

Synthesis and Characterization of Silicate Polymers

By Camilla G. Sønderby*, Morten E. Simonsen and Erik G. Søgaard



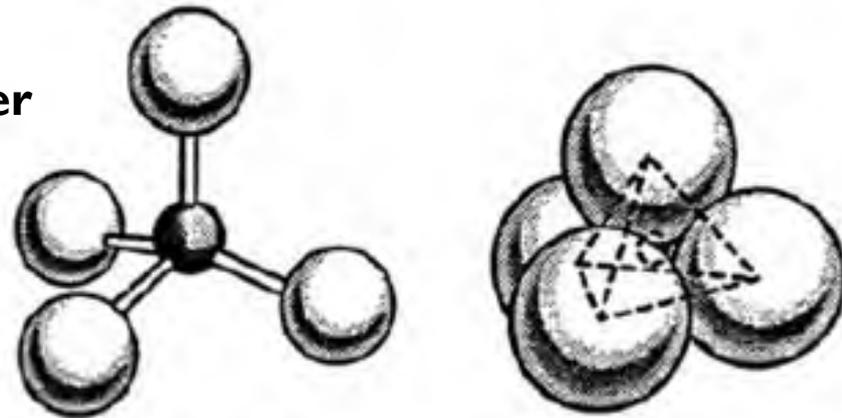
Outline of the presentation

Synthesis of the silicate polymer

Application for the silicate polymer
sol-gel process
possible reactions for the dissolution

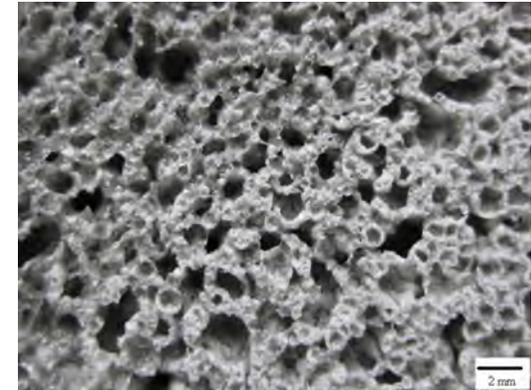
Charaterization of the silicate polymer

pH measurement
Viscosity investigation
SEM analysis
Compressive strength
FT-IR investigations
XRD analysis



Concluding remarks

Synthesis of the silicate polymer - applications



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

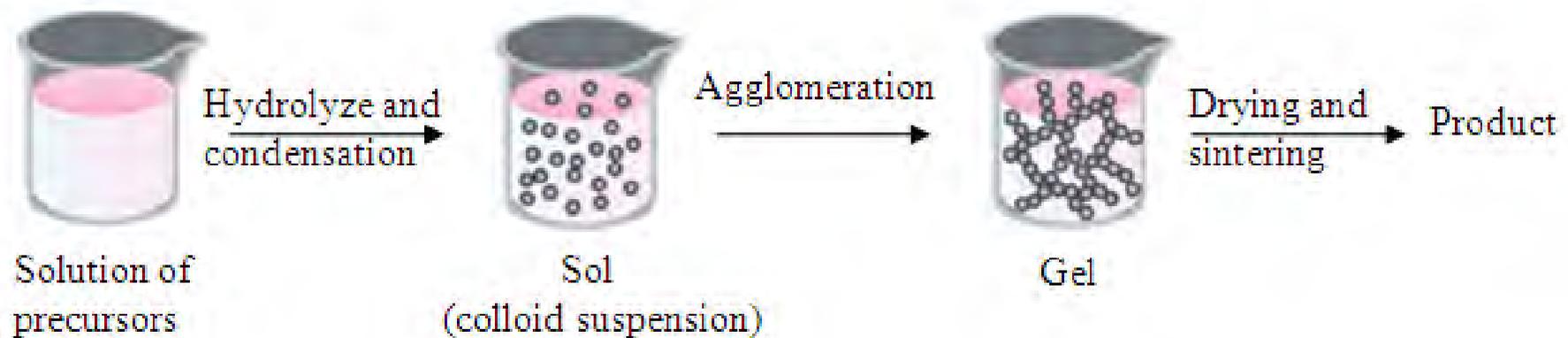
Variation in preparation conditions of the inorganic polymers can result in wide variety of properties, including:

