On the Effects of Water Content on the Structure and Thermo-Mechanical Properties of Geopolymers

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Introduction

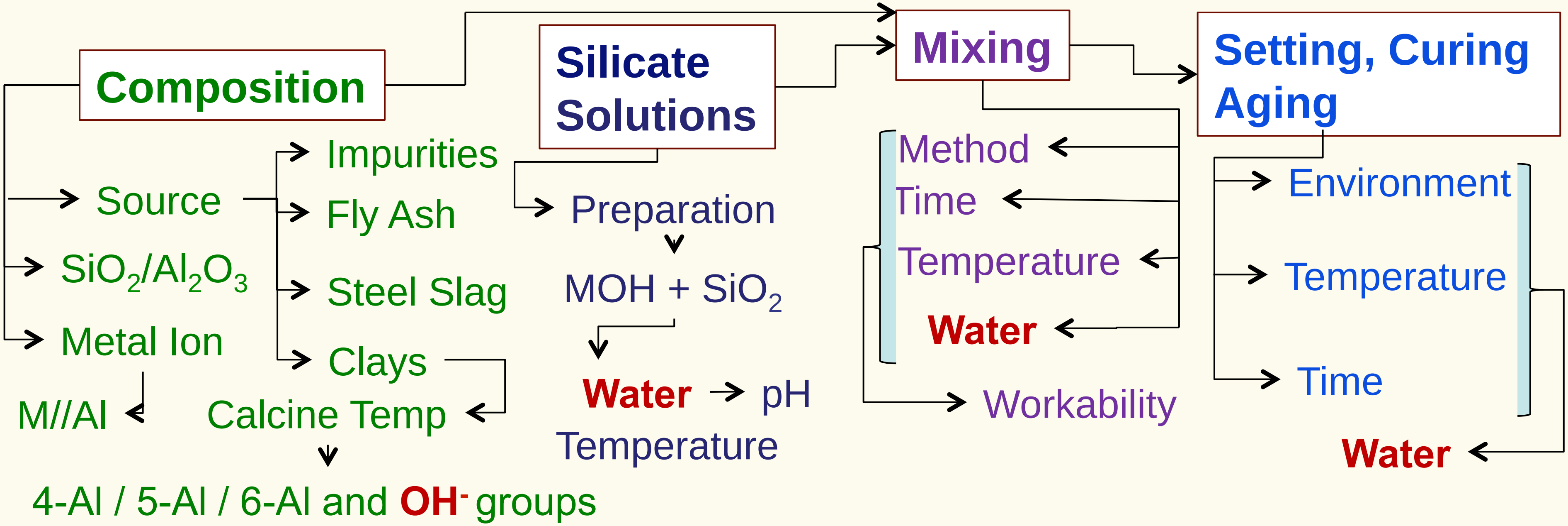
Compressive Strength *Example*

Various metakaolin and metakaolinite GPs.

SiO_2/Al_2O_3 ratio	Alkali activator ratio	Water Ratio	MK calcination temperature (°C)	Curing temperature (°C) / curing time (hr) /Aging (days)	**Maximum compressive strength, (MPa)**
1.08 - 3	Na/Al=0.5 - 2	H_2O/SiO_2 =2.8	750	75 /24 / 7	**62 ±3**
2.5 - 5	Na/Al=0.8 – 1.6	H_2O/Na_2O = 13.6	750	40/ ≤72/ NS	**~25**
4	Na/Al=1.1	H_2O/Al_2O_3 = 11	NS	85/ 2/NS	**74**
2.5 - 3.8	Na/Al=0.7 - 1.2	H_2O/Al_2O_3 = 12-16	NS	85/2 / NS	**48**
2.5 - 4.3	Na/Al=1	H_2O/Na_2O = 11	NS	40/20/ 7	**~82**
2.5 - 4.3	K/Al=1	H_2O/Na_2O = 11	NS	40/20/ 7	**~82**
2.3 - 4	Na/Al=1	H_2O/Al_2O_3 = 11	NS	40/20/NS	**~75**
2	Na/Al=1	H_2O/Al_2O_3 = 9.4	750	60/24/10	**70**
2.5-5	Na/Al=1	H_2O/Al_2O_3 = 11-13	750	80/48/1	**37**
2.5-5	K/Al=1	H_2O/Al_2O_3 = 11-13	750	80/48/1	**33**

Introduction

Numerous parameters affect final product



Commonly used compositions of SiO_2/Al_2O_3 =2 - 4 and H_2O/Al_2O_3 = 11-13 molar ratios.

Introduction

- Water is necessary for dissolution and mobility of monomeric species, however increasing water contnet decreases polymerization rate.
- Geopolymer products contains water
  - in large pores and intergranual space (Free water)
  - within the small network pores,
  - hydrating charge balancing cations
  - OH^- groups
- Water content is often altered to increase workability of mixtures.

Introduction

Motivation

Carry on systematic study on the effects of water content or $H_2O/(SiO_2 + Al_2O_3)$ molar ratios on the structure and properties of geopolymers with various chemical compositions including SiO_2/Al_2O_3 and metal activators (K and Na)

Sample Preparation

- Metakaolin (MK) - MetaMax® (BASF catalysts LLC, NJ)

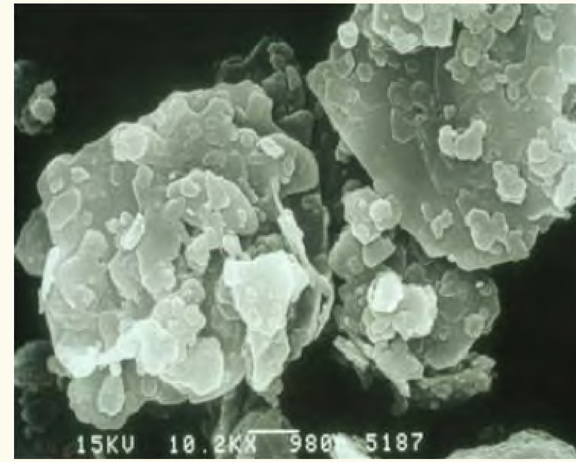
  SiO_2/Al_2O_3 = 2.05 molar ratio

  Average particle size 1.2 μm

  Less than 3.7 % impurities

  TiO_2 - 1.7 %

  350-410 m^2/g



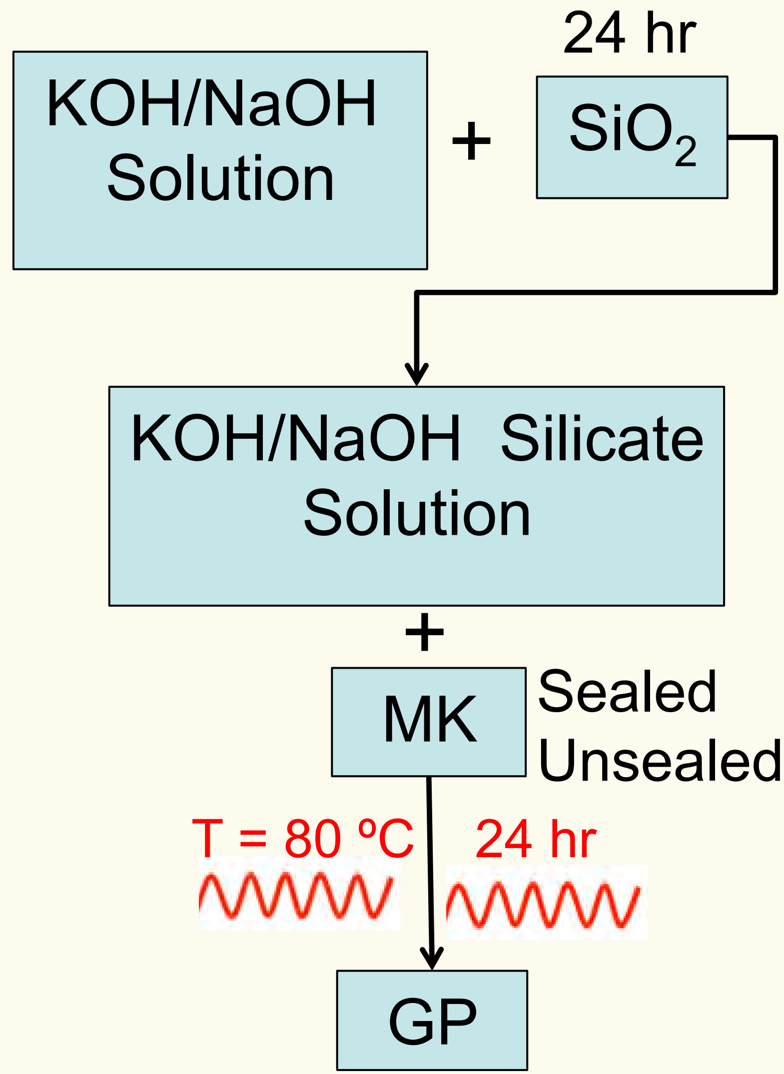
Chemical Composition	SiO_2	Al_2O_3	Na_2O	K_2O	TiO_2	Fe_2O_3	CaO	MgO	P_2O_5	SO_3	LOI
Percent	53.0	43.8	0.23	0.19	1.70	0.43	0.02	0.03	0.03	0.03	0.46

