AALBORG UNIVERSITY

Synthesis and Characterization of Silicate Polymers

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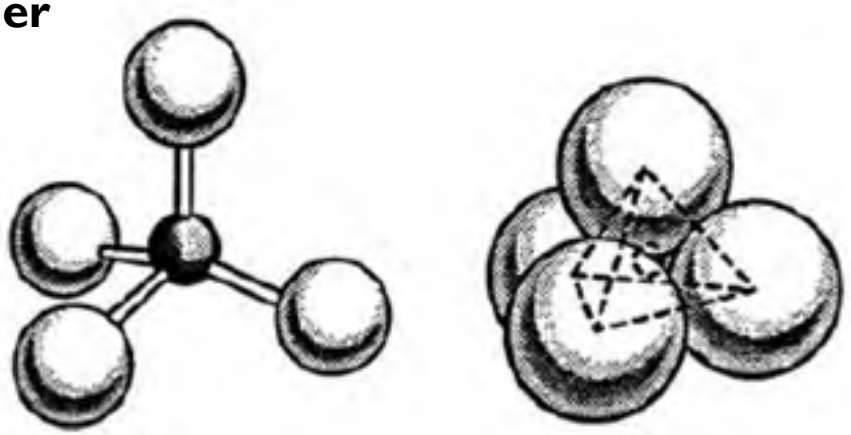
Outline of the presentation

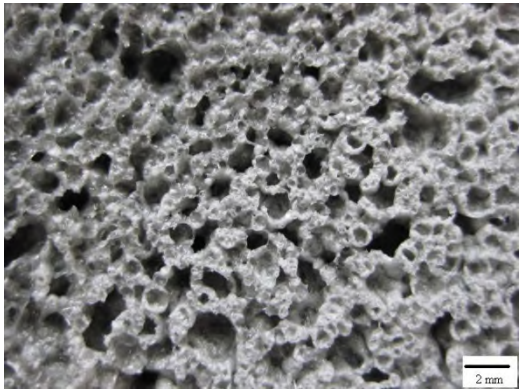
Synthesis of the silicate polymer
- Sol-gel process and
- possible reactions for the dissolution

Characterization of the silicate polymer
- pH measurement
- Viscosity investigation
- SEM analysis
- Compressive strength
- FT-IR investigations
- XRD analysis
- XPS analysis
- Thermal analysis
- Si^{89} –NMR analysis
- ESI-MS

Concluding remarks



Synthesis of the silicate polymer - applications



The development of the inorganic polymers is a promising technology that may be used in many applications.

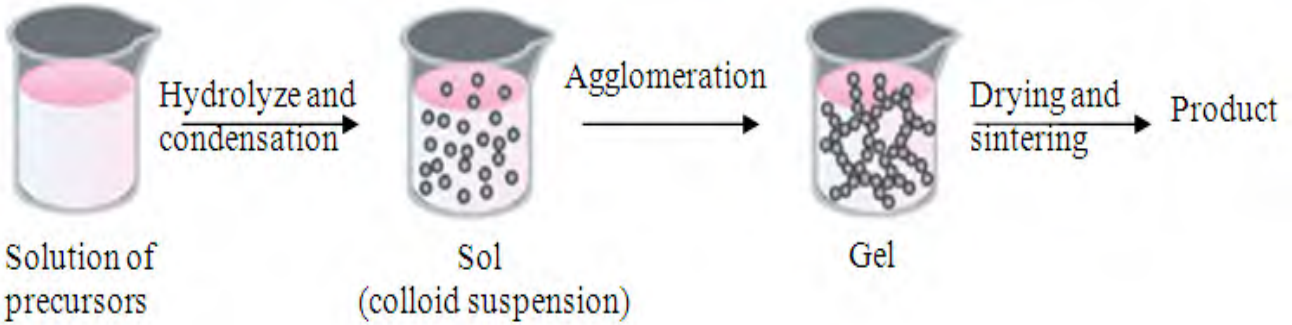
Variation in preparation conditions of the inorganic polymers can result in wide variety of properties, including:

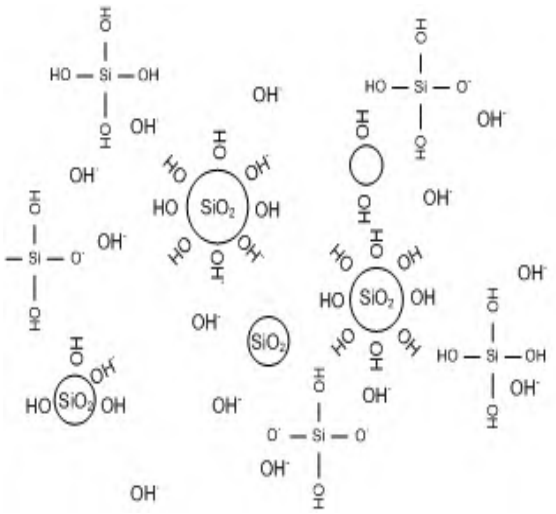
- High compressive strength
- Fire resistance
- Low thermal conductivity

These advantages make inorganic polymers a promising technology for new construction materials.

Synthesis of inorganic silicate polymer

The silicon precursor in the sol-gel process is produced in situ by dissolution of silica particles by KOH





	50_50	55_45	60_40	65_35	70_30	75_25
Microsilica [g]	50	55	60	65	70	75
Water [g]	50	45	40	35	30	25
KOH [g]	11.1	12.1	13.2	14.3	15.4	16.5
Concentration [M]	3.88	4.75	5.82	7.21	9.00	11.65

Synthesis of silicate polymers

The synthesis of the inorganic polymers is thought to be a result of the dissolution of the surface of the amorphous silica particles by hydroxide resulting in formation of soluble silica particles in the solution.

$$SiO_2 + 2H_2O \rightarrow H_4SiO_4 \quad (1)$$

$$SiO_2 + H_2O + OH^- \rightarrow H_3SiO_4^- \quad (2)$$

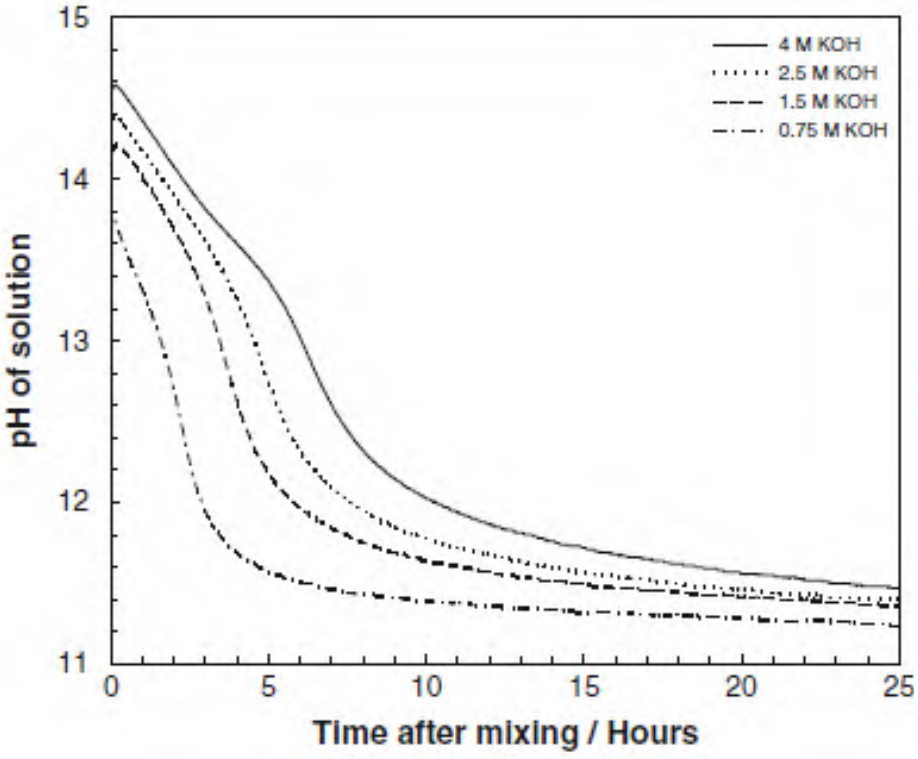
$$H_3SiO_4^- + OH^- \rightarrow H_2SiO_4^{2-} + H_2O \quad (3)$$