- High compressive strength
- Fire resistance
- Low thermal conductivity

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

Synthesis of silicate polymers

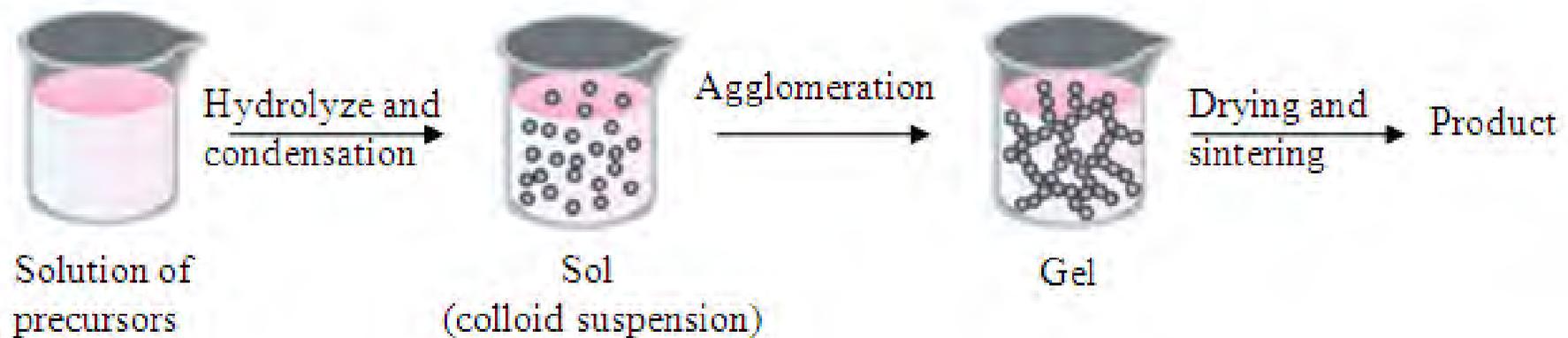
The inorganic polymer is made from a sol-gel route.



In general, the sol-gel process involves the transition of a system from a liquid or sol (colloidal suspension) into a solid gel phase.

Synthesis of silicate polymers

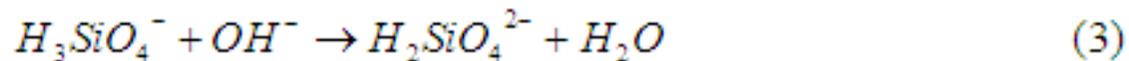
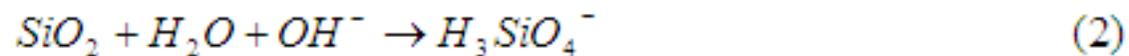
The inorganic polymer is made from a sol-gel route.



Synthesis of the silicate polymer is made from amorphous silica in alkaline solution. In this investigation the polymers were made by mixing 200 g amorphous silica with 200 mL of concentrated solution of potassium hydroxide (0,75- 4,0 M)

Synthesis of silicate polymers

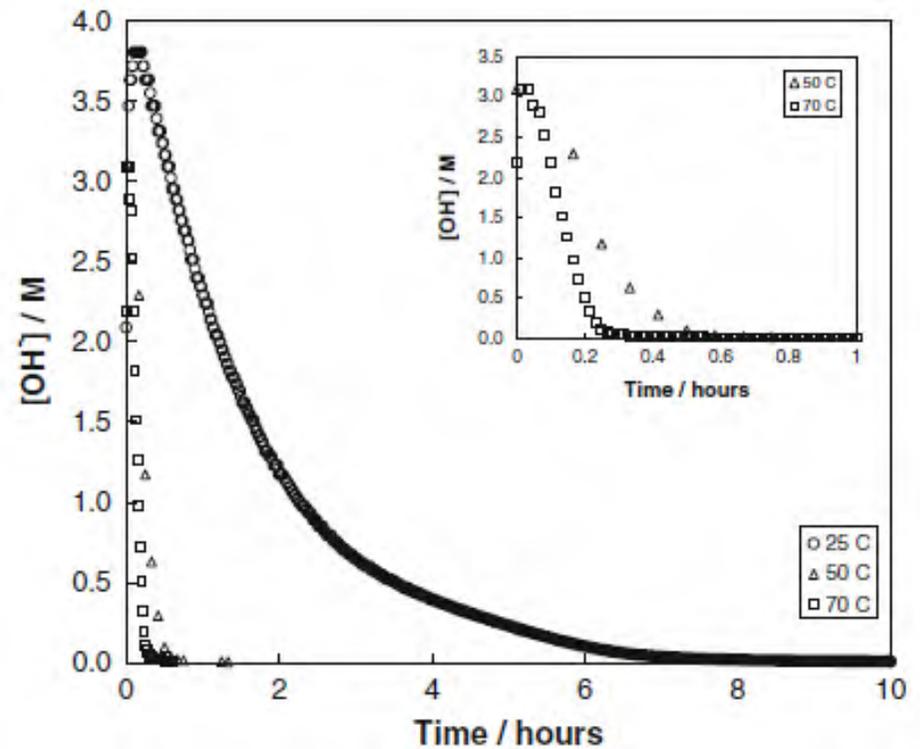
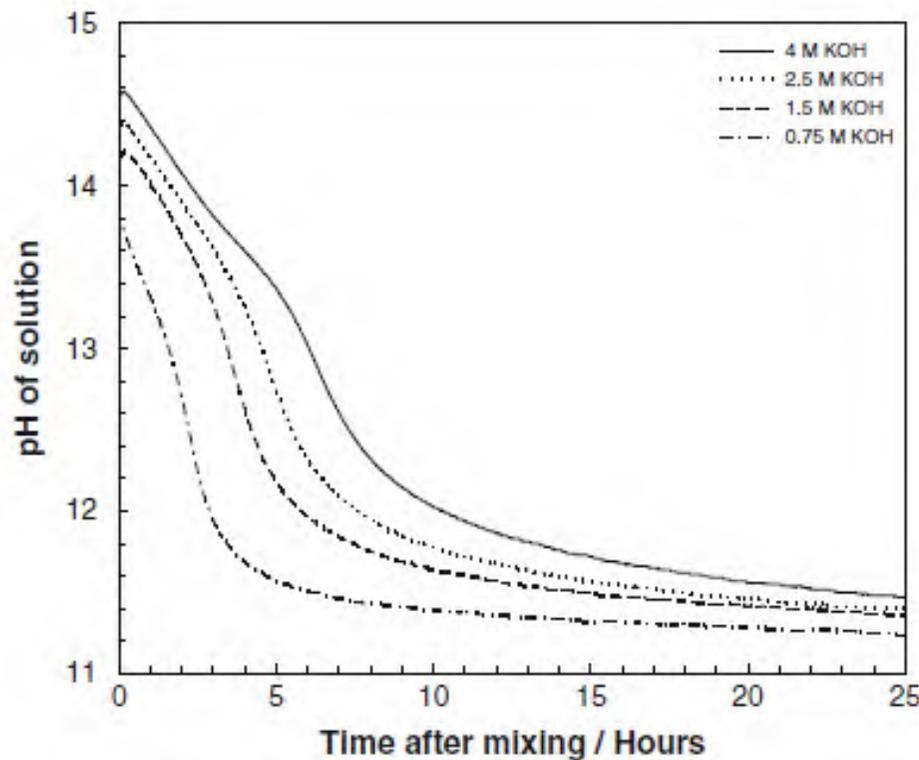
The synthesis of the inorganic polymers is thought to be a result of the dissolution of the surface of the amorphous silica particles by hydroxide resulting in formation of soluble silica particles in the solution.