- Amorphous fumed **SiO_2**(Alfa Aesar, MA)
- KOH (Mallinckrodt Chemicals, NJ)
- NaOH (Mallinckrodt Chemicals, NJ)
- Deionized water

http://www2.basf.us/functional_polymers/kaolin/products/metamax/index.htm

Sample Preparation

	SiO_2/Al_2O_3	$H_2O/(Al_2O_3+SiO_2)$	H_2O/Al_2O_3	Sample Label
KOH - K/Al=1	2.5	2.0	7.0	K-2.5-2
		3.0	10.5	K-2.5-3
		3.144	**11.0**	**K-2.5-3.14**
		4.0	14.0	K-2.5-4
	3.0	2.0	8.0	K-3-2
		2.75	**11.0**	**K-3-2.75**
		3.0	12.0	K-3-3
		4.0	16.0	K-3-4
	4.0	2.0	10.0	K-4-2
		2.2	**11.0**	**K-4-2.2**
		3.0	15.0	K-4-3
		4.0	20.0	K-4-4
NaOH -Na/Al=1	2.5	2.0	7.0	
		3.0	10.5	Na-2.5-3
		3.144	**11.0**	**Na-2.5-3.14**
		4.0	14.0	Na-2.5-4
	3.0	2.0	8.0	Na-3-2
		2.75	**11.0**	**Na-3-2.75**
		3.0	12.0	Na-3-3
		4.0	16.0	Na-3-4
	4.0	2.0	10.0	Na-4-2
		2.2	**11.0**	**Na-4-2.2**
		3.0	15.0	Na-4-3
		4.0	20.0	Na-4-4



Sample setting (ageing)

Characterization

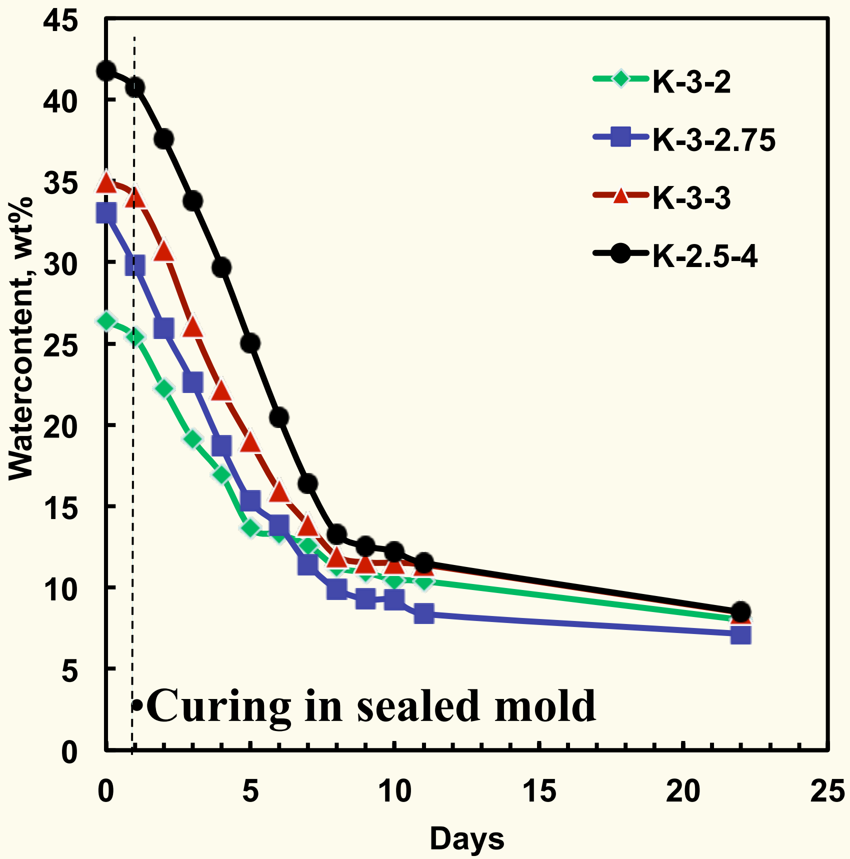
Structural Characterization

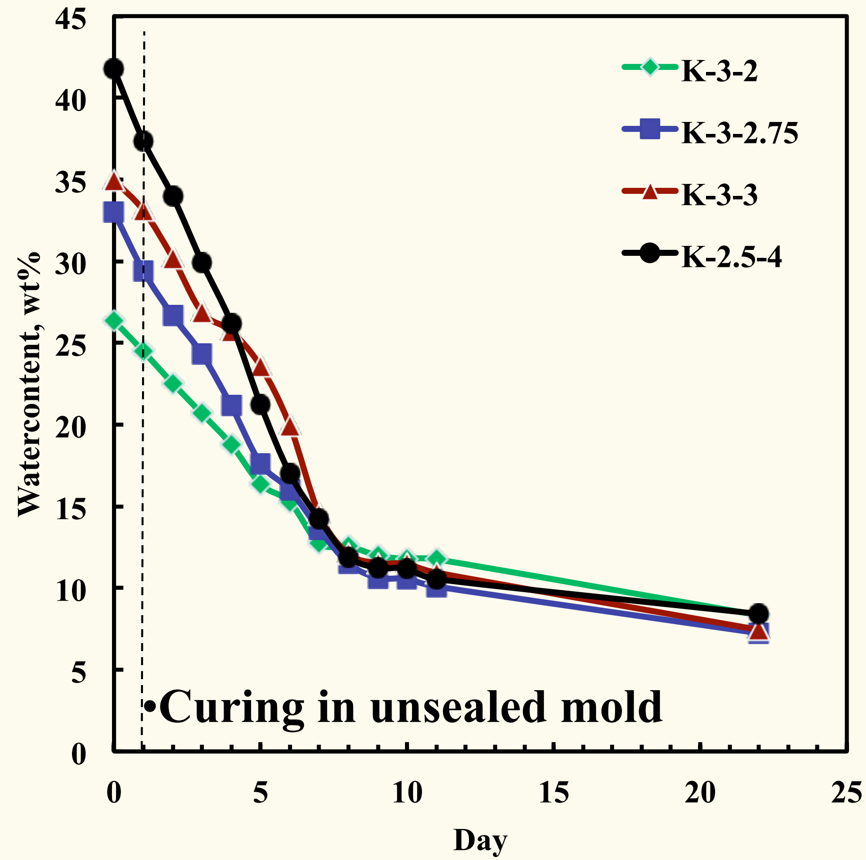
- X-Ray Diffraction (XRD)
- ^{27}Al Nuclear Magnetic Resonance (NMR)
- Scanning Electron Microscopy (SEM)
- Density by Alcohol Immersion

Thermal and Mechanical Properties

- Thermo-Gravimetric (TGA)
- Thermo-Mechanical Analysis (TMA)
- Thermal Constant Analysis (TCA)
- Compression Test

