

INSTITUT
GÉOPOLYMÈRE

APPLICATION OF Ca-BASED GEOPOLYMER WITH BLAST- FURNACE SLAG. A REVIEW

Joseph DAVIDOVITS

SECOND INTERNATIONAL
SLAG VALORISATION SYMPOSIUM
THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT



Geopolymer

inorganic macromolecules

**not gel,
or unknown structure
or colloids,**

Geopolymer

inorganic macromolecules

---

alkaline polymerization

acidic polymerization

Geopolymer

inorganic macromolecules

---

alkaline

(Ca, Na, K)-geopolymer

Geopolymer

inorganic macromolecules

Portland CSH

geopolymer NaASH

Until 1999

***2nd Geopolymer Conference,
GP' 99, Saint-Quentin***

**geopolymers = advanced
knowledge
in alumino-silicate chemistry**

Since 2002

3rd Geopolymer Conference

GP' 2002, Melbourne

**everything that was not Portland
cement was called Geopolymer.**

2005

4th Geopolymer Conference, GP ' 2005

Saint-Quentin,

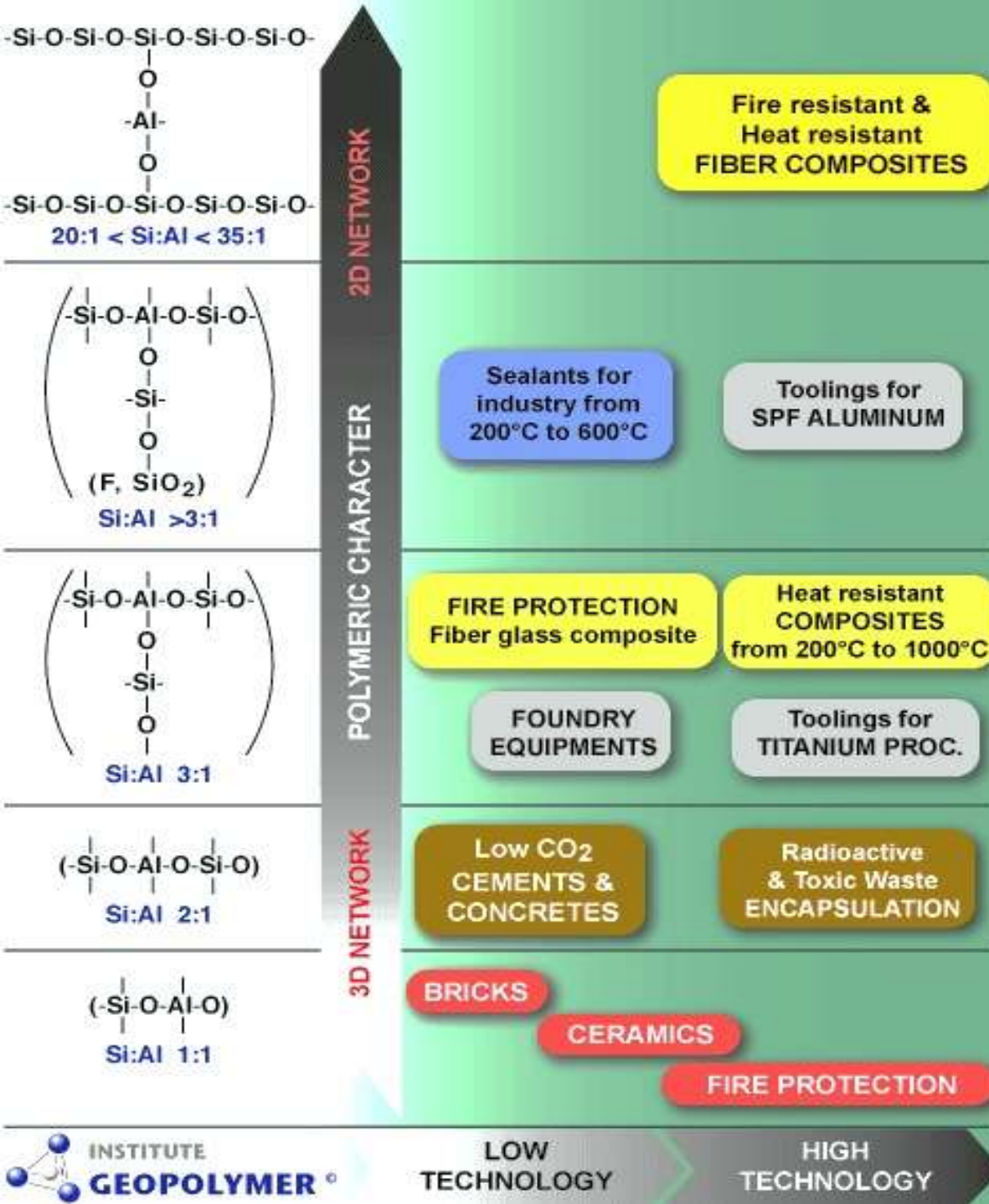
**separate session for
alkali-activated materials AAM.**