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

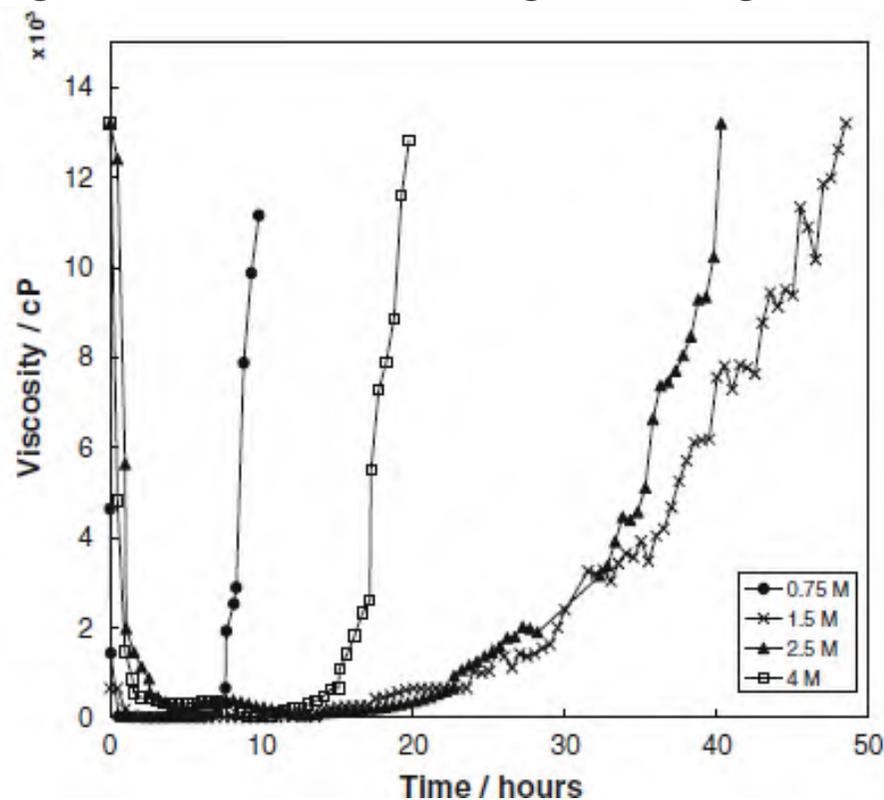
Characterization of silicate polymers – pH measurements