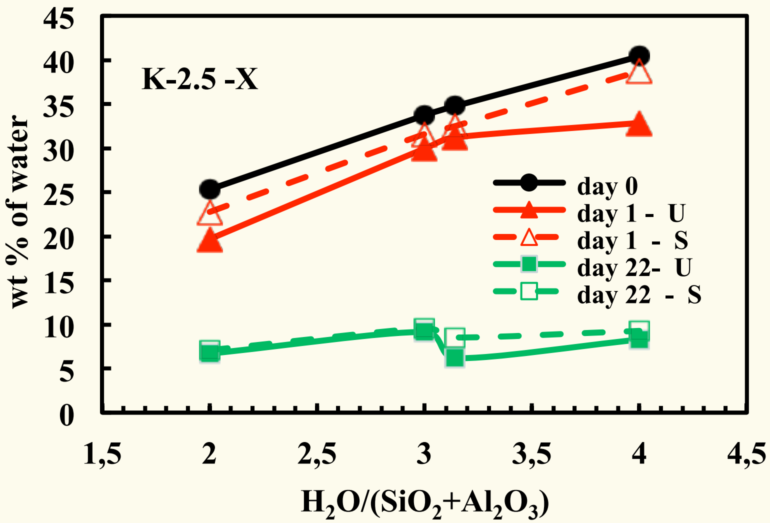
Kinetics of Water Loss

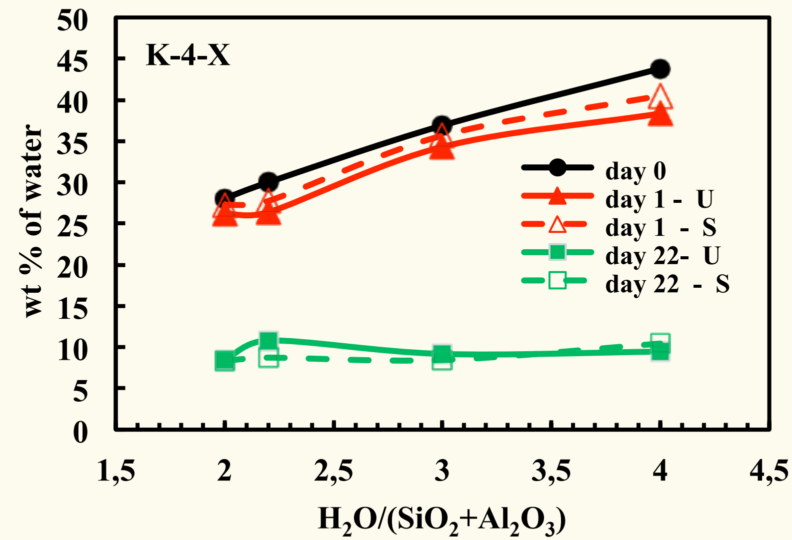


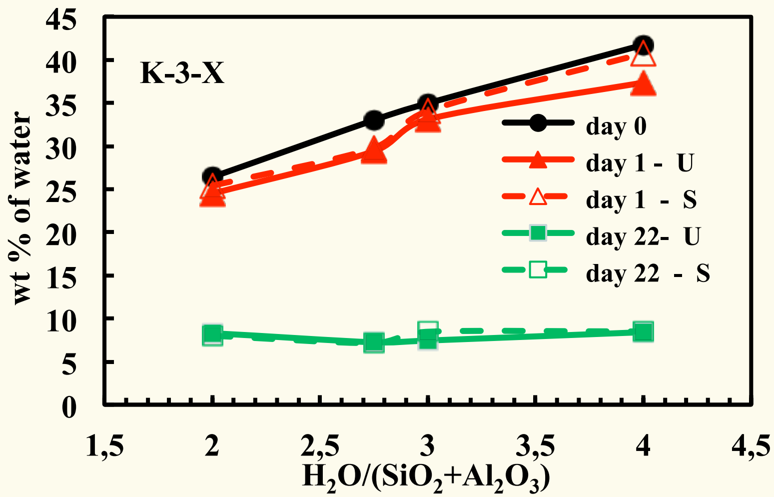


- Weight measurements before and after processing for > 20 days
- Typical trends seen in all samples

Kinetics of Water Loss

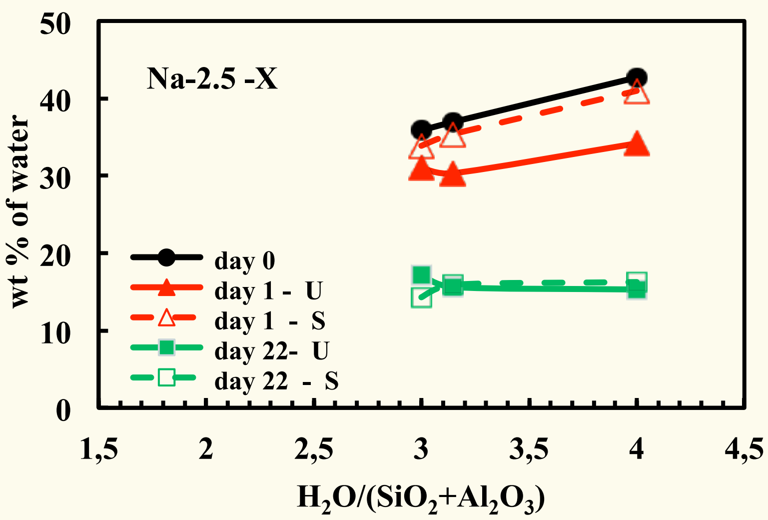


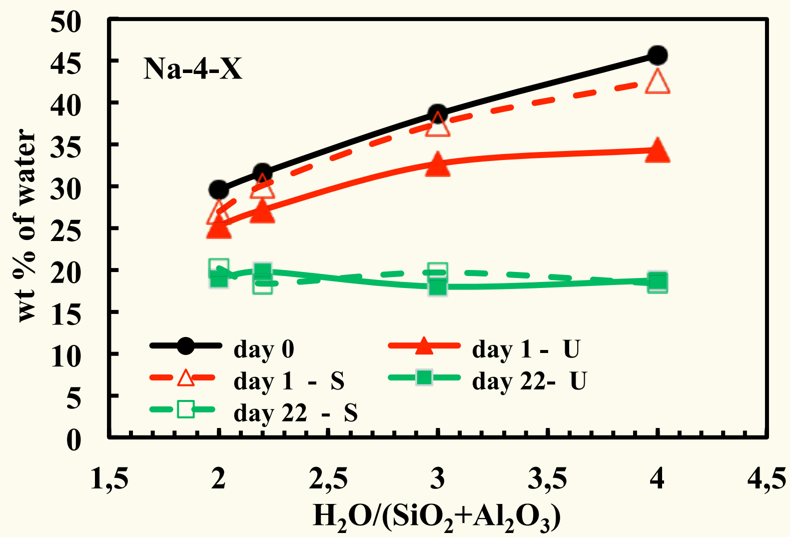


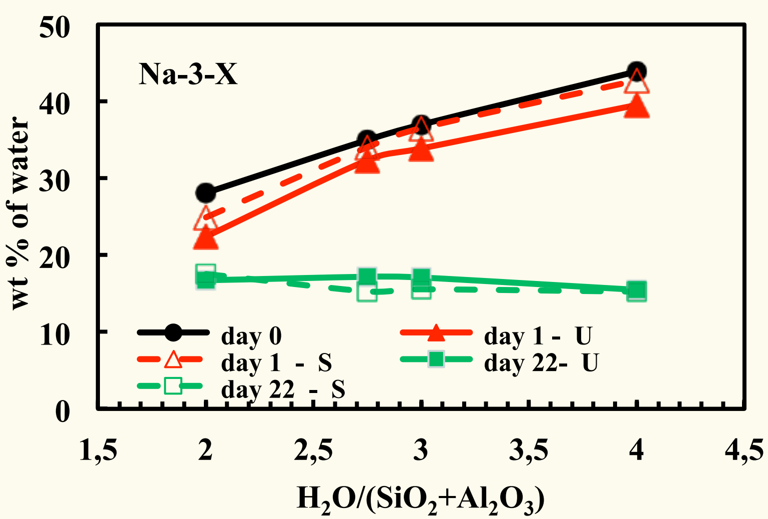


The change of wt% of water remaining in K-activated geopolymers with SiO_2/Al_2O_3 =2.5-4 during curing in unsealed (labeled as U) and sealed (labeled as S) molds as a function of initial water content, i.e. $H_2O/(SiO_2 + Al_2O_3)$ ratio. Day-0 denotes samples after mixing, day-1 after curing, and day-22 after aging for 22 days.