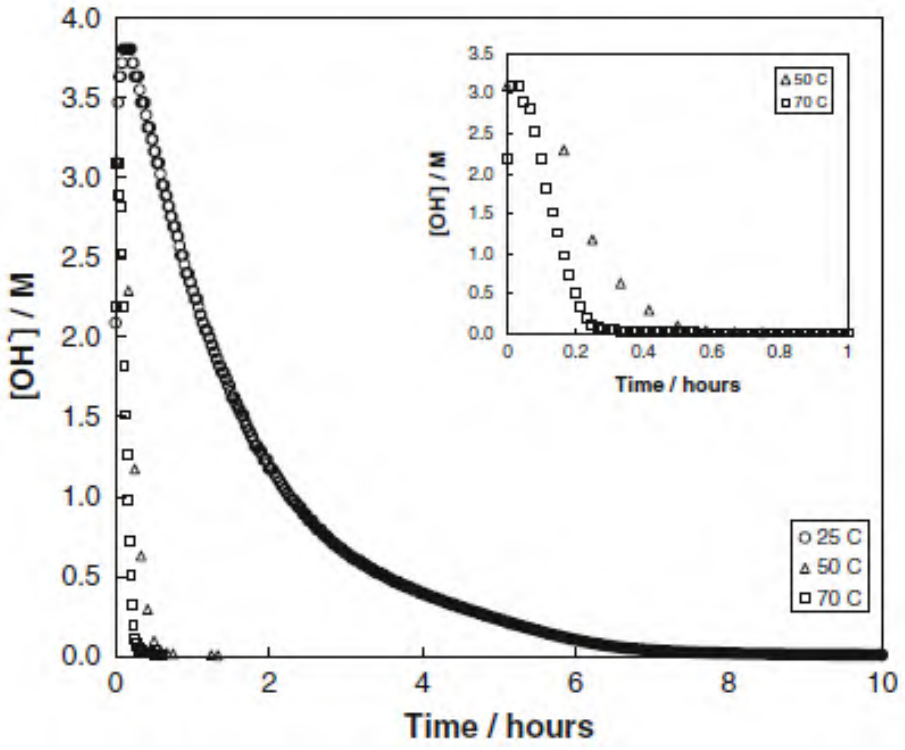
$$SiO_2 + 2OH^- \rightarrow H_2SiO_4^{2-} \quad (4)$$

These reactions suggests that H_2O and OH^- are consumed during the dissolution process resulting in a decrease in pH.

Characterization of silicate polymers – pH measurements

In order to investigate the synthesis of silicate polymer in greater detail pH of the solution was studied during synthesis.





Synthesis and characterization of silicate polymer

Viscosity measurement

Adsorption of OH^- ions of the surface of the silica particles (Negatively charged particles)

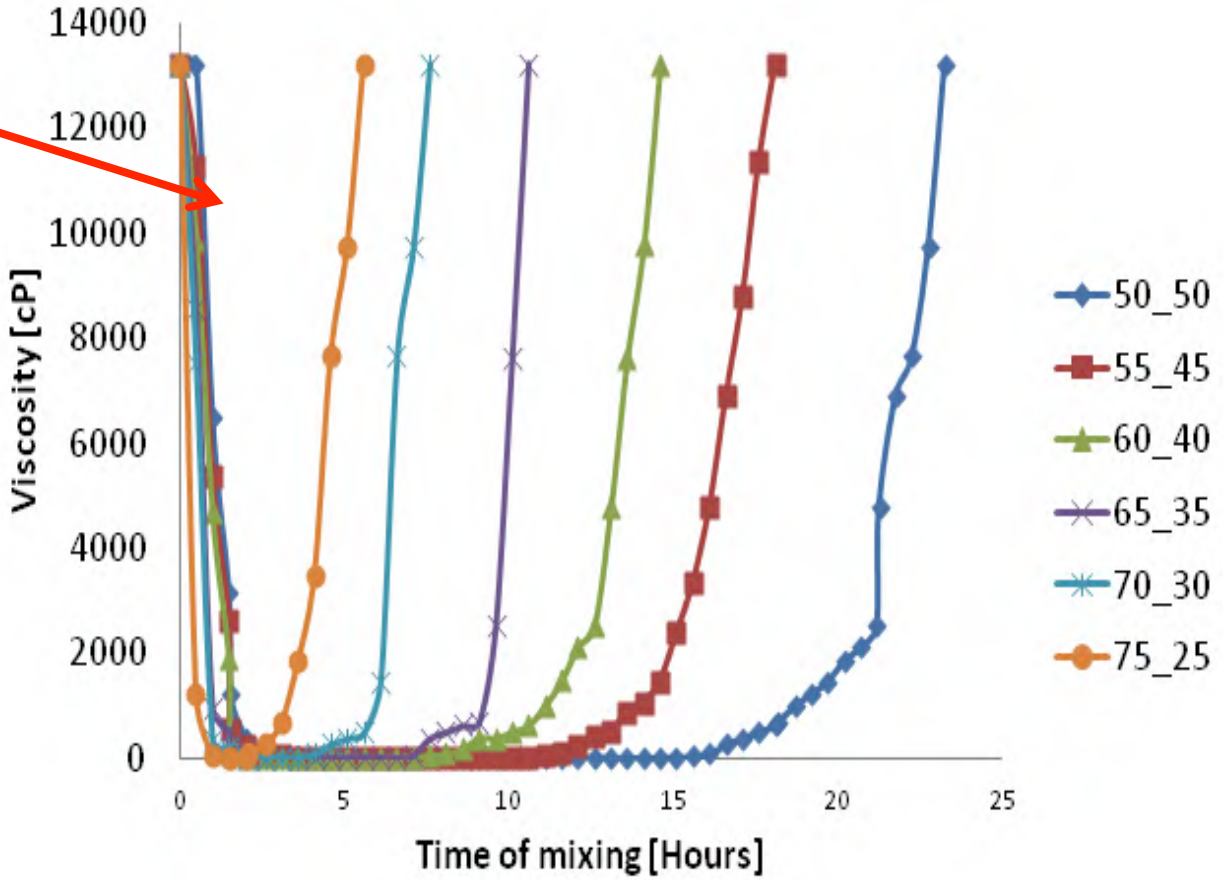
↓

Viscosity decrease (repulsion between particles)

Dissolution of silica particles (Particles decrease in size and number)