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



Charaterization of silicate polymer – viscosity

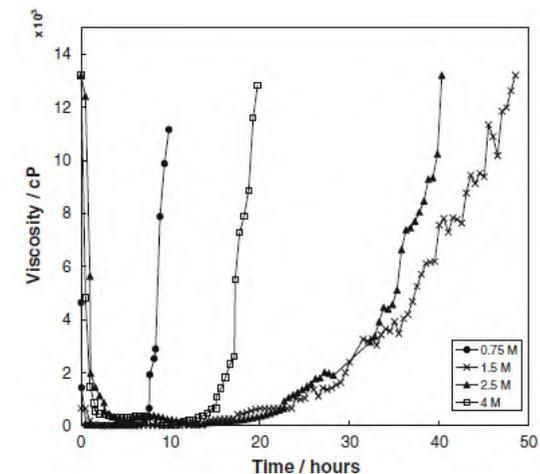
The viscosity development during the synthesis of the inorganic polymers was investigated during both the dissolution stage and the gelation state.



Charaterization of silicate polymer - viscosity

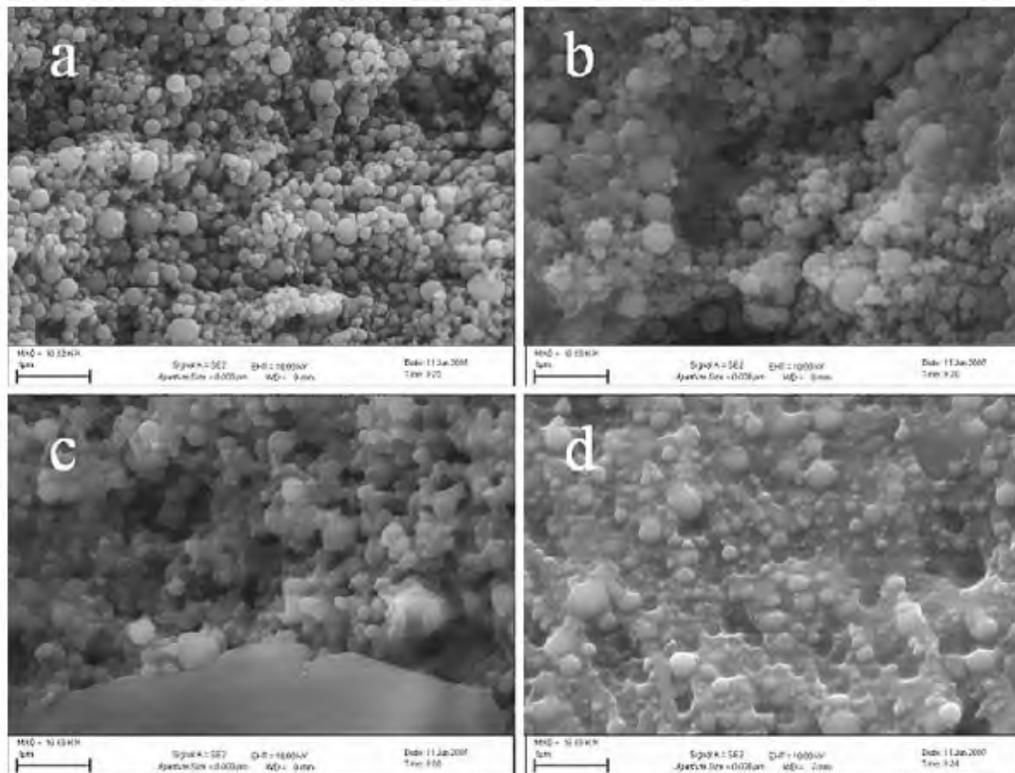
The decrease in viscosity is thought to be due to processes occurring during the initial dissolution step.

- Adsorption of OH^- ions on the surface of silica particles resulting in negatively charged particles. As the solution consists of only negatively charged particles surrounded by positively charged cations the particles will be repelled by one another and hence the viscosity will decrease.
- Dissolution of the silica particles will cause the particles to decrease in size and number resulting in an additional decrease in viscosity.