Kinetics of Water Loss

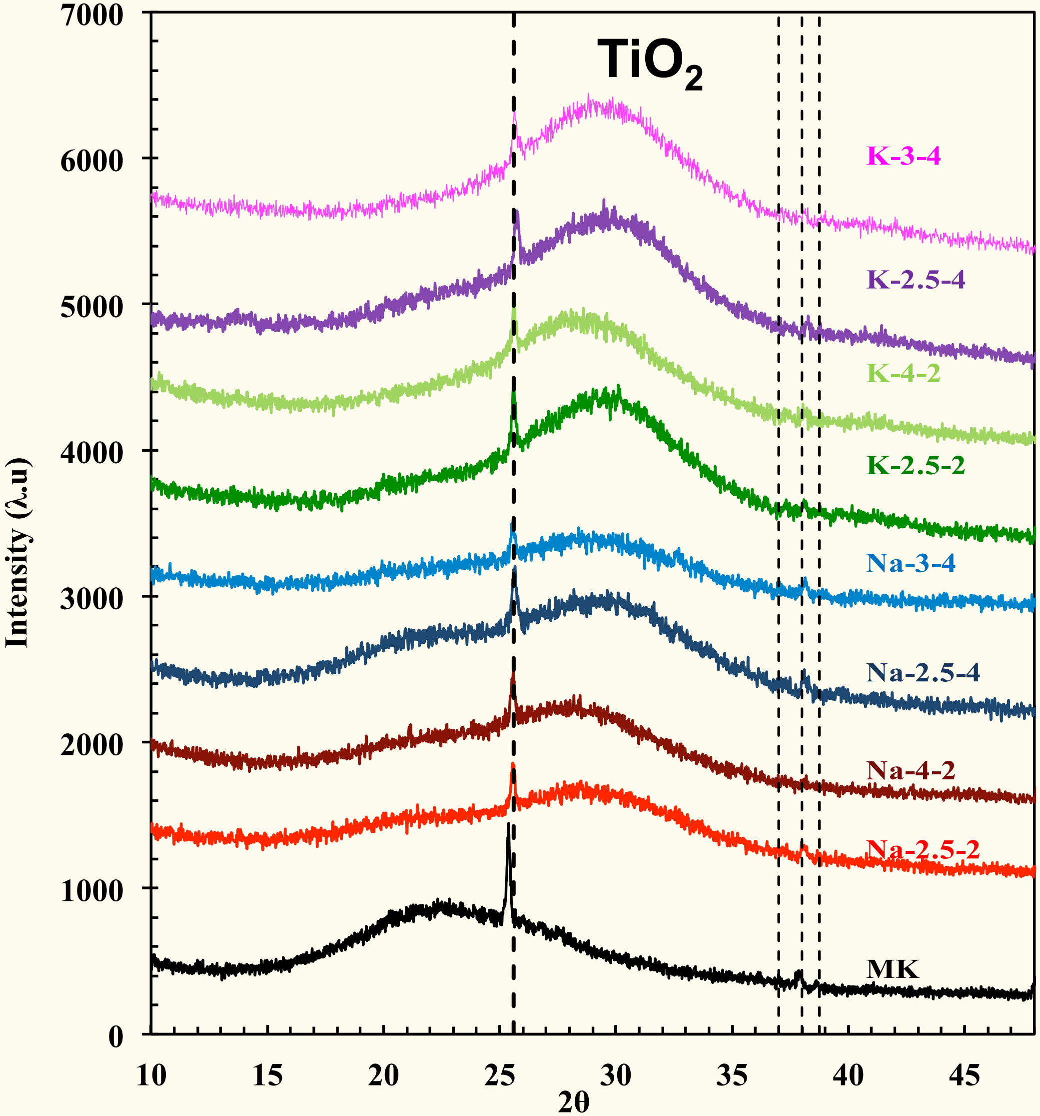






The change of wt% of water remaining in Na-activated geopolymers with SiO_2/Al_2O_3 =2.5-4 during curing in unsealed (labeled as U) and sealed (labeled as S) molds as a function of initial water content, i.e. $H_2O/(SiO_2 + Al_2O_3)$ ratio. Day-0 denotes samples after mixing, day-1 after curing, and day-22 after aging for 21 days.

Structural Changes-XRD



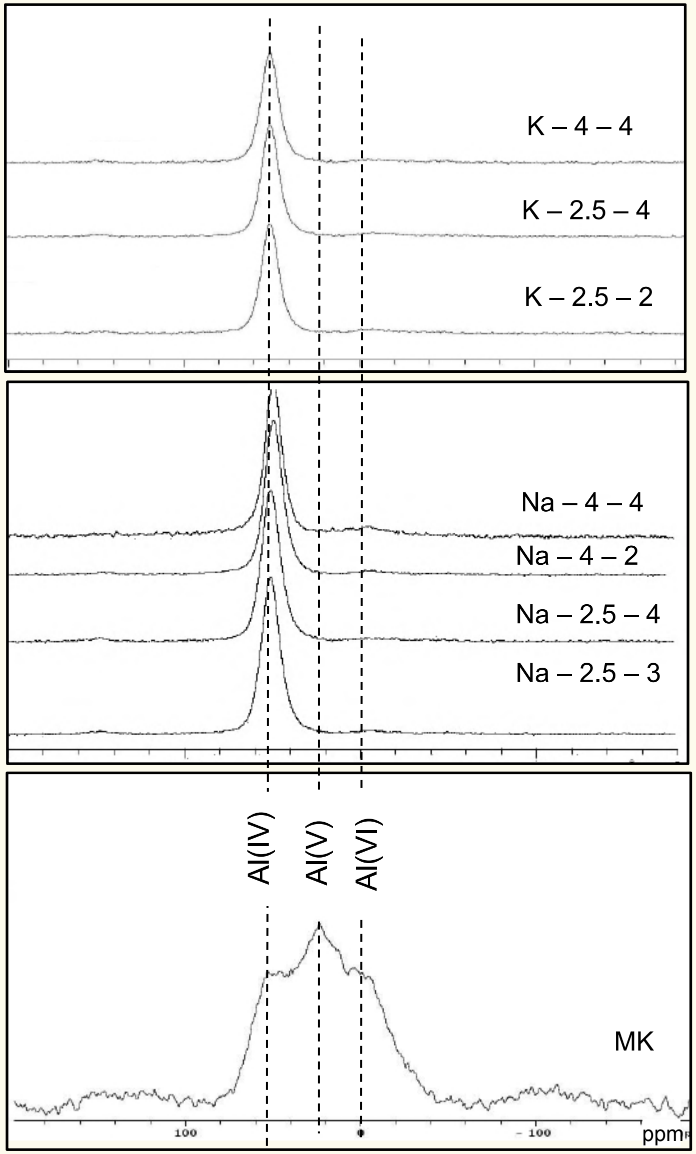
XRD of selected K- and Na-based geopolymers after curing and aging for 21 days. For comparison, XRD of the virgin MK is also shown in the figure.

Vertical dashed lines indicate position of XRD peaks for TiO_2 (anatase).