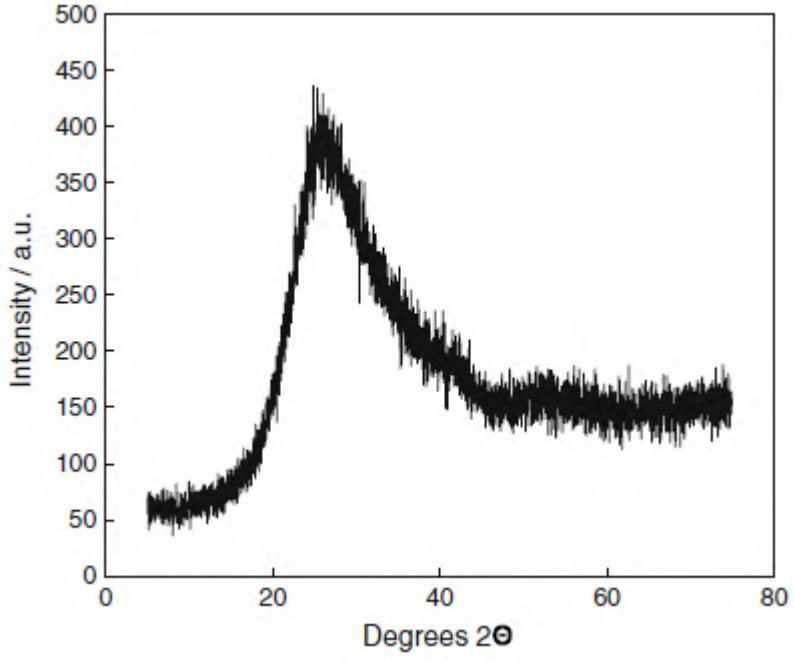
↓

Additional viscosity decrease



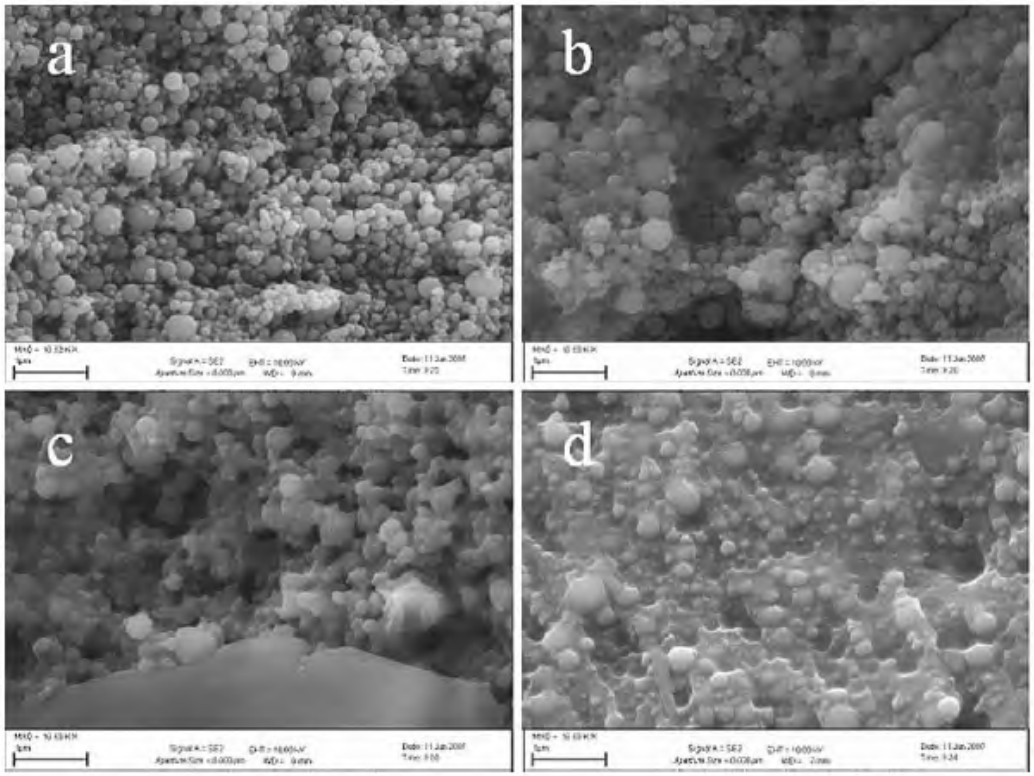
Characterization of silicate polymer – XRD

The silicate polymer is X-ray amorphous, since the main characteristic of the XRD spectra is a featureless bump centered at 20-40 ° 2θ. A typical XRD spectrum is shown in the figure below.



Charaterization of silicate polymer – SEM analysis

SEM images of the inorganic polymers supports the dissolution – gelation model as a significant change in the particle size of the silica particles is observed when different concentrations of hydroxide was used.



a: 0,75 M KOH
b: 1,50 M KOH
c: 2,50 M KOH
d: 4,00 M KOH

Synthesis and characterization of inorganic silicate polymer

Compressive strength

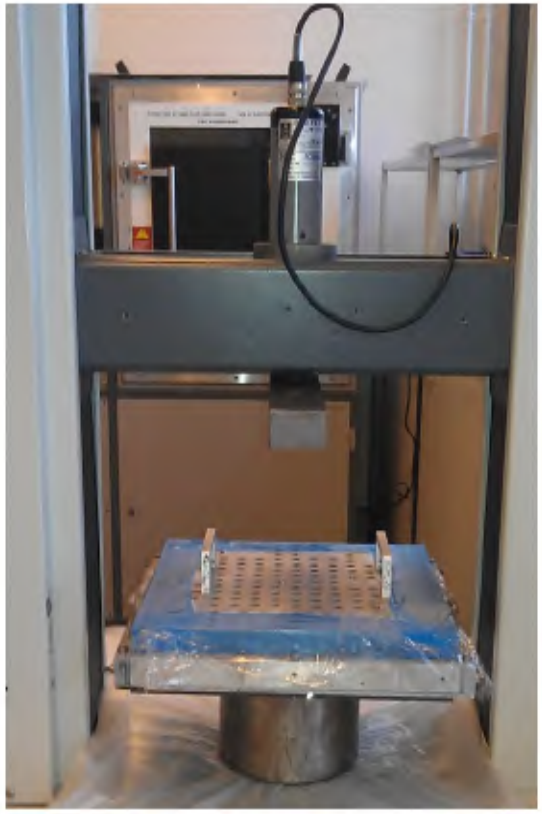
It is the capacity of materials to withstand axially directed pushing forces.
When the limit of the inorganic silicate polymer is reached the material is crushed.

Three different preparation methods were used:

1. silica + alkaline solution
   cast in a mould

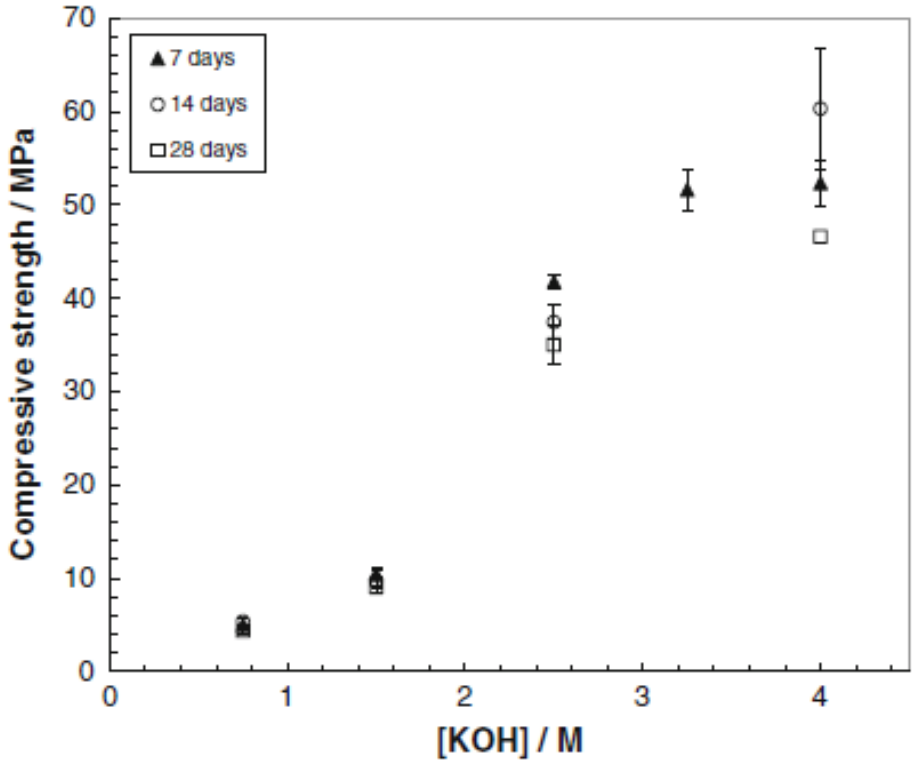
2. silica + alkaline solution
   stirring 4 hours
   cast in a mould

3. silica + alkaline solution
   stirring 4 hours
   adding different materials
   cast in a mould



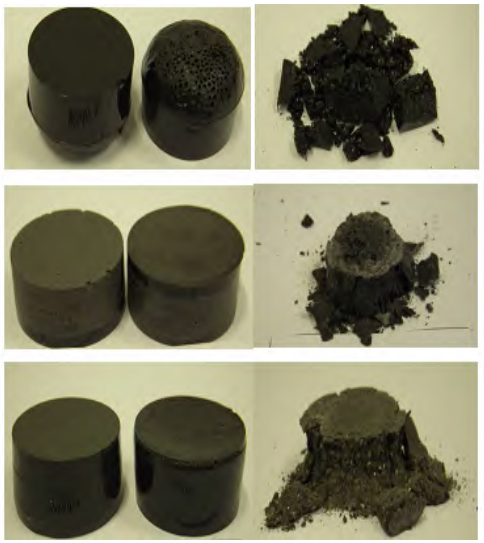
Characterization of silicate polymers – Compressive strength

The results of the compressive strength of the inorganic polymer was strongly related to the concentration of potassium hydroxide used in the synthesis.