Charaterization of silicate polymer – SEM analysis

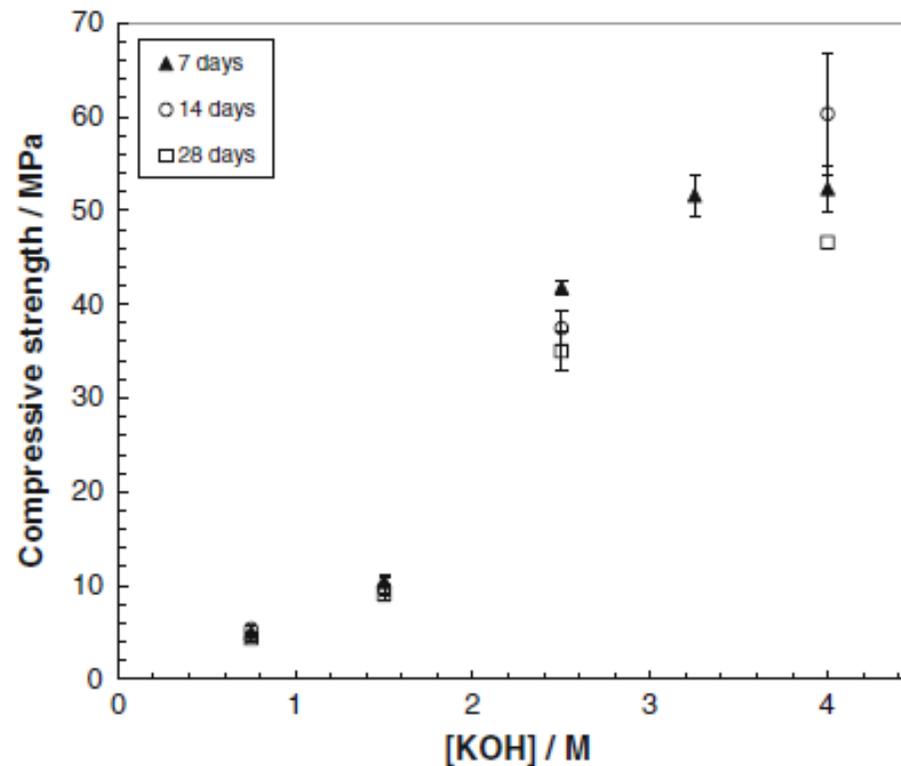
SEM images of the inorganic polymers supports the dissolution – gelation model as a significant change in the particle size of the silica particles is observed when different concentrations of hydroxide was used.



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

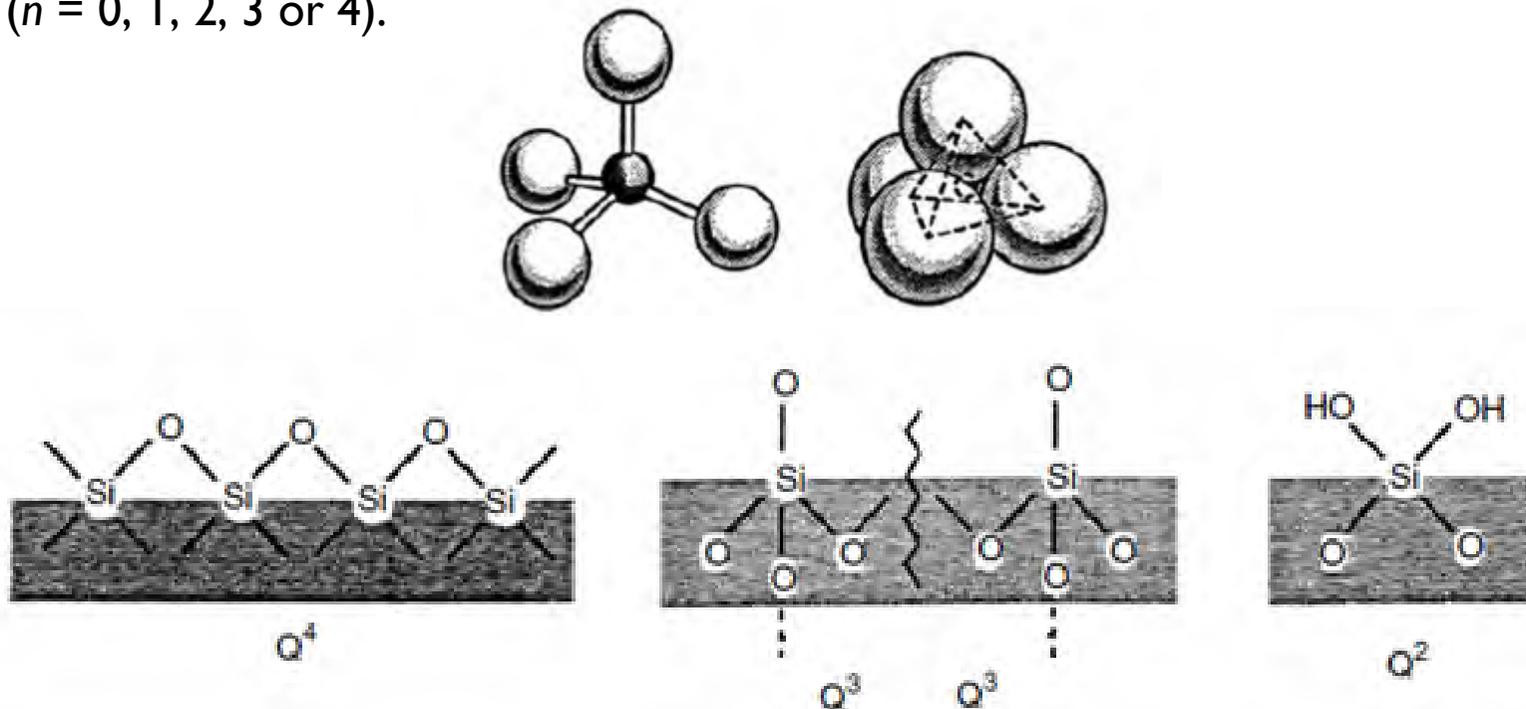
Charaterization of silicate polymers – Compressive strength

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



Characterization of silicate polymer – FT-IR

The inorganic polymers are composed from Si-O tetrahedrons which are connected via corner sharing bridging oxygens. The connectivity of the tetrahedron is specified by the number of bridging oxygens. Tetrahedron with n bridging oxygens are denoted Q^n ($n = 0, 1, 2, 3$ or 4).

