Geopolymers

Chemistry of Geopolymers of
the
Institute of Rock Structure and Mechanics
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Republic

What are they?

1. Geopolymers are inorganic polymers based on specific properties of thermally treated double layered clayed minerals (e.g.kaolinit, nakrit, dicket).

2. Poly-condensation occurs by effect of alkali aqueous solutions on **thermally transformed** clayed materials. Ions of aluminum and silicon are on the beginning hydrated and later form chaining structures at ambient temperature, ending by the formation of solid three dimensional network.

Thermal treatment

- Temperature of the clay thermal treatment depends on various factors:

a) Morphology of kaolinitic clay.

b) Average particle size of clayed mineral.

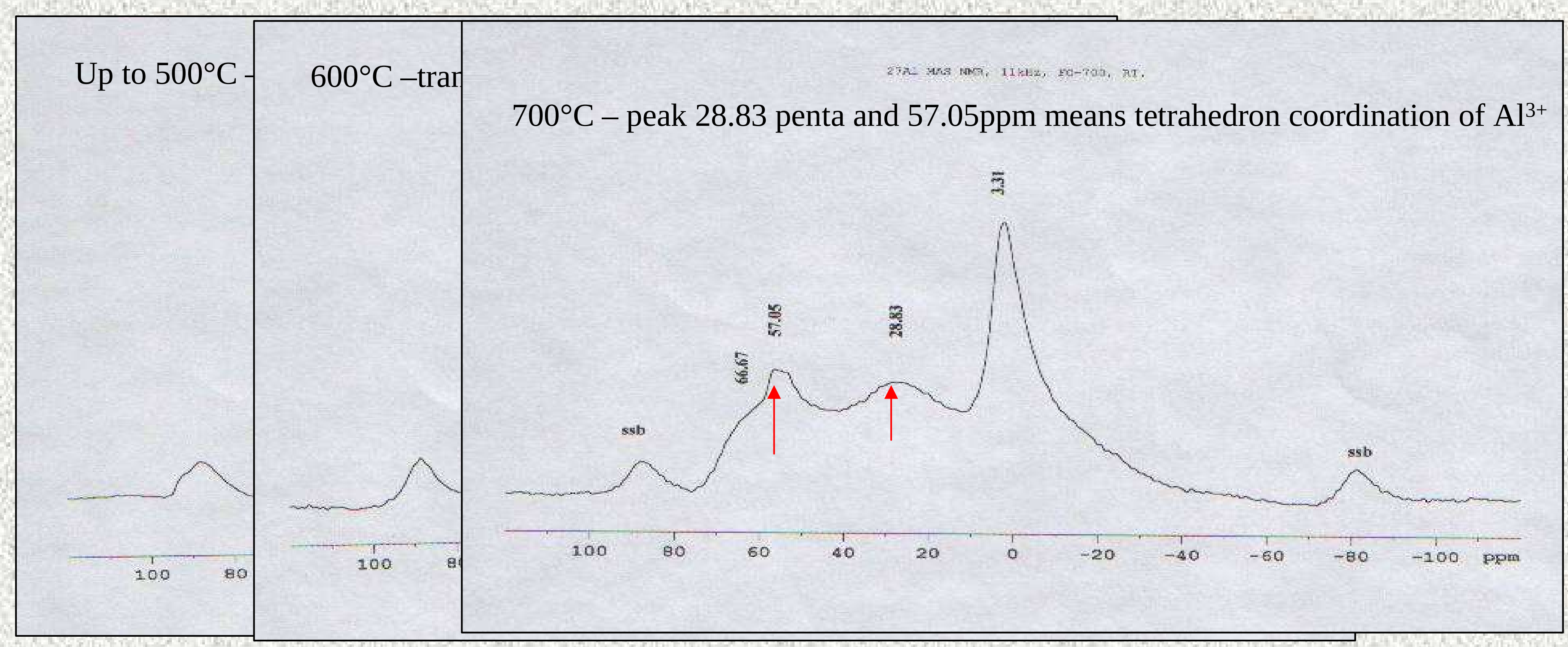
c) Temperature bellow the point of spinel or mullite formations.