Synthesis and characterization of silicate polymer

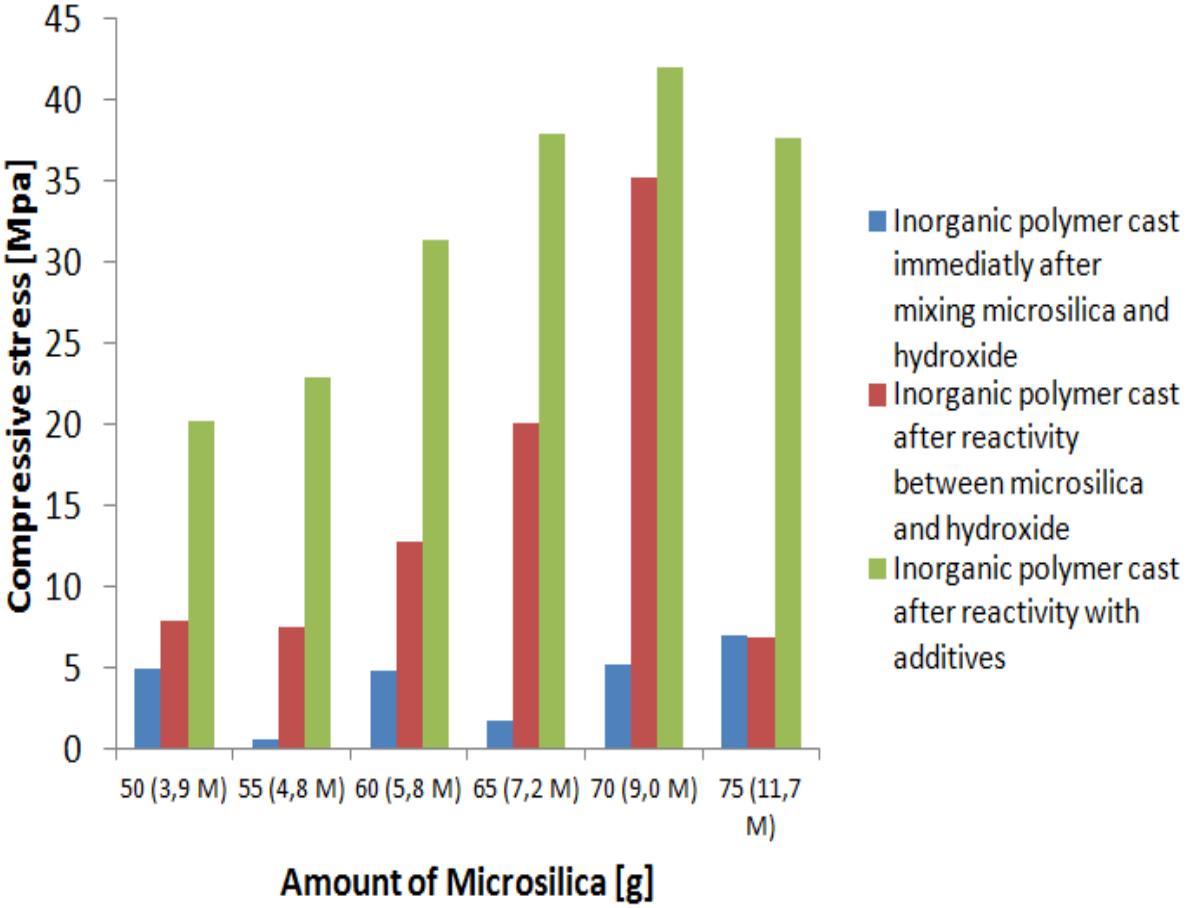
Compressive strength



$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$$

$$Si^0 \rightarrow Si^{4+} + 4e^-$$

$$4H_2O + Si^0 \rightarrow 2H_2 + Si(OH)_4$$

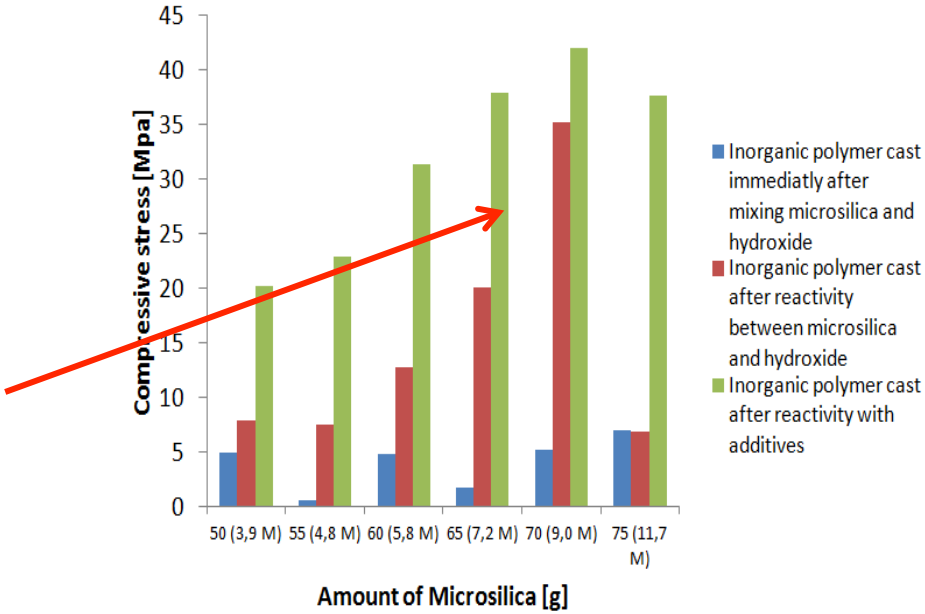


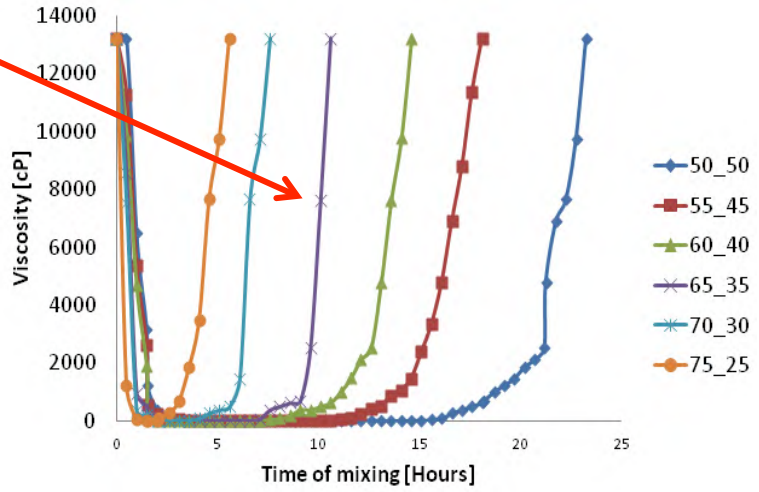
Synthesis and characterization of inorganic silicate polymer

The mixture 65_35 would be the optimal mixture for using as inorganic silicate polymer as binder
The mixture has a relative high compressive strength, especially when different materials are added.

The mixture has a low viscosity for approx. 6 hours.