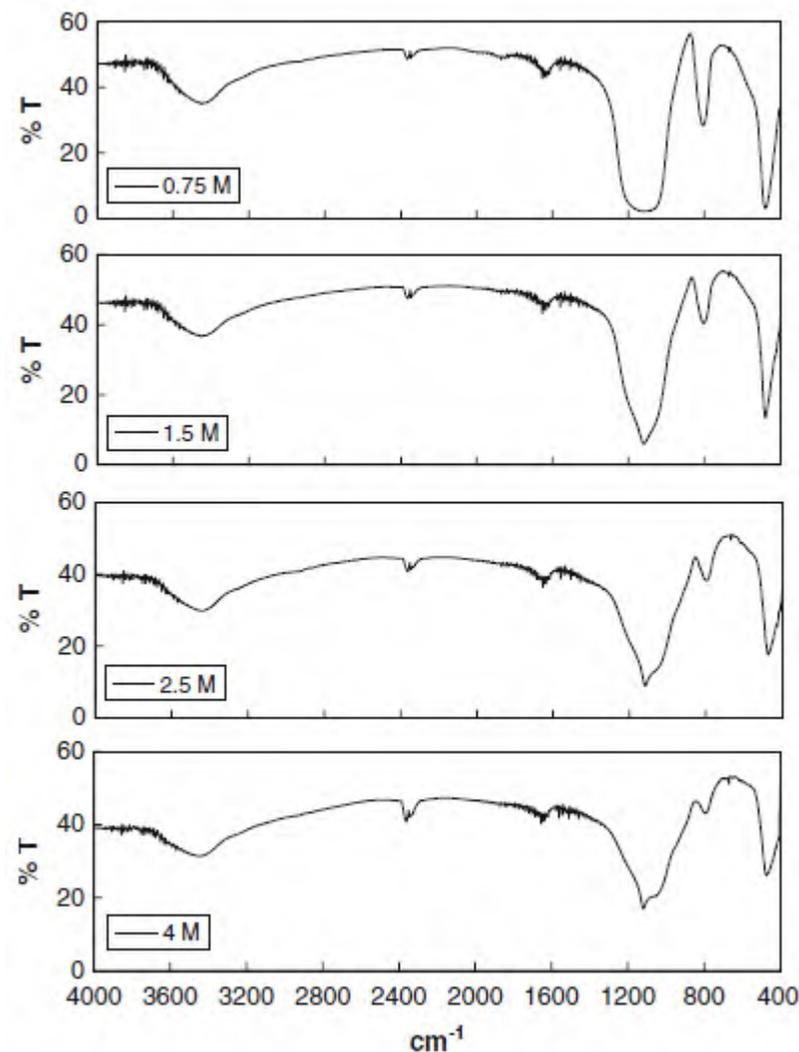


Characterization of silicate polymer – FT-IR

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 numbers, indicating the transformation of Q^4 units to Q^3 and Q^2 units.

Si-O stretching 1000-1200 cm^{-1}
 Si-O stretching: 1100 cm^{-1} (Q^4)
 Si-O stretching 1050 cm^{-1} (Q^3)