Shift in amorphous halo

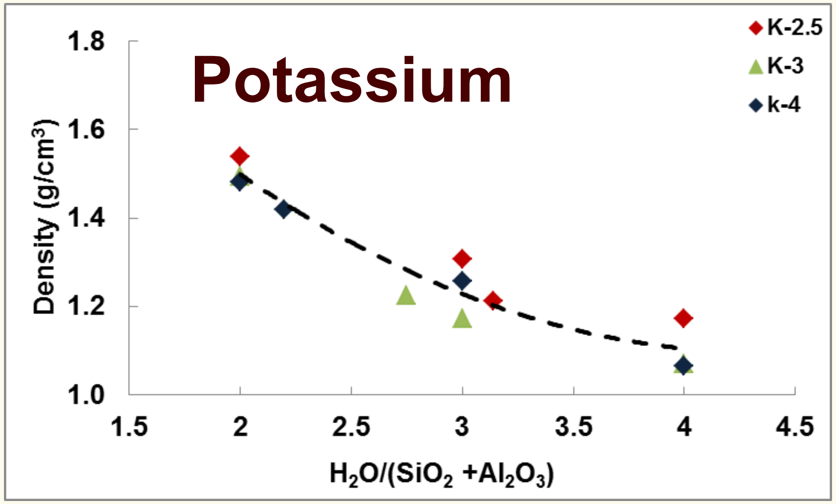
22ºϴ to ~ 28 ºϴ

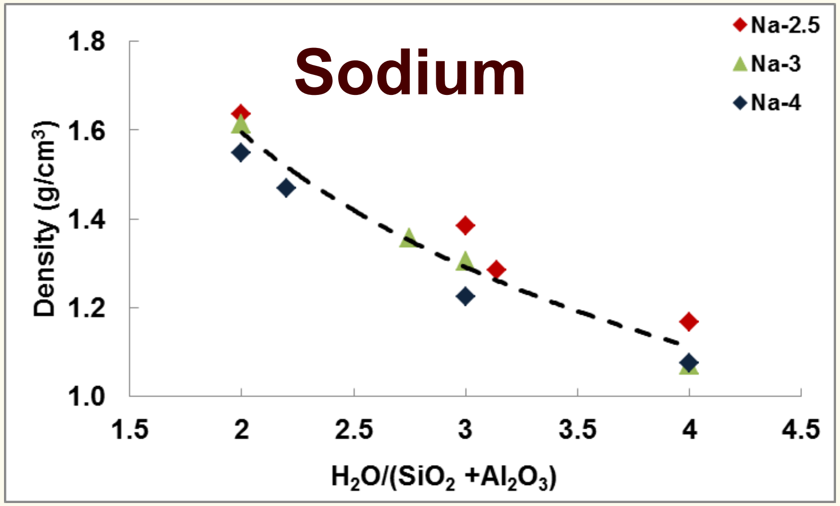
Structural Changes-^{27}Al MAS NMR

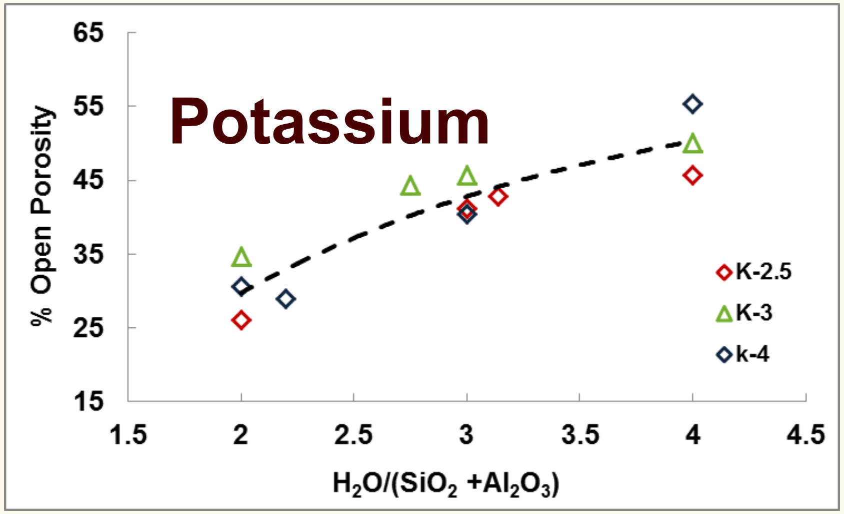


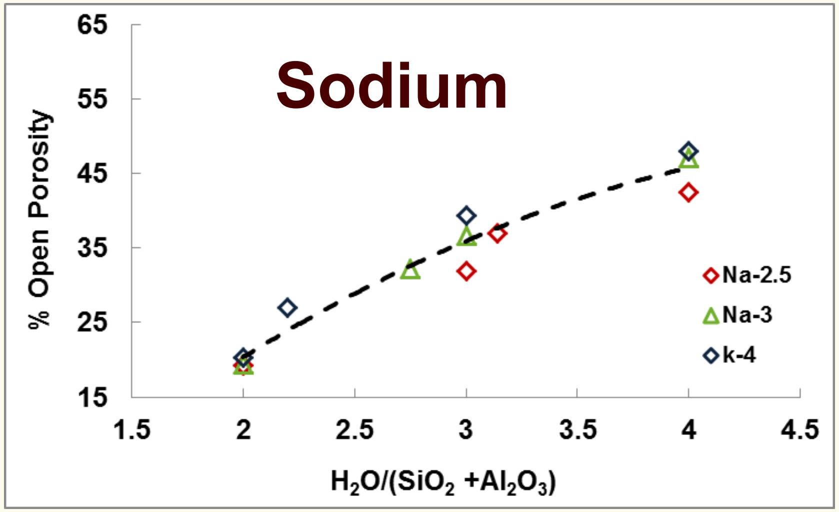
^{27}Al MAS-NMR of virgin MK, and selected K- and Na- activated geopolymer samples after curing and aging for 21 days. Dashed lines mark Al(IV), Al(V) and Al(VI) -coordinated Al referred to an external standard of $[Al(H_2O)_6]^{3+}$.