Thermal investigations of the mixture 65_35 are important for different applications

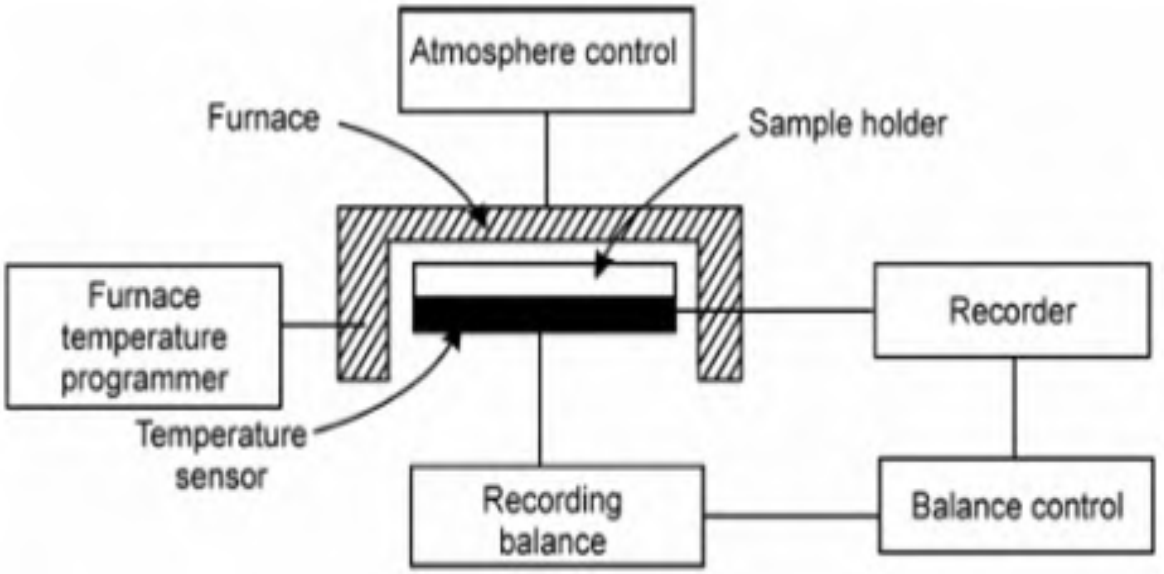




Thermal changes of the inorganic silicate polymer

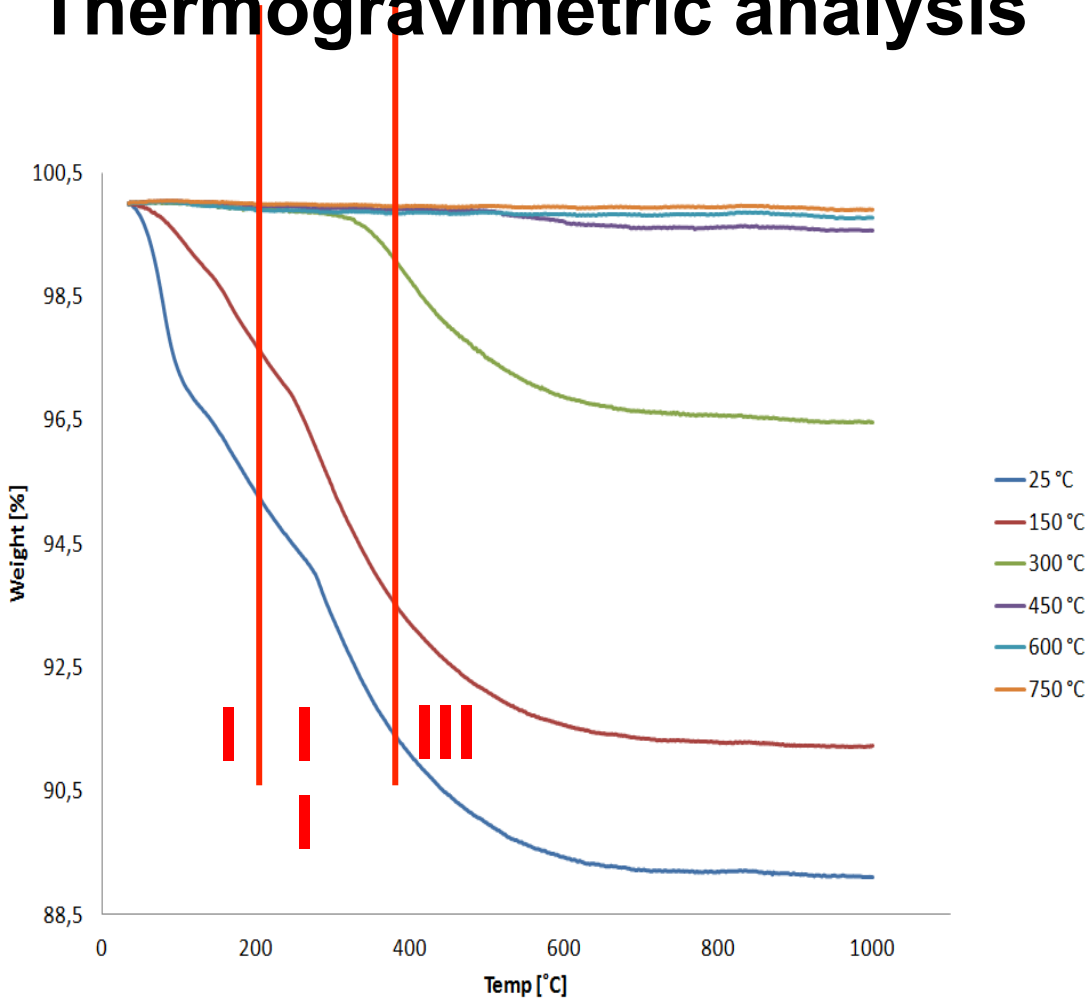
Thermogravimetric analysis (TGA)

TGA is a technique on which a sample weight is monitored as a function of temperature. The sample is subjected to a controlled temp. program in a controlled atm.