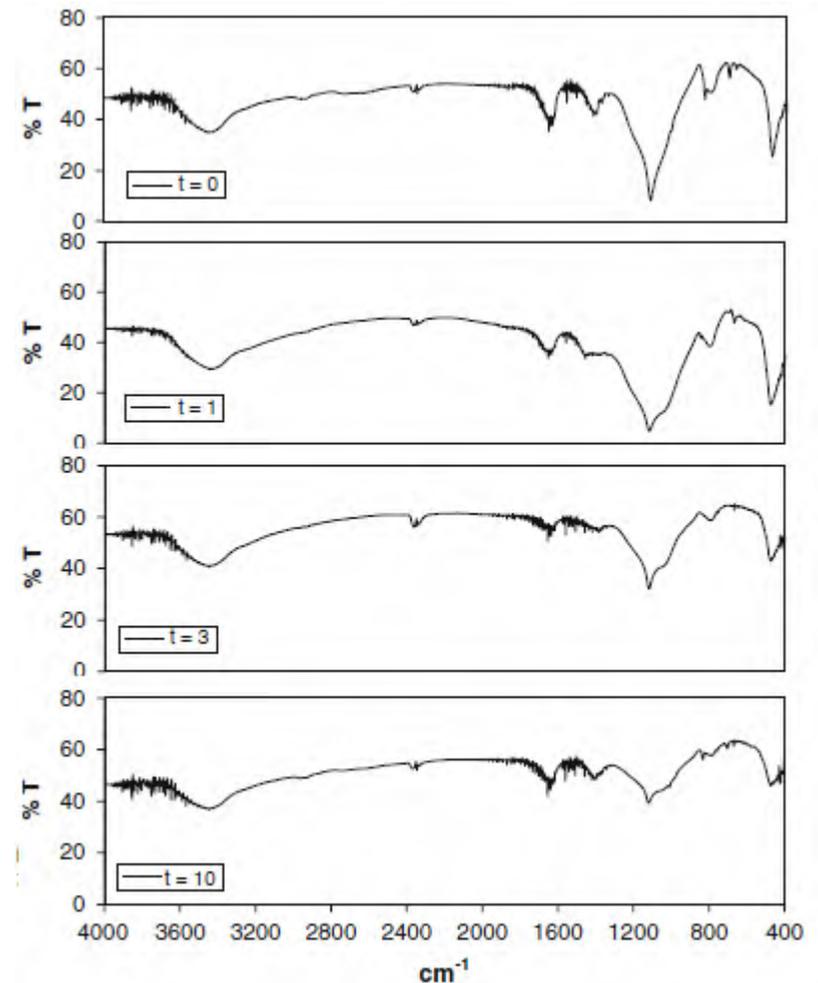
Si-O bending: 890-975 cm^{-1}
 Si-O bending: 800 cm^{-1}
 Si-O bending: 900 cm^{-1} (Q^2)



Charaterization of silicate polymer -FTIR

The observed change in FT-IR spectra from mainly consisting of Q^4 units to Q^3 and Q^2 with increasing concentration of KOH has been applied to investigate the change in composition during preparation.

It is seen that the intensity of the Q^4 peak located at 1120 cm^{-1} decreases significantly during the reaction.



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 $20-40^\circ 2\theta$. A typical XRD spectrum is shown in the figure below.

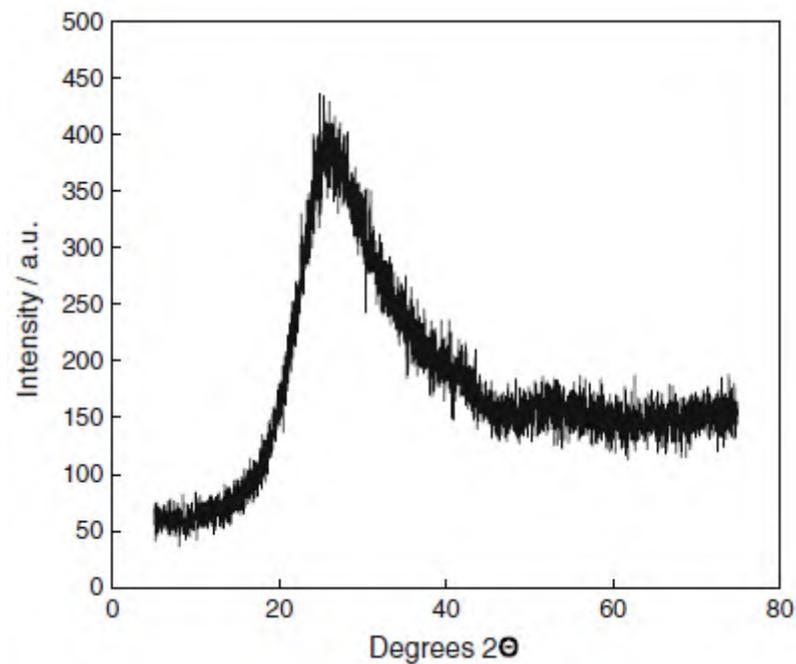


Fig. 1. ESI-MS spectra of the KOH based inorganic polymer reaction solution in negative scanning mode optimized in the spectral region around 500 m/z, a) after 15 min, b) 2 hours, c) 8 hours, and d) after 12 hours of mixing.

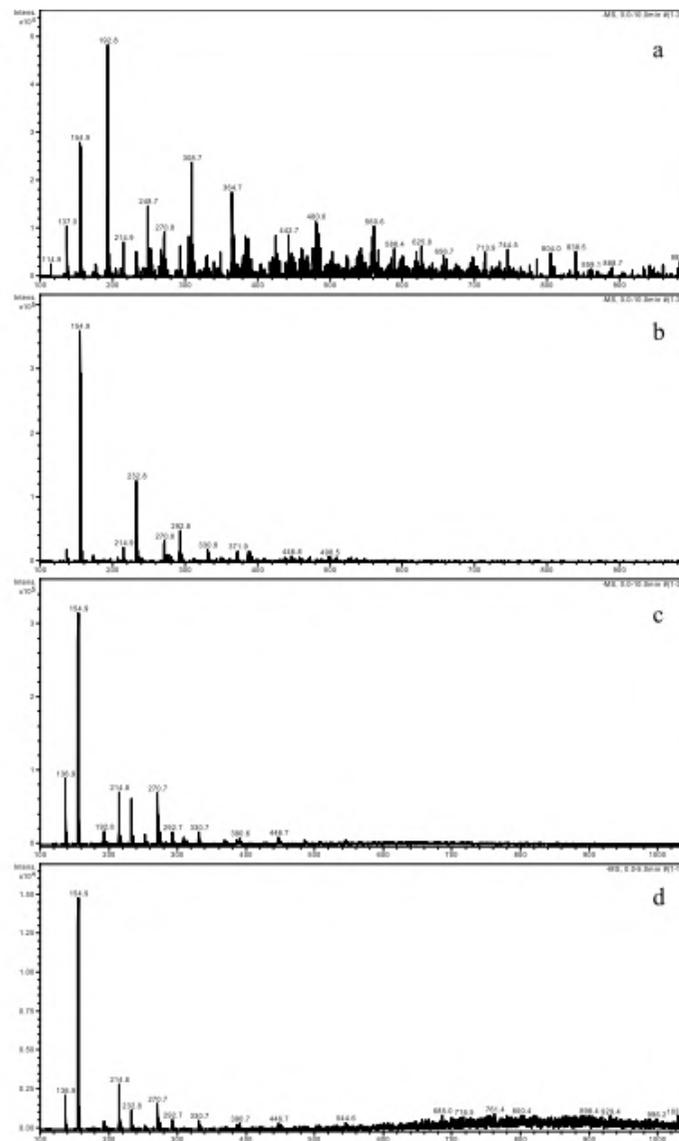


Table 1. Identified molecule ions in the reaction solution of KOH based inorganic polymers in negative scanning mode. - H₂O denotes dehydroxylation resulting in the formation of an oxo group.

Nr.	m/z	Compound	Intensity	Possible structures
1	77	SiO ₂ (OH) ⁻	< 5	• - 1 H ₂ O
2	95	SiO(OH) ₃ ⁻	< 5	•
3	137	Si ₂ O ₄ (OH) ⁻	29	— - 2 H ₂ O
4	155	Si ₂ O ₃ (OH) ₃ ⁻	100	— - 1 H ₂ O
5	173	Si ₂ O ₂ (OH) ₅ ⁻	< 5	—
6	193	Si ₂ O ₃ (OK)(OH) ₂ ⁻	5	— - 1 H ₂ O
7	215	Si ₃ O ₅ (OH) ₃ ⁻	24	 - 1 H ₂ O  - 2 H ₂ O
8	233	Si ₃ O ₄ (OH) ₅ ⁻	22	  - 1 H ₂ O
9	249	Si ₂ O ₂ (OK) ₂ (OH) ₃ ⁻	< 5	—
10	253	Si ₃ O ₅ (OK)(OH) ₂ ⁻	< 5	 - 1 H ₂ O  - 2 H ₂ O
11	271	Si ₃ O ₄ (OK)(OH) ₄ ⁻	22	  - 1 H ₂ O
12	275	Si ₄ O ₇ (OH) ₃ ⁻	< 5	 - 2 H ₂ O  - 2 H ₂ O  - 3 H ₂ O
13	293	Si ₄ O ₆ (OH) ₅ ⁻	6	 - 1 H ₂ O  - 1 H ₂ O  - 2 H ₂ O
14	309	Si ₃ O ₄ (OK) ₂ (OH) ₃ ⁻	< 5	  - 1 H ₂ O
15	331	Si ₄ O ₆ (OK)(OH) ₄ ⁻	6	 - 1 H ₂ O  - 1 H ₂ O  - 2 H ₂ O
16	371	Si ₅ O ₇ (OH) ₇ ⁻	< 5	
17	387	Si ₄ O ₅ (OK) ₂ (OH) ₅ ⁻	< 5	   - 1 H ₂ O
18	391	Si ₅ O ₈ (OK)(OH) ₄ ⁻	< 5	
19	425	Si ₄ O ₅ (OK) ₃ (OH) ₄ ⁻	< 5	   - 1 H ₂ O
20	443	Si ₄ O ₄ (OK) ₃ (OH) ₆ ⁻	< 5	
21	447	Si ₅ O ₇ (OK) ₂ (OH) ₅ ⁻	< 5	
22	481	Si ₄ O 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.

The formation of soluble silica species results 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.

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 numbers, Indicating the transformation of Q^4 units to Q^3 and Q^2 units.

The silicate polymer is X-ray amorphous, since the main characteristic of the XRD spectra is a featureless bump centered at $20\text{-}40^\circ 2\theta$.