- Generally below 750 °C with 4-6 hours dwell.
- Thermally treated kaolin is known as metakaolin

MAS- NMR analyses - ^{27}Al transition

The stage of transition from natural [6] Al^{3+} coordination to oxygen to [4] and [5] Al^{3+} is determined by ^{27}Al MAS-NMR analyses. Sanz at al., JACS (1998)

Example of changing aluminum coordination at different temperature of treatment.



Why thermal treatment?

- The alkali aqueous solution effects on clayed mineral **only** if aluminum ion is in four / five fold coordination to the oxygen.
- Hydration of tetra/penta coordinated formations of both clayed participants occurs in relatively short time (10 to 15 minutes when intensively mixed) and is expresed by dissolution of the clayed particles in alkali aqueous solutions.
- The stage of dehydrated kaolin was described in ceramic literature as $Al_2O_3.2SiO_2$ but in case of geopolymer theory the dehydration is only a first step of changes – the second one is more important – aluminum ion transformation. For such a state was offered new formula of metakaolin $Al_2O_2Si_2O_5$ (Davidovits).

Thermal activation

$$Al_2O_3.2SiO_2.2H_2O \xrightarrow[\text{Heat}]{} Al_2O_2Si_2O_5 + 2H_2O$$

Dehydration and change of Al coordination: octahedral → tetrahedral

Hydration by alkali aqueous solution

$$Al_2O_2Si_2O_5 \xrightarrow{OH^-} [Si(OH)_4 \,.\, Al(OH)_4]^-$$

$$[Si(OH)_4 \,.\, Al(OH)_4]^- \xrightarrow{OH^-} (OH)_3\text{-}\,Si - O - \overset{(-)}{Al}\text{-}(OH)_3$$

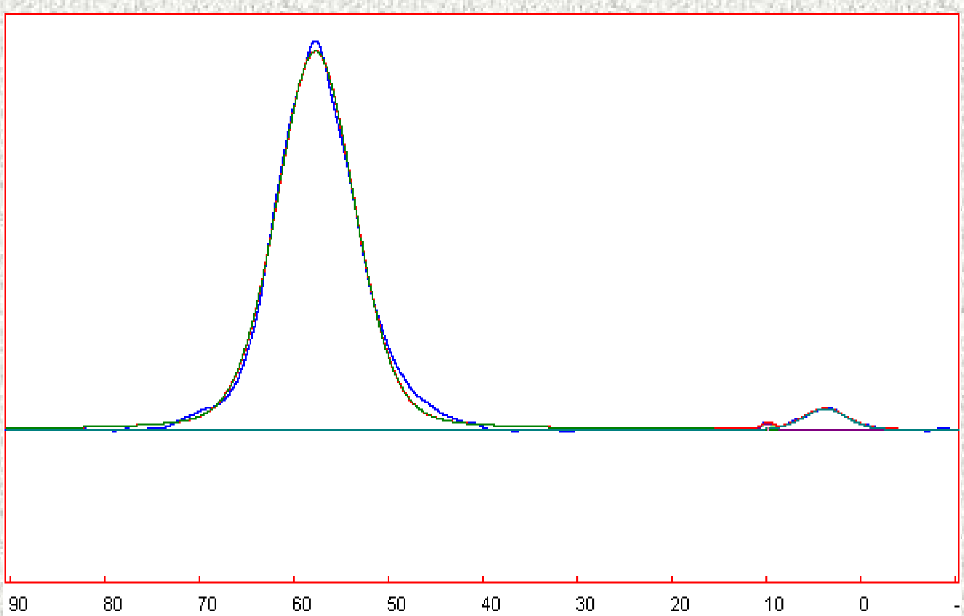
dimer

Poly-condensation and equilibration of negative charge by alkalis

$$n[\,(OH)_3\text{-}\,Si - O - \overset{(-)}{Al}\text{-}(OH)_3] \xrightarrow[-\,n\,H_2O]{+\,n\,Na^+} n\,[\text{-}O - Si - O - \overset{(-)}{Al}\text{-}\,O\text{-}]$$