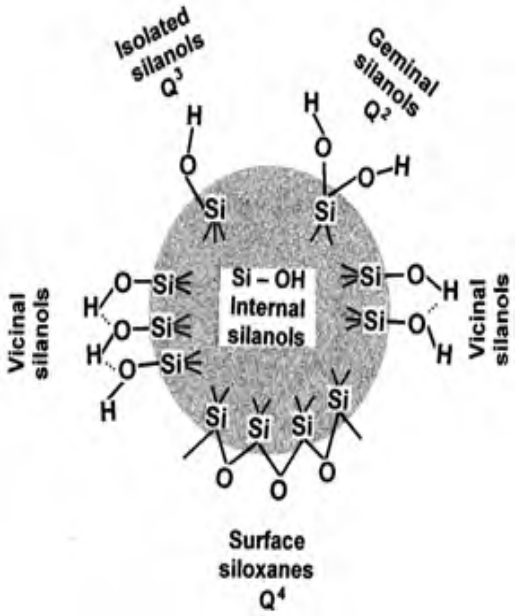


Thermal changes for the inorganic silicate polymer

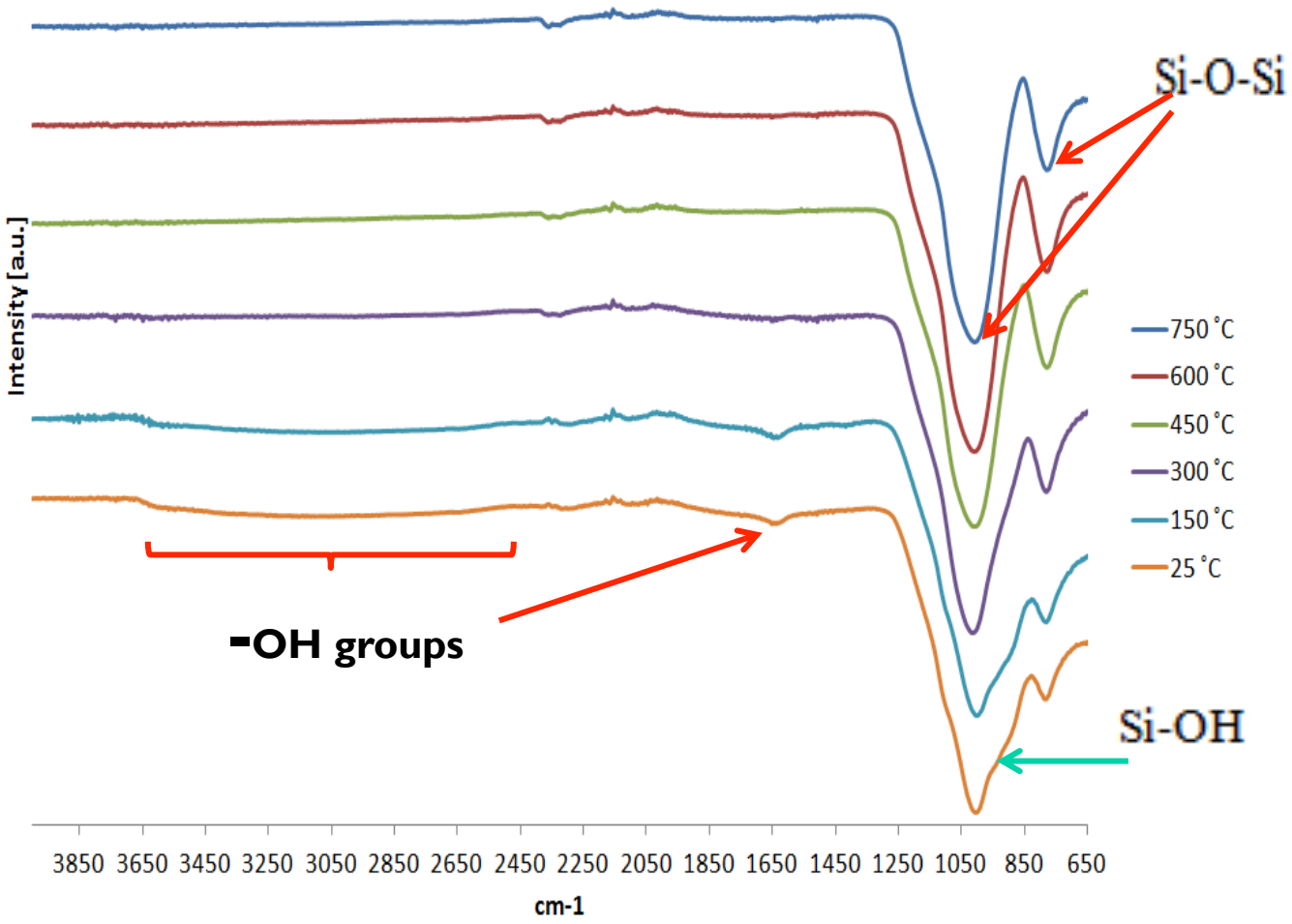
Thermogravimetric analysis



Inorganic silicate polymer:
- **Physically bound water**
- **Chemically bound water**
- **Hydroxyl groups**



FT-IR investigation

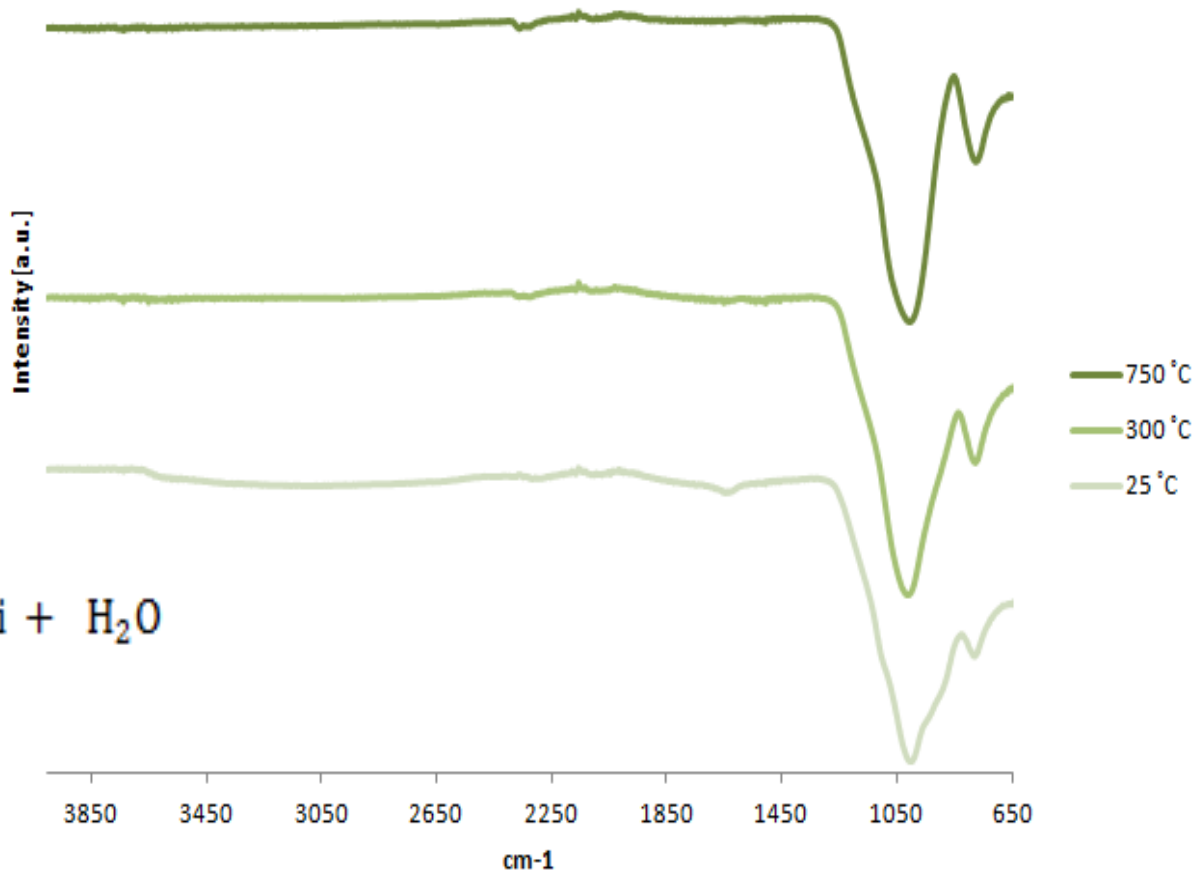


Thermal changes for the inorganic silicate polymer

FT-IR investigation

OH-groups and Si-OH were dimishing with higher temp

Si-O-Si- groups were increasing with higher temp.



$$\text{Si-OH} + \text{Si-OH} \rightarrow \text{Si-O-Si} + H_2O$$

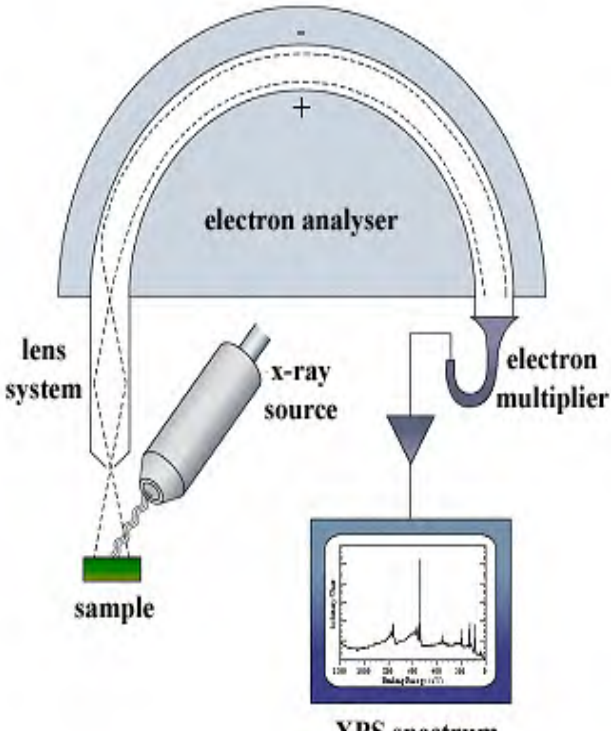
Thermal changes for the inorganic silicate pol

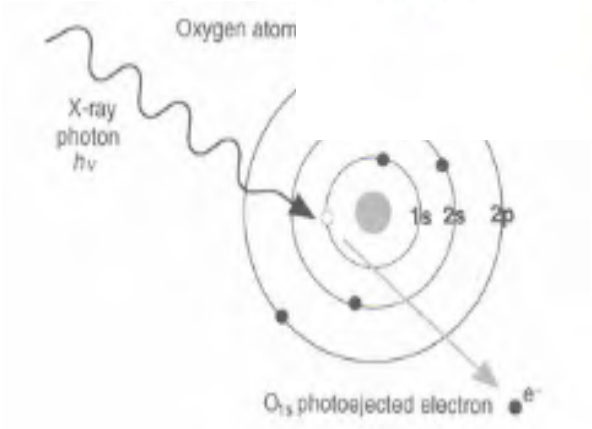
XPS analysis

X-ray photoelectron spectroscopy is used to study the composition and chemical state of a surface.

When the material is bomarbed with X-rays, photoelectrons may be emitted from the topmost surface.

The kinetic energy of the photoelectron is measured by a spectometer.