Structural Changes-Density and Open Porosity

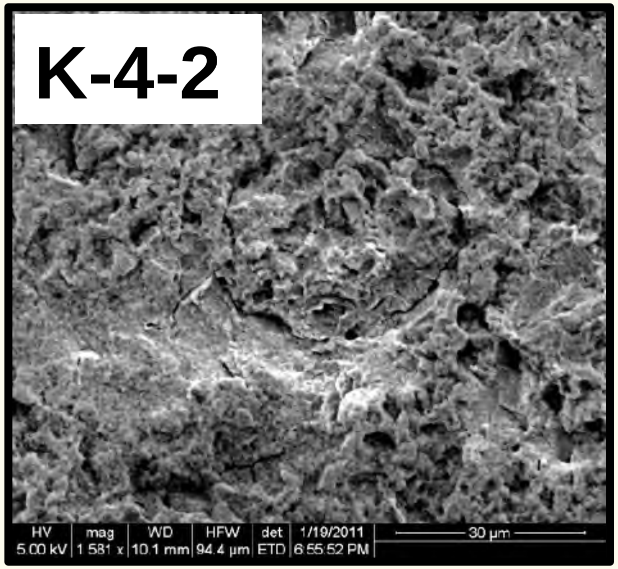


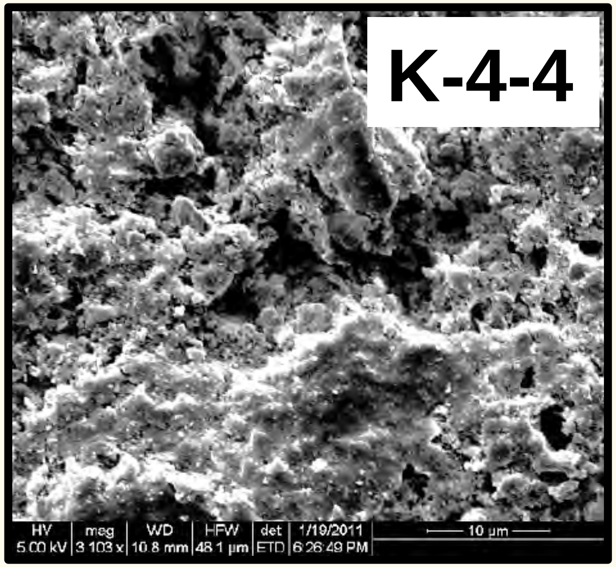


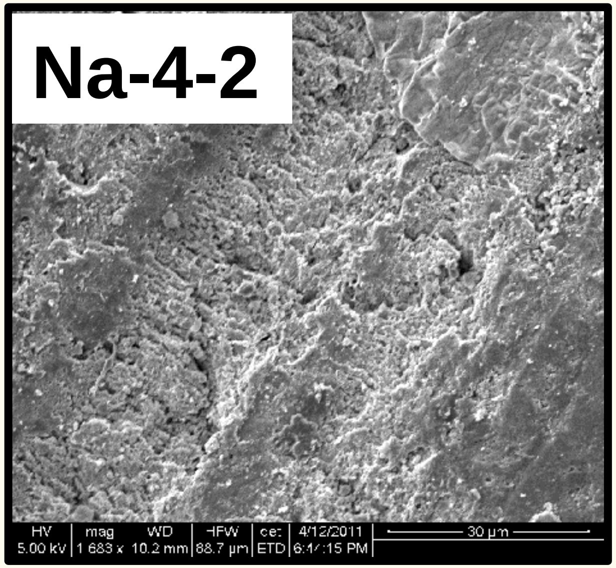


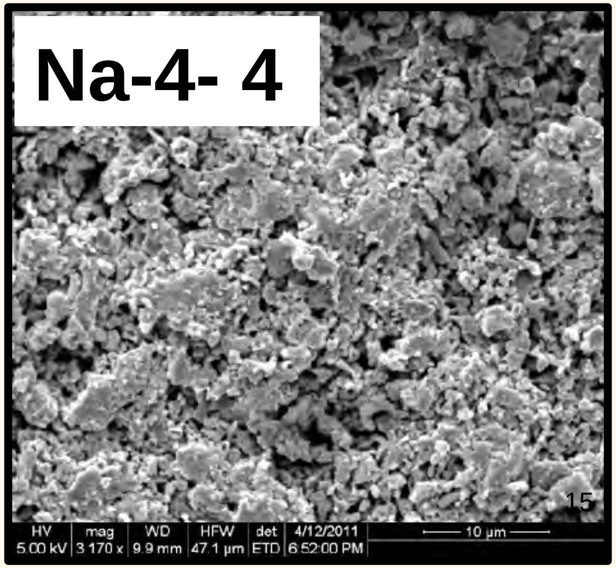


Microstructure-SEM



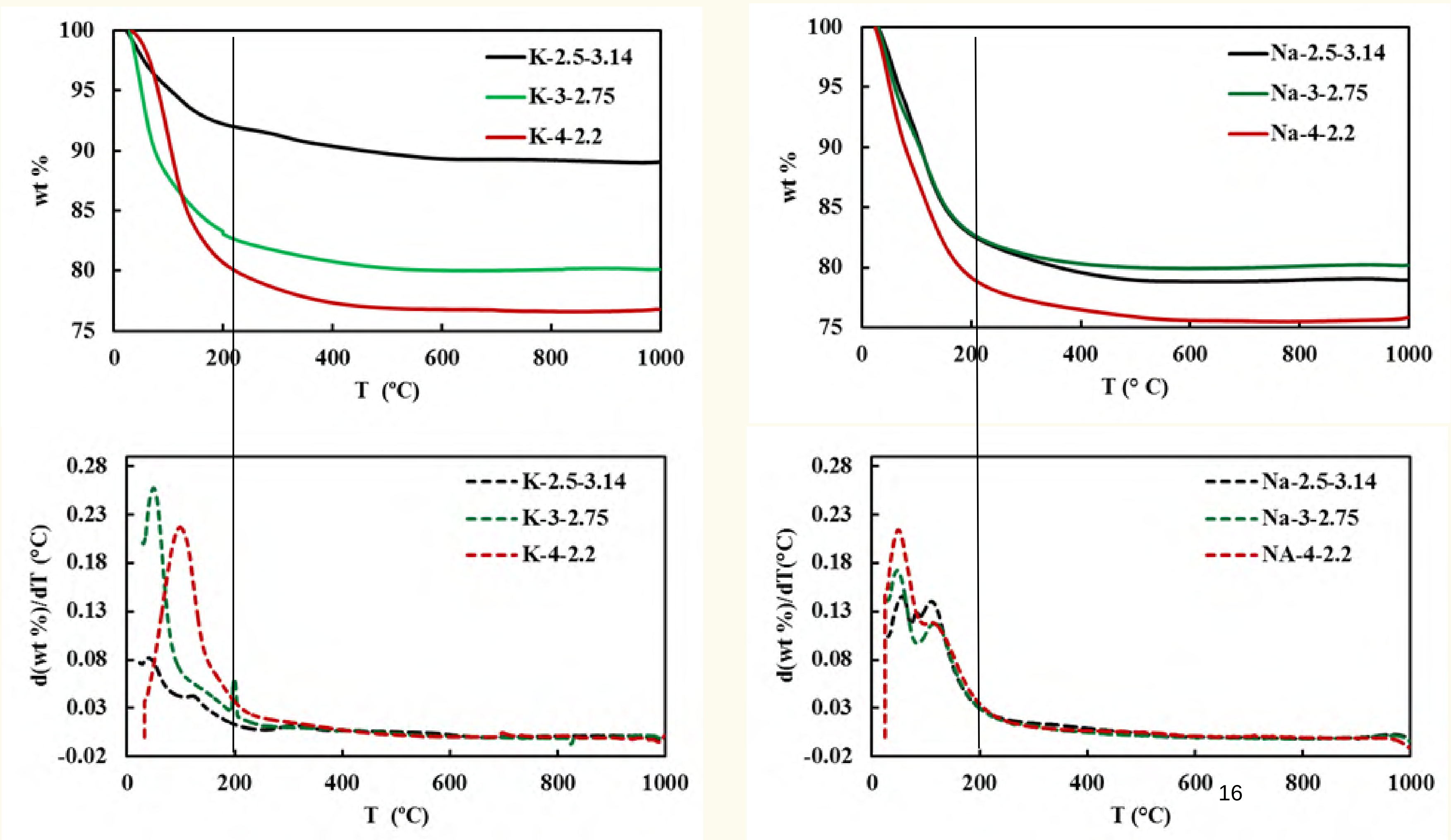




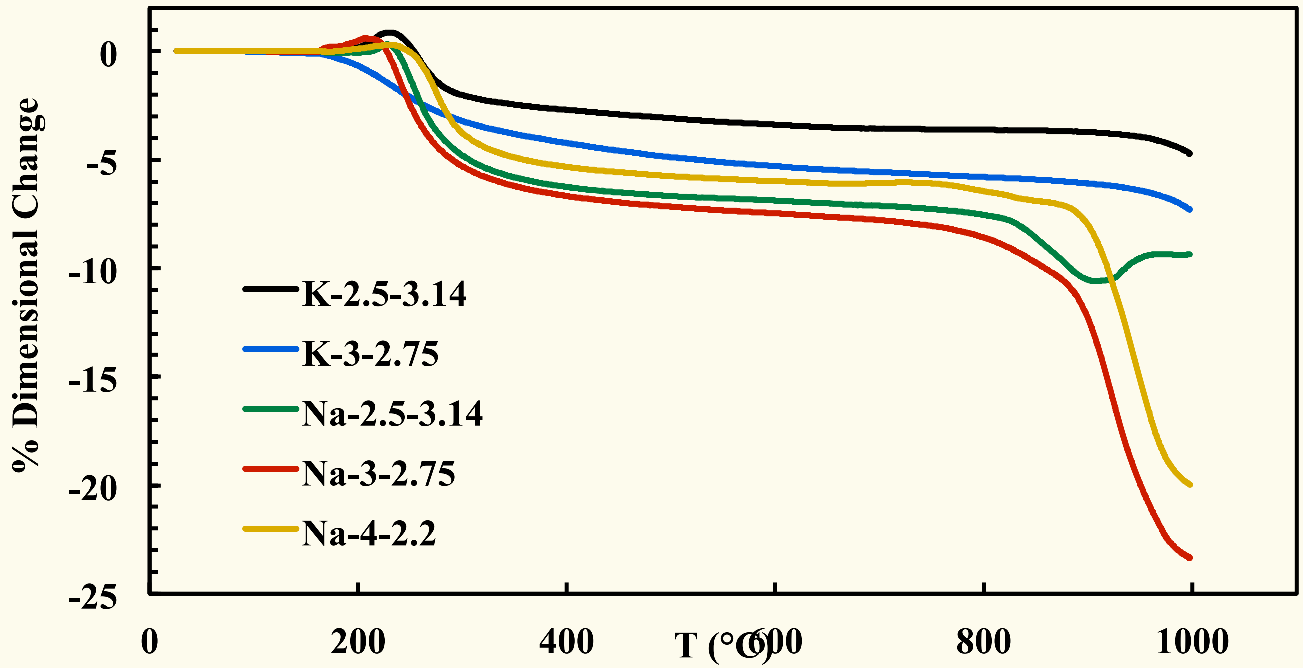


Thermal Characterization - TGA

Most water is lost at T ≤ 200 °C

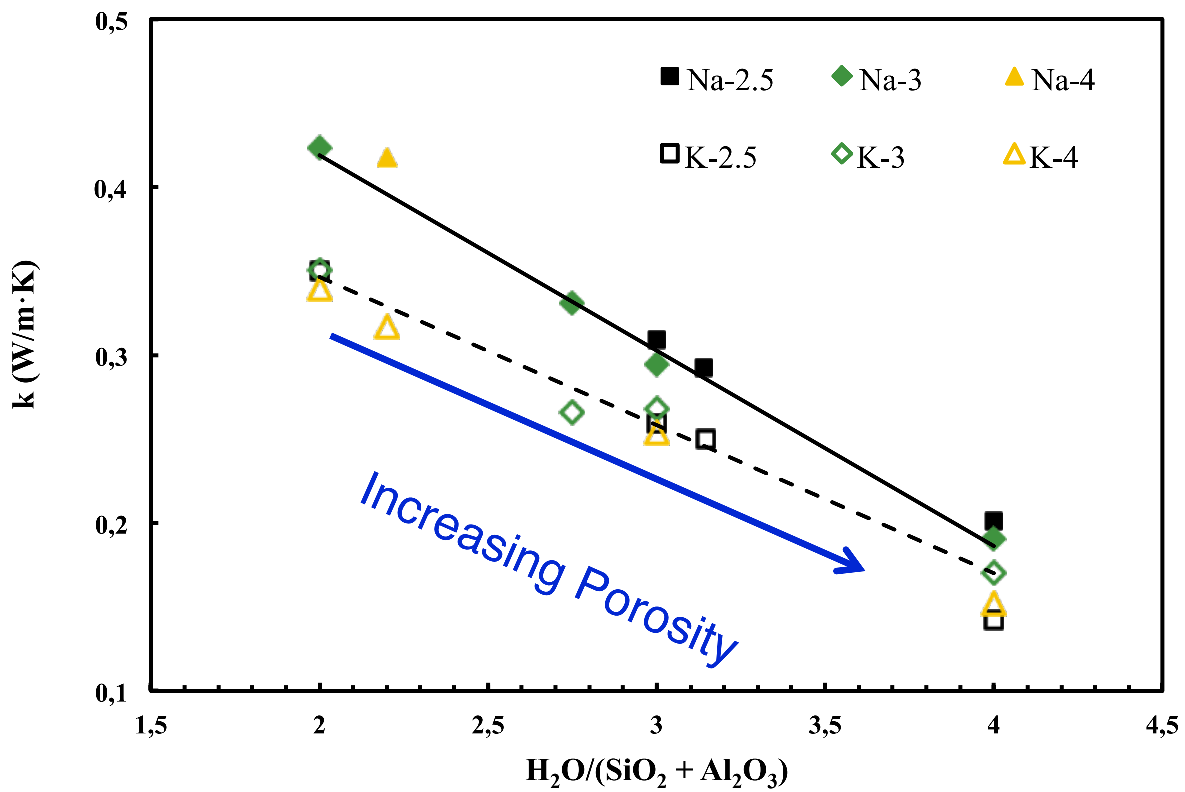


Thermal Characterization - TMA



- Aging may minimize dimensional changes
- Dimensional changes of 3% to 20% reported in literature