oligomers

^{27}Al MAS NMR pattern

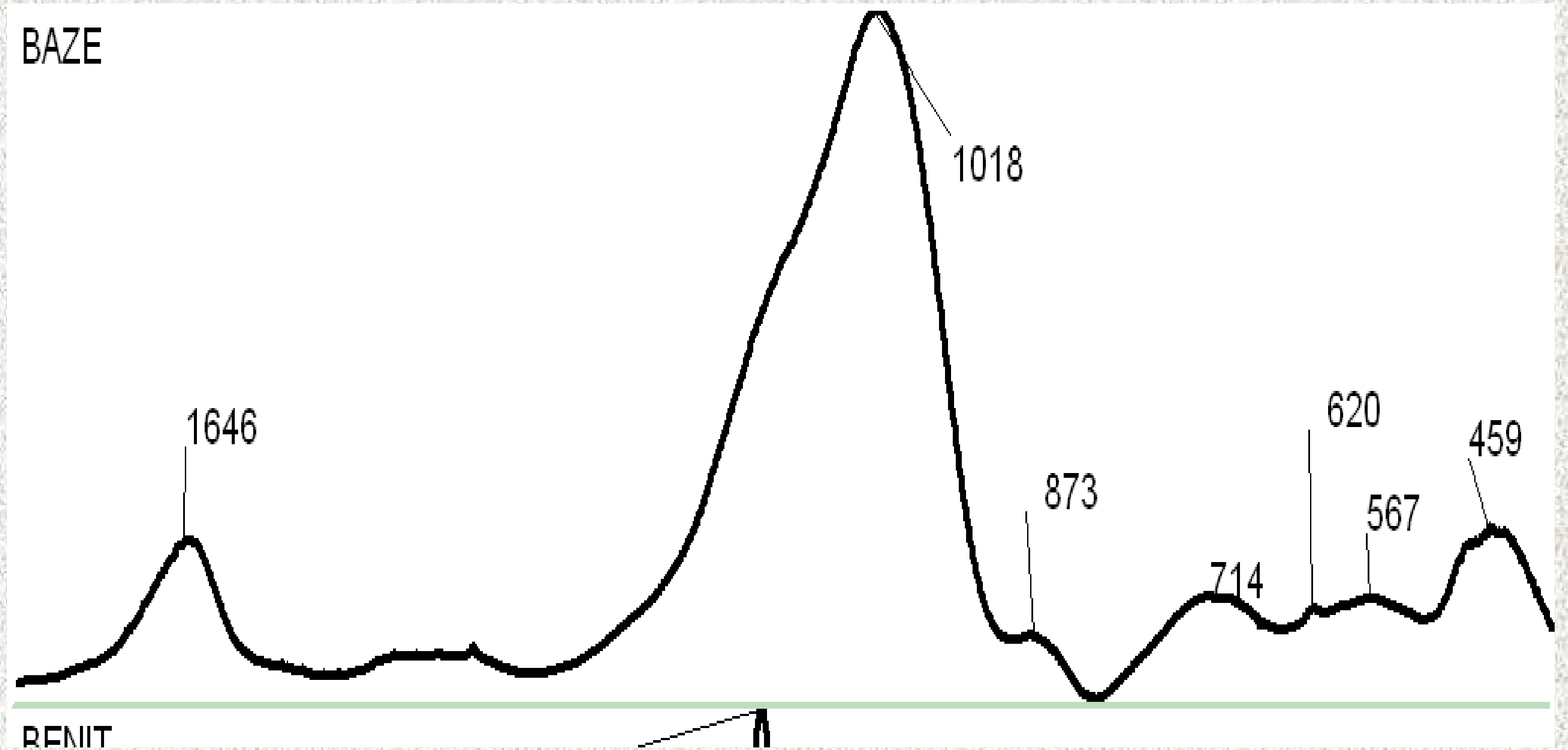


Geopolymer prepared from activated Czech kaolin Sedlec Ia – all alumina ions are tetra coordinated in respect to oxygen (= 58 ppm).