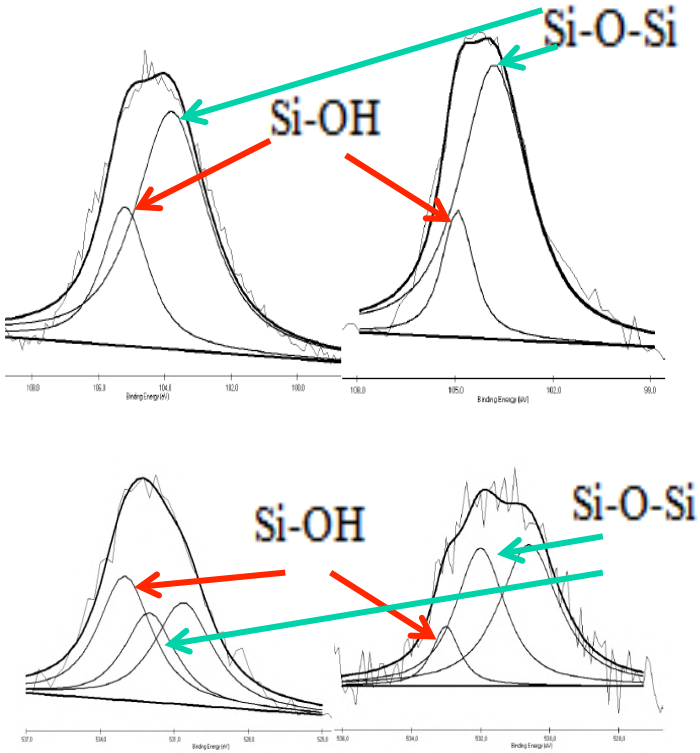
$$E_B = hv - E_K - W$$

Thermal changes for the inorganic silicate polymer

Sample	XPS peak Components	Si 2p	
		Si 2p 1/2 (Si-OH)	Si 2p 3/2 (Si-O-Si)
25 °C	Binding energy	105.2	103.8
	FWHM	1.660	2.600
	Relative content	27.17	72.83
150 °C	Binding energy	105.0	103.8
	FWHM	1.148	2.494
	Relative content	17.65	82.35

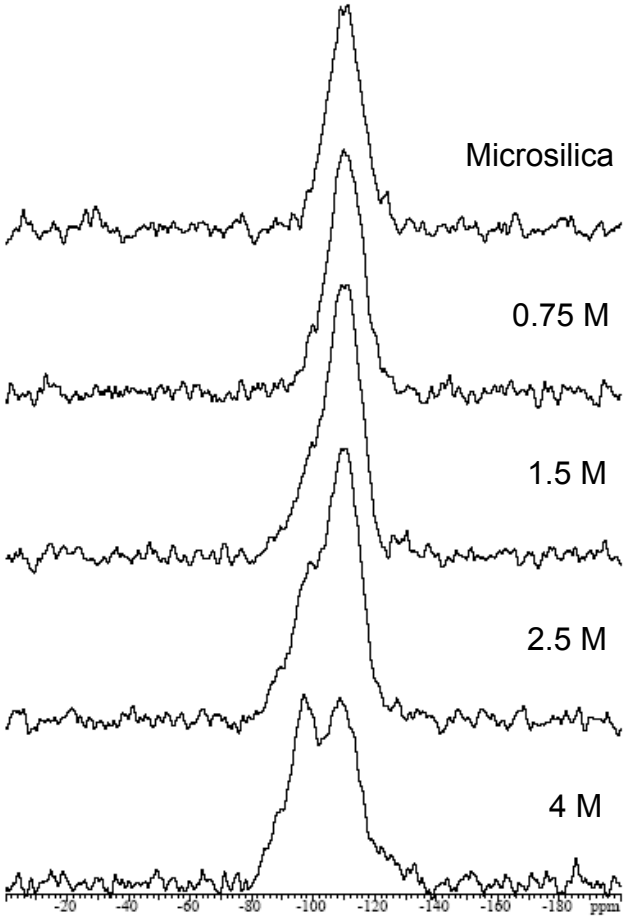
Sample	XPS peak Components	O1s		
		Si-OH	Si-O-Si	Si-O-X
25 °C	Binding energy	533	532	530.63
	FWHM	2.59	2.48	2.81
	Relative content	38.43	27.26	34.31
150 °C	Binding energy	533	532	530.59
	FWHM	0.95	1.69	2.05
	Relative content	9.82	40.23	49.95

25 °C 150 °C

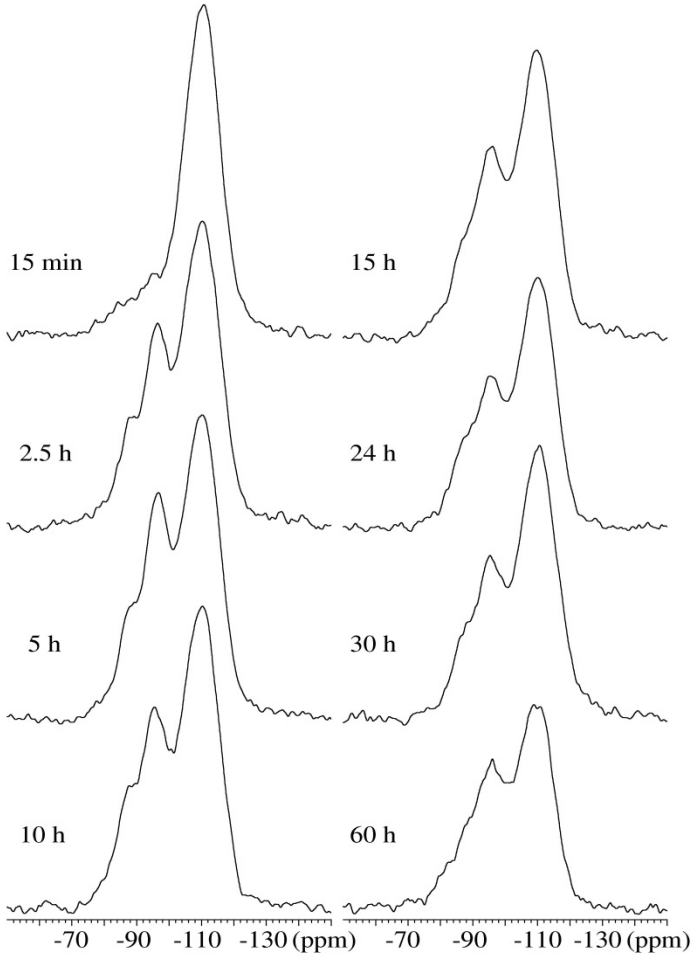


Fitting of Si 2p and O 1s peak showed that Si-OH groups were diminishing and the amount of Si-O-Si groups were increasing

^{29}Si MAS NMR spectra of the inorganic polymers synthesized using different KOH concentrations. The ^{29}Si MAS NMR spectra were recorded using a one pulse experiment on a Varian-INOVA 200 spectrometer (200 MHz, 4.7 T).



^{29}Si MAS NMR spectra' of an inorganic polymer synthesized using 4 M KOH obtained at different times after mixing