Thermal Characterization - Thermal Conductivity

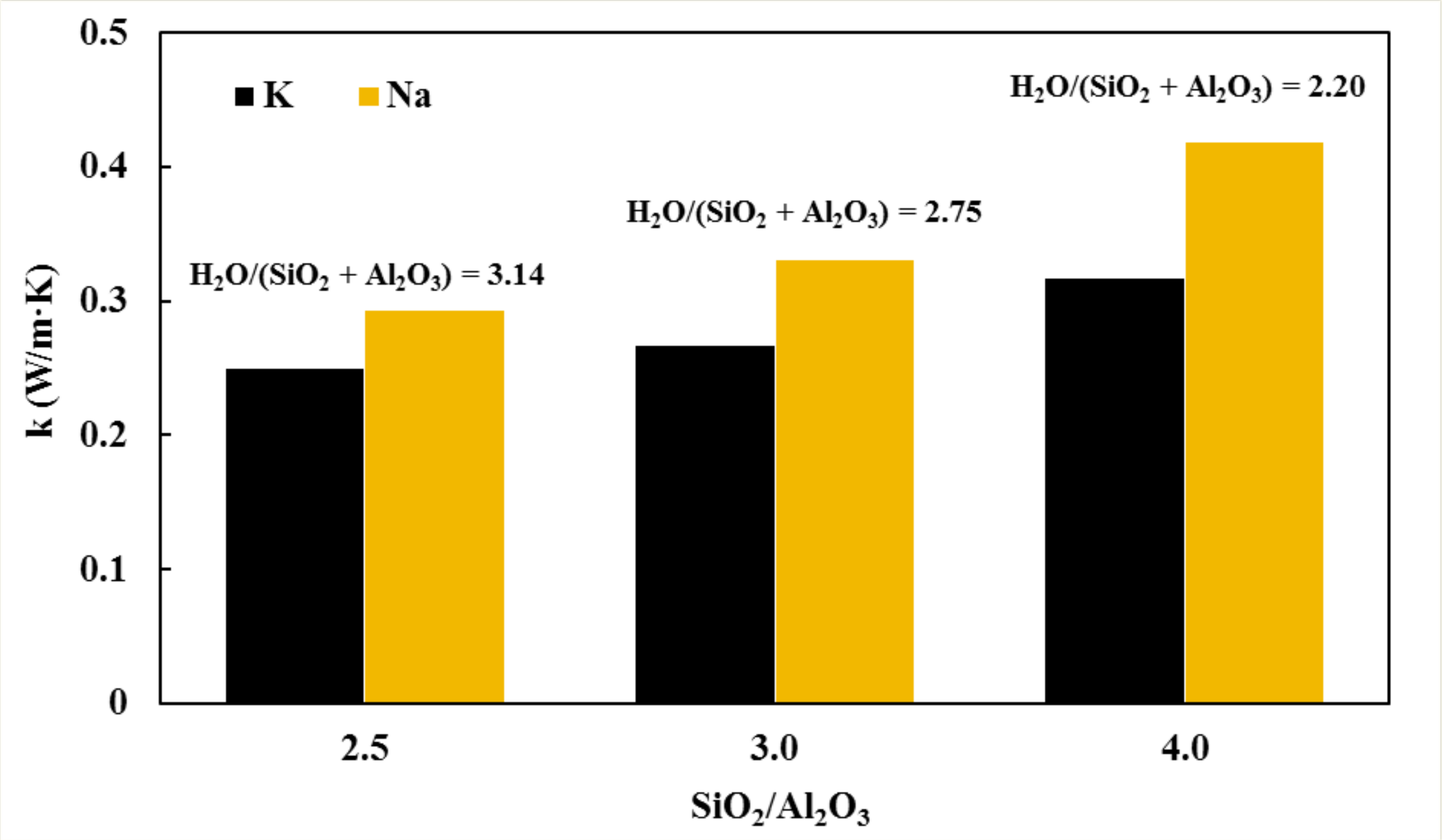


At Room Temperature

Increased porosity governs thermal conductivity.

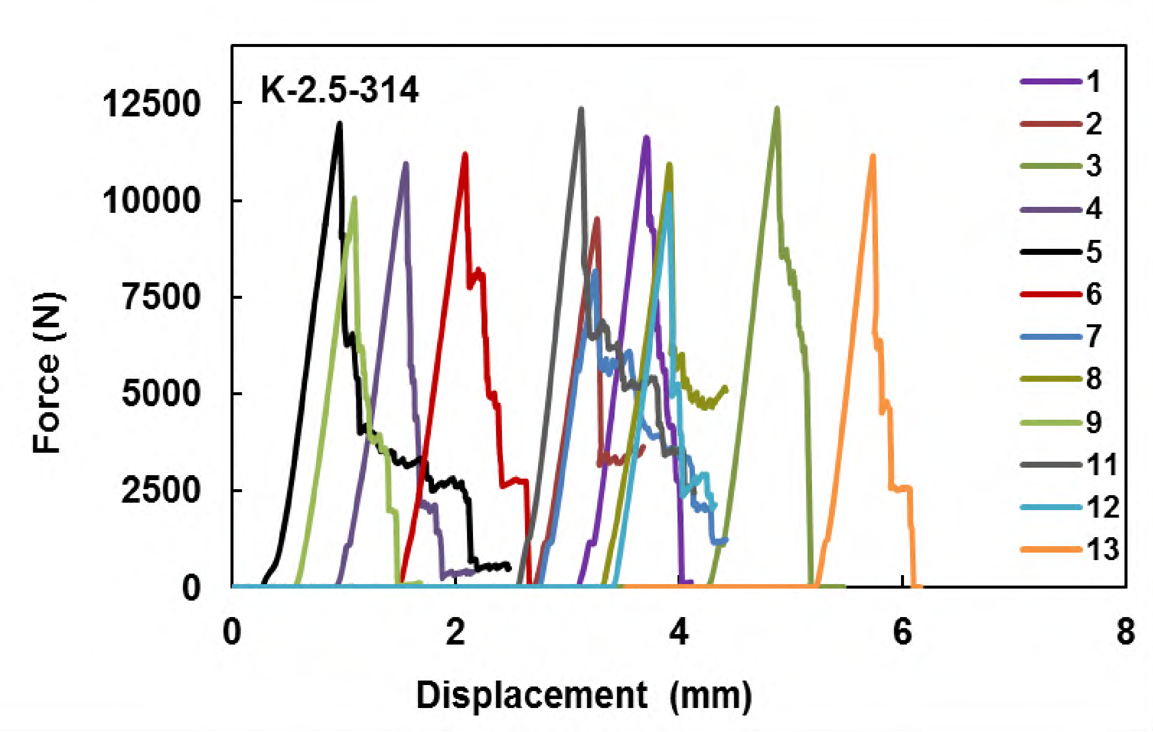
Si content does not play a role in thermal conductivity.

Thermal Conductivity $H_2O/Al_2O_3 = 11$

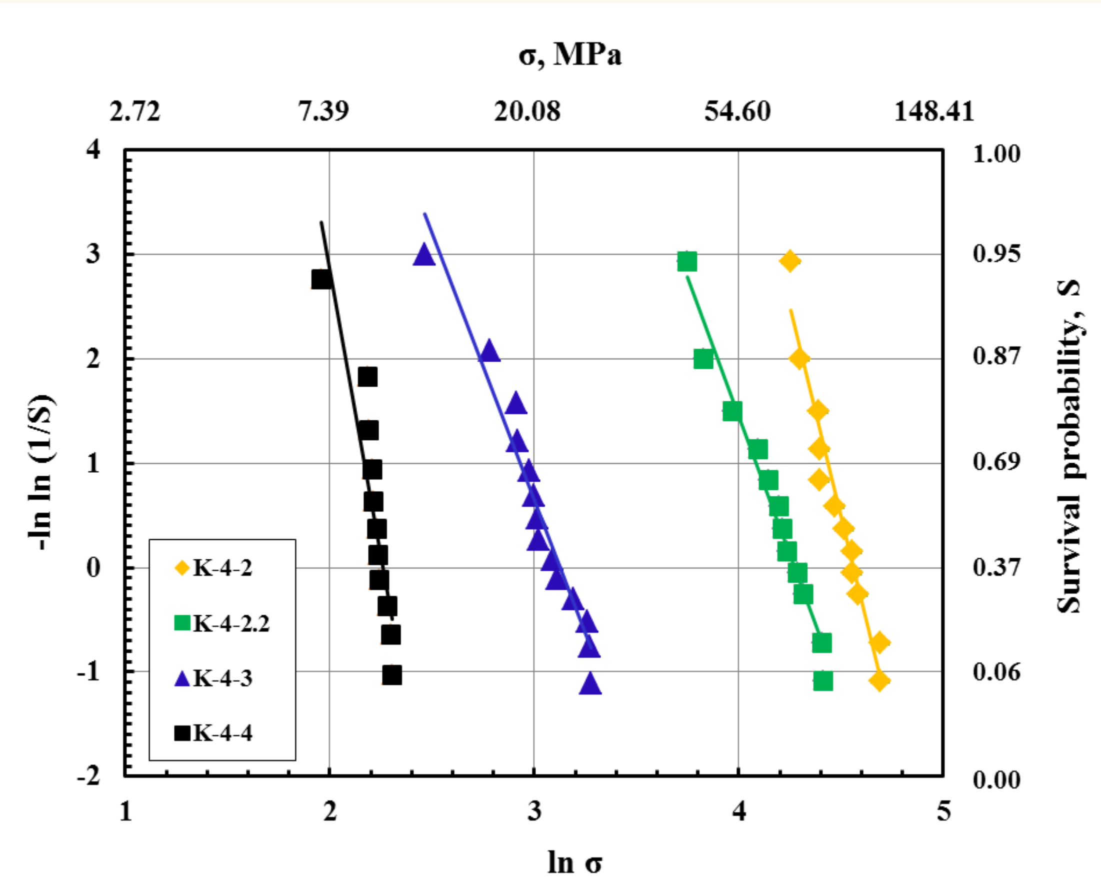


Increasing thermal conductivity with increasing Si content gives misconception that SiO_2/Al_2O_3 is the governing mechanism

Mechanical Properties
Compressive strength

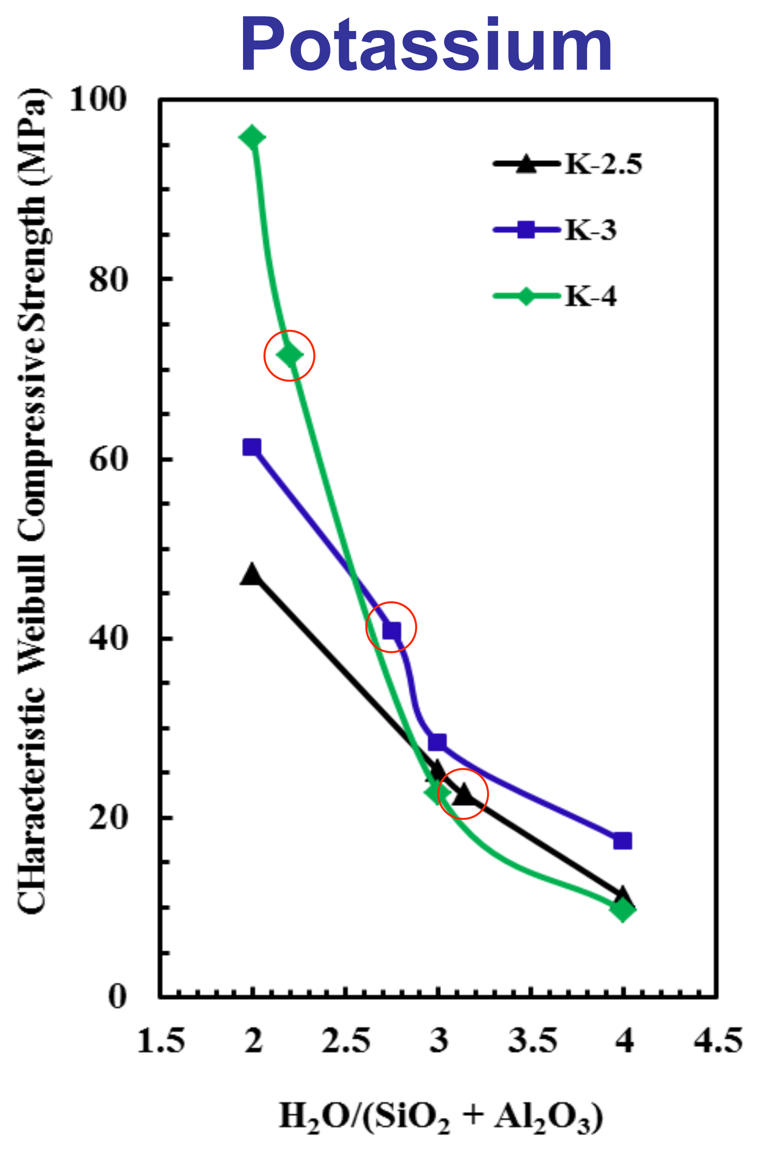


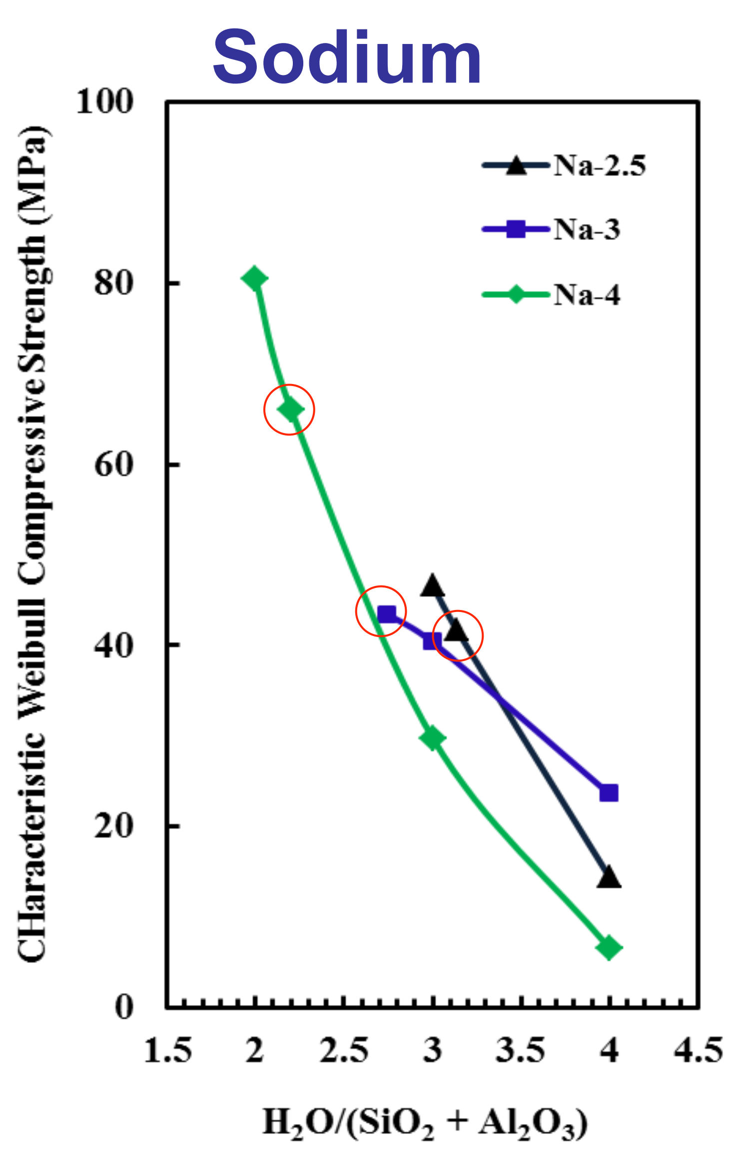
Mechanical Properties
Compressive strength



Sample	Characteristic	Weibull
	Characteristic strength (MPa)	Weibull Modulus
K-4-2	**95.80**	**7.98**
K-4-2.2	79.49	5.31
k-4-3	22.74	5.10
K-4-4	9.6	10.97

Mechanical Properties Compressive strength





Summary

- Water is the governing factor in density and porosity.
- Residual Water after ageing (setting) : 6-10% K-GPs 15-20% Na=GPs
- Si content does not have significant impact on density.
- Aging is an important processing step for full geopolymerization.
- $H_2O/(SiO_2 + Al_2O_3)$ ratio governs thermal conductivity and a lesser degree the activation ion (Na or K).
- SiO_2/Al_2O_3 has no effect on thermal conductivity.
- Compressive strengths strongly affected by $H_2O/(SiO_2 + Al_2O_3)$ especially at high $H_2O/(SiO_2 + Al_2O_3)$
- Thermal and mechanical properties of GPs can be easily altered simply by using different amounts of water in preparing activated solutions.

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