Characterization

- The formation of 3D netting of purely inorganic matters means dominantly amorphous character of alumino-silicates. (The amorphous character do not permit the use of common name of alumina-silicate because alumina-silicates are strictly denominated for their crystal forms).
- The bonds Si-O-Al are confirmed by FTIR analyses at specific deformed valence vibrations (1065-980 $cm^{-1)}$. Phaira J.W. a Van Deventera J.S.J. (Int.Journal of Minerals, 66, 2002, pp.121-143).
- The natural rate of $2SiO_2$: Al_2O_3 in kaolinit (120 : 102) could be changed by addition of soluble alkali silicates which varieties the final geopolymer property.

FTIR analysis



Vibrations at 1018 cm^{-1} is a proof of geopolymer Si-O, Al-O bonding

Codification of valence vibrations

maximum (cm-1)			
3446	**3440**	**–OH**	**OH in molecule**
1637	1636	H–O–H	H2O
1431	1438	O–C–O / CO3	CaCO3
1170	1170	Si–O–Si	SiO2
1030	**1033**	**Si–O–Si** **Al–O–Si**	**geopolymer**
797	795	Si–O–Si	SiO2
777	778	Si–O–Si	SiO2
713		**Al–O**	**geopolymer**
467	**467**	**Al–O, Si–O**	**geopolymer**

Properties of geopolymers

- Comparable compressive strengths with other cementitious materials (Portland cement, gypsum, lime):
  - Experimentally proved **strength – up to 75 MPa.**
- **Low porosity**:
  - Porosity depends on particle size and curing during the setting and hardening (experimentally, with clayed particles D_{50}= 2.83μm, matrix total porosity = 2.0 %.)
- **Amorphous hydrated products**.
  - Hydrated products differ considerably from cement's structure (C-S-H gel + crystal phases).
- Expressed in **Fire resistance up to 1150°C**.
- And in **Resistance to the brisk temperature changes**.

Fire resistance test

The geopolymer composite made from alternated layers of geopolymer and cotton fabrics. Hot side + 900 °C , thickness of the plate 12 mm and resistance measured expresed in minutes when cold side temperature reaches 140°C. Time was 8 minutes 57 seconds. Distance of the burner 5 cm (pict.2) and 15 cm (pic.1) when the resistance grows up to 38 minutes.

