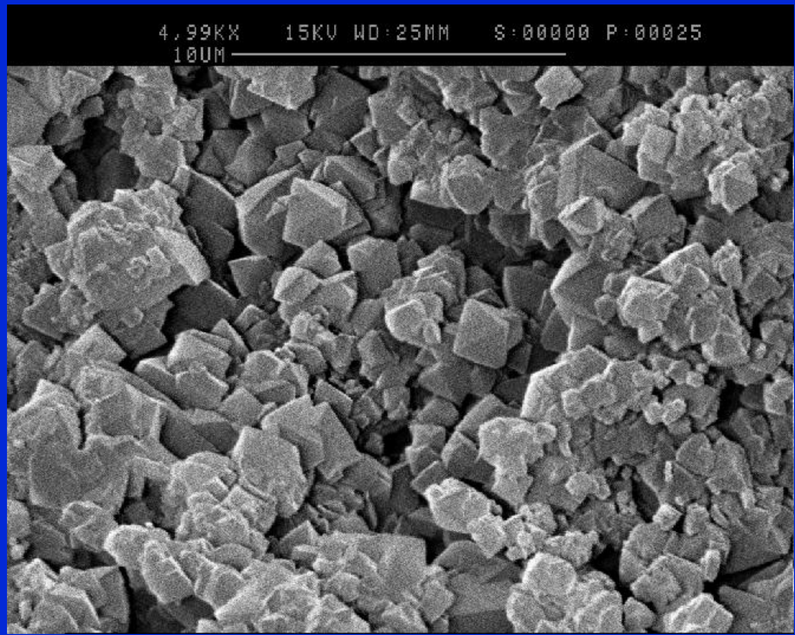
Microstructure – SEM

(Low Strength Category)



Si 25

Porous microstructure



Higher magnification of Si 25

EDAX – **Zeolite P**

Conclusions

- **Amorphous -> crystalline transformation occur in some mixtures**
- **High Al_2O_3 ($SiO_2/Al_2O_3 = 2.5$) and High Na_2O ($Na_2O/SiO_2 = 1.4$) favours amorphous → crystalline transformation**
- **$Na_2O.Al_2O_3.3.8SiO_2.13H_2O$ – no tendency towards phase transformation**
- **Tentative relationship between development of crystalline phases and low strengths**
- **Initial mix formulation – key parameter**
- **findings can be relevant to the practical phase development of geopolymer systems under initial prolonged exposure to mild temperatures and high humidity levels.**

THANK YOU