My decision

**No more participation
to alkali-activation conferences.**

alka **STOP** **ste**

Ge **!!**



**Ca-based
Geopolymer cement
chemistry =
alkalination of slag**

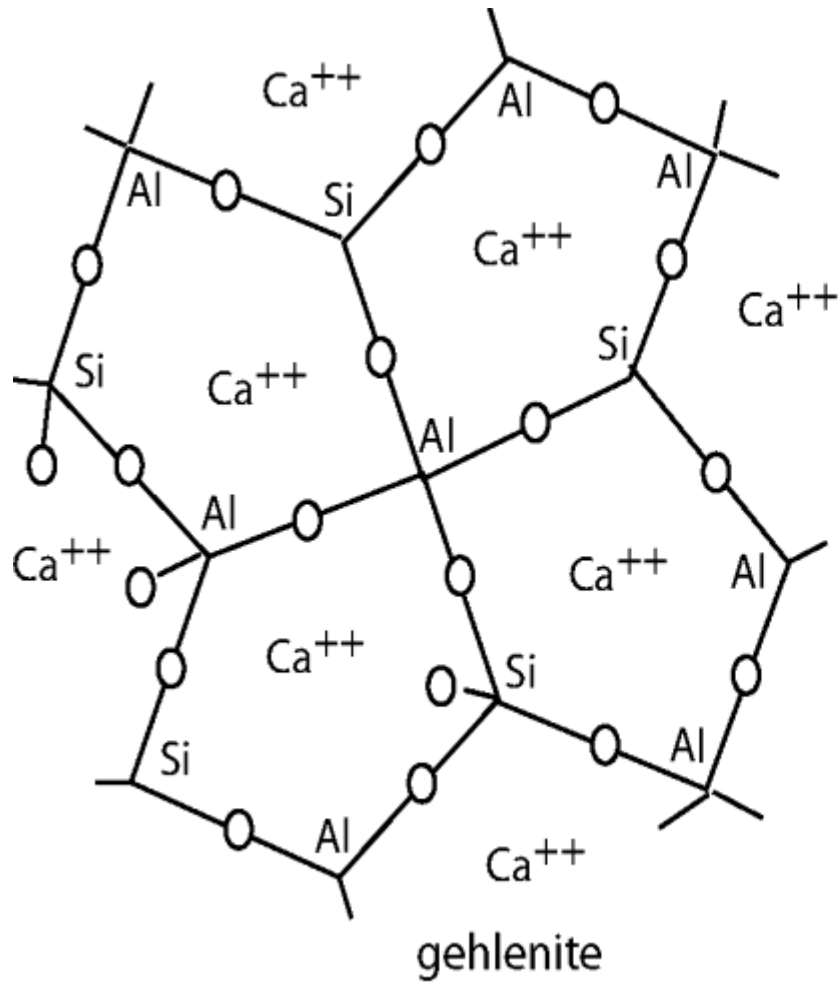
Alkali-activation : first 2 steps of geopolymerization *in alkaline milieu*

- 1) *alkalination*: alumino-silicates + alkali**
- 2) Depolymerisation of silicates into oligomers (oligo-sialates, oligo-siloxo)**

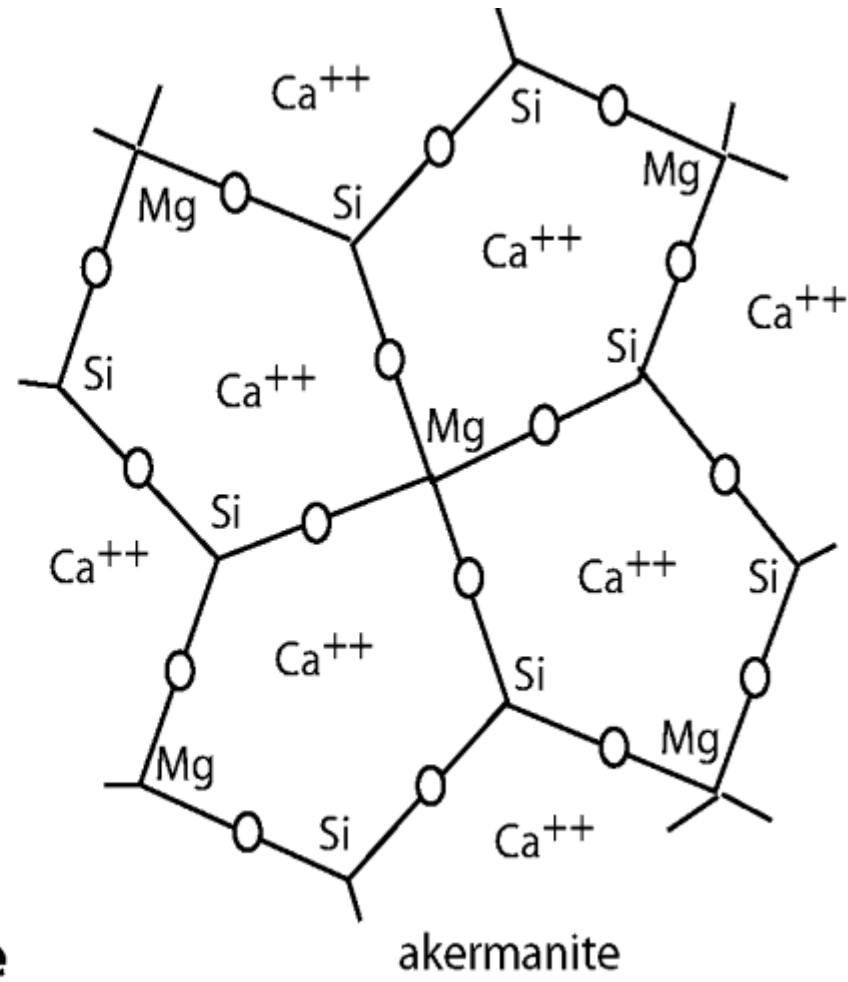
Geopolymerization *in alkaline milieu*

- 1) *alkalination*: alumino-silicates + alkali
- 2) Depolymerisation of silicates into oligomers (oligo-sialates, oligo-siloxo)
- 3) Inter-reaction of oligo-sialates/oligo-siloxo**
- 4) Polycondensation into poly(sialates)**
- 5) Reticulation, networking**
- 6) Geopolymer solidification**

Blast furnace slag