Influence of different type of incorporated tissue

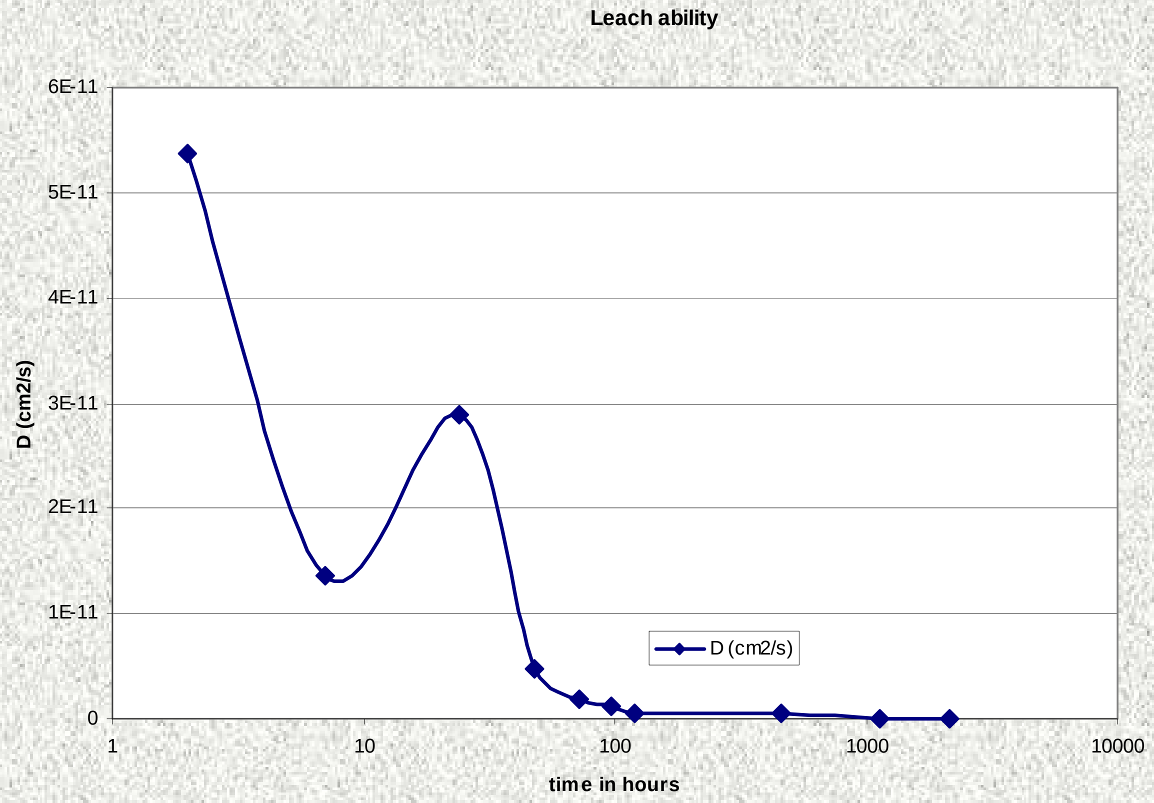
From the left : The composite with cotton fabrics, central plate with none organized fibers and right plate includes rectangular tissue.

Properties of geopolymers

- The **geopolymer matrix could be filled** by large types of additives (incorporated or encapsulated into the matrix).
- Shrinkage varieties according to the quantity of the additives from 0.5 - 10 % of length.
- Incorporation of radioactive waste:
- Expressed by **low leaching ability** proved in cooperation of our laboratory with Nuclear Research Institute Rez:

1. On radioactive waste from nuclear power station
2. Radioactive isotope ^{134} Cs incorporated into the geopolymer matrix.

Leach ability of radioactive ^{134}Cs



Properties of geopolymers

- **Freeze-thaw resistance**.
  - Depends on porosity and quantity of additives.
  - Lowering porosity or contrary open porosity structure.

- **High resistance against** the aggressive medium (alkalis and acids) due to the insoluble 3D netting of alumino-silicates.
- Geopolymers based on sodium activated metakaolin are affected by **efflorescence** if submerged in water or if placed in high humidity conditions.

Efflorescence problems

- Highly movable ion of sodium and its proportion to the activated aluminum ion could cause efflorescence on the solid surfaces.
- Also certain complementing chemicals in additives (especially in case of different sort of waste) effect the efflorescence.
- The clayed materials with high proportion of complementing minerals and inorganic impurities also often affect efflorescence.
- The alkali solution (combination of soluble sodium silicate and sodium hydroxide) should be well calculated to balance the negative charge of penta/tetra coordinated aluminum ion and its quantity.
- Usually could be use the range of 0.75 – 0.80, molar quantity of Na/Al

- **Recommended solution**: Activation by **potassium**

Conclusion

- The advantage of geopolymer matrix is in extremely wide varieties of use from its binding capability up to the inhibitions of hazardous metals and encapsulation of very different waste.
- In the mean time it is also disadvantage because unfortunately in many works the geopolymer is presented like all problems resolving material.

Thank you for your attention