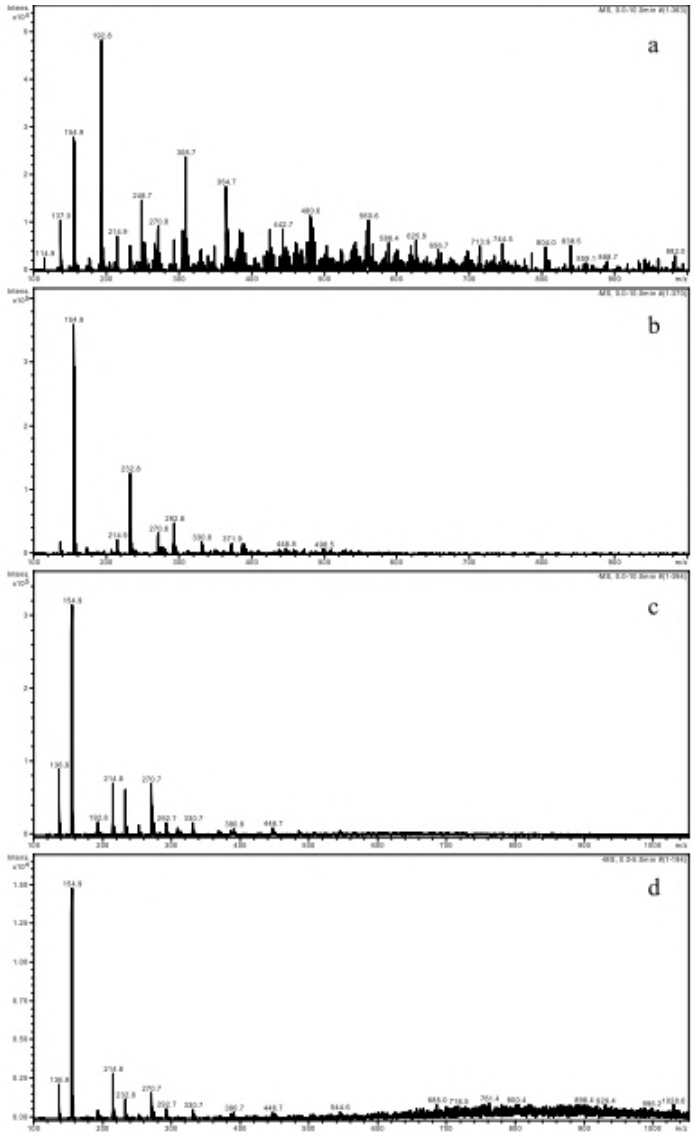
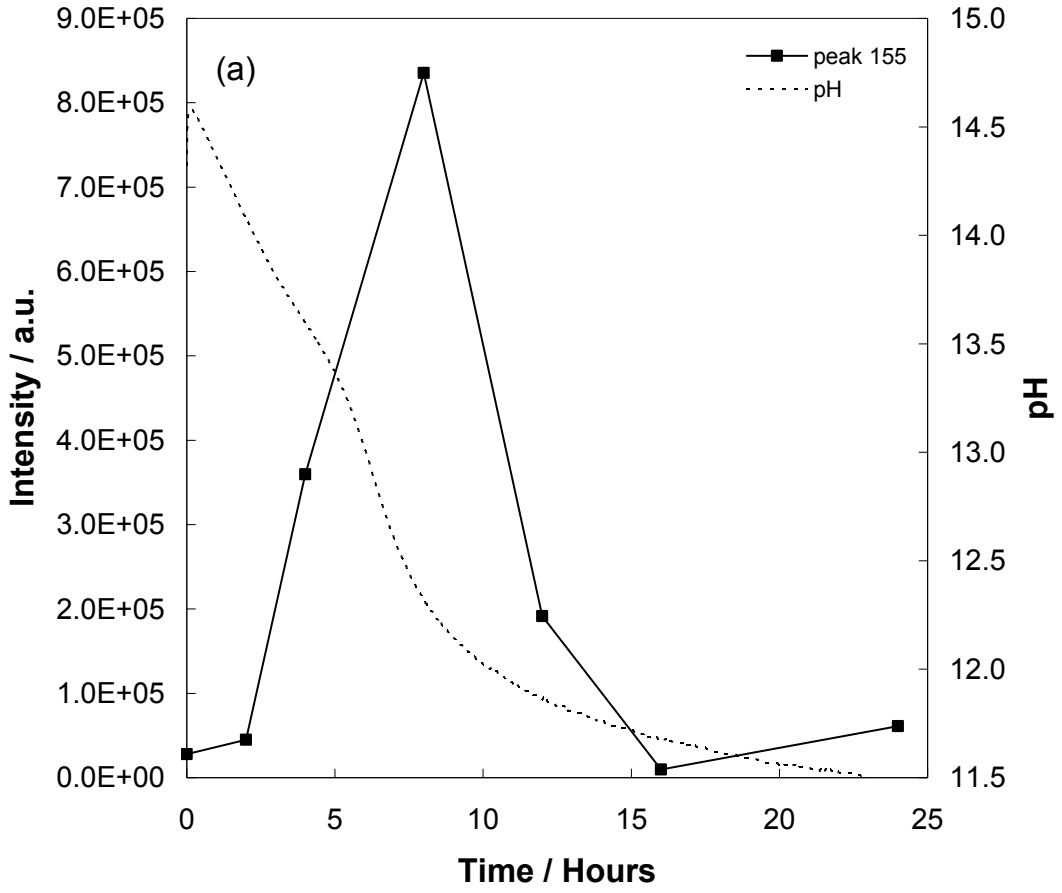


Fig. 1. ESI-MS spectra of the KOH based inorganic polymer reaction solution in negative scanning mode optimized in the spectral region around 500 m/z, a) after 15 min, b) 2 hours, c) 8 hours, and d) after 12 hours of mixing.



Evolution of the intensity of the most dominant molecule ion in the reaction solution of the inorganic polymer synthesized from microsilica and 4 M KOH. Reprinted with permissions from Elsevier (Original printed in Simonsen et al., Inter J Mass Spec (2009) 1-2, 78-85). Copyright 2009 Elsevier.

Table 1. Identified molecule ions in the reaction solution of KOH based inorganic polymers in negative scanning mode. – H_2O denotes dehydroxylation resulting in the formation of an oxo group.

Nr.	m/z	Compound	Intensity	Possible structures
1	77	$SiO_2(OH)^-$	< 5	• - 1 H_2O
2	95	$SiO(OH)_3^-$	< 5	•
3	137	$Si_2O_4(OH)^-$	29	— - 2 H_2O
4	155	$Si_2O_3(OH)_3^-$	100	— - 1 H_2O
5	173	$Si_2O_2(OH)_5^-$	< 5	—
6	193	$Si_2O_3(OK)(OH)_2^-$	5	— - 1 H_2O
7	215	$Si_3O_5(OH)_3^-$	24	△ - 1 H_2O ⌒ - 2 H_2O
8	233	$Si_3O_4(OH)_5^-$	22	△ ⌒ - 1 H_2O
9	249	$Si_2O_2(OK)_2(OH)_3^-$	< 5	—
10	253	$Si_3O_5(OK)(OH)_2^-$	< 5	△ - 1 H_2O ⌒ - 2 H_2O
11	271	$Si_3O_4(OK)(OH)_4^-$	22	△ ⌒ - 1 H_2O
12	275	$Si_4O_7(OH)_3^-$	< 5	□ - 2 H_2O ⏃ - 2 H_2O ∿ - 3 H_2O
13	293	$Si_4O_6(OH)_5^-$	6	□ - 1 H_2O ⏃ - 1 H_2O ∿ - 2 H_2O
14	309	$Si_3O_4(OK)_2(OH)_3^-$	< 5	△ ⌒ - 1 H_2O
15	331	$Si_4O_6(OK)(OH)_4^-$	6	□ - 1 H_2O ⏃ - 1 H_2O ∿ - 2 H_2O
16	371	$Si_5O_7(OH)_7^-$	< 5	
17	387	$Si_4O_5(OK)_2(OH)_5^-$	< 5	□ ⏃ ∿ - 1 H_2O
18	391	$Si_5O_8(OK)(OH)_4^-$	< 5	
19	425	$Si_4O_5(OK)_3(OH)_4^-$	< 5	□ ⏃ ∿ - 1 H_2O
20	443	$Si_4O_4(OK)_3(OH)_6^-$	< 5	∿
21	447	$Si_5O_7(OK)_2(OH)_5^-$	< 5	
22	481	$Si_4O_4(OK)_4(OH)_5^-$	< 5	∿

Concluding remarks

The synthesis of the inorganic binder is a result of dissolution of the surface of the amorphous silica by hydroxide resulting in formation of soluble silica species (oligomers).

The formation of soluble silica species results also in a decrease in the viscosity due to: Adsorption of OH^- ions on the surface of the silica particles resulting in negatively charged particles. Dissolution of the silica particles causes the particles to decrease in size and number.

Gel-formation due to oligomers turning into polymers could increase viscosity and results in the important increased compressive strength

The results of the compressive strength of the inorganic polymer was strongly related to the concentration of potassium hydroxide used in the synthesis.

FT-IR investigation of the silicate polymers showed that an increase in the hydroxide concentration used in the synthesis shifts the position toward lower wave numbes, Indicating the transformation of Q^4 units to Q^3 and Q^2 units.

Thermal investigations showed that already dried samples could decrease their amounts of physically and chemically bound water as well as surface hydroxyl groups at higher temperature

The silicate polymer is X-ray amorphous, since the main characteristic of the XRD spectra is a featureless bump centered at 20-40 ° 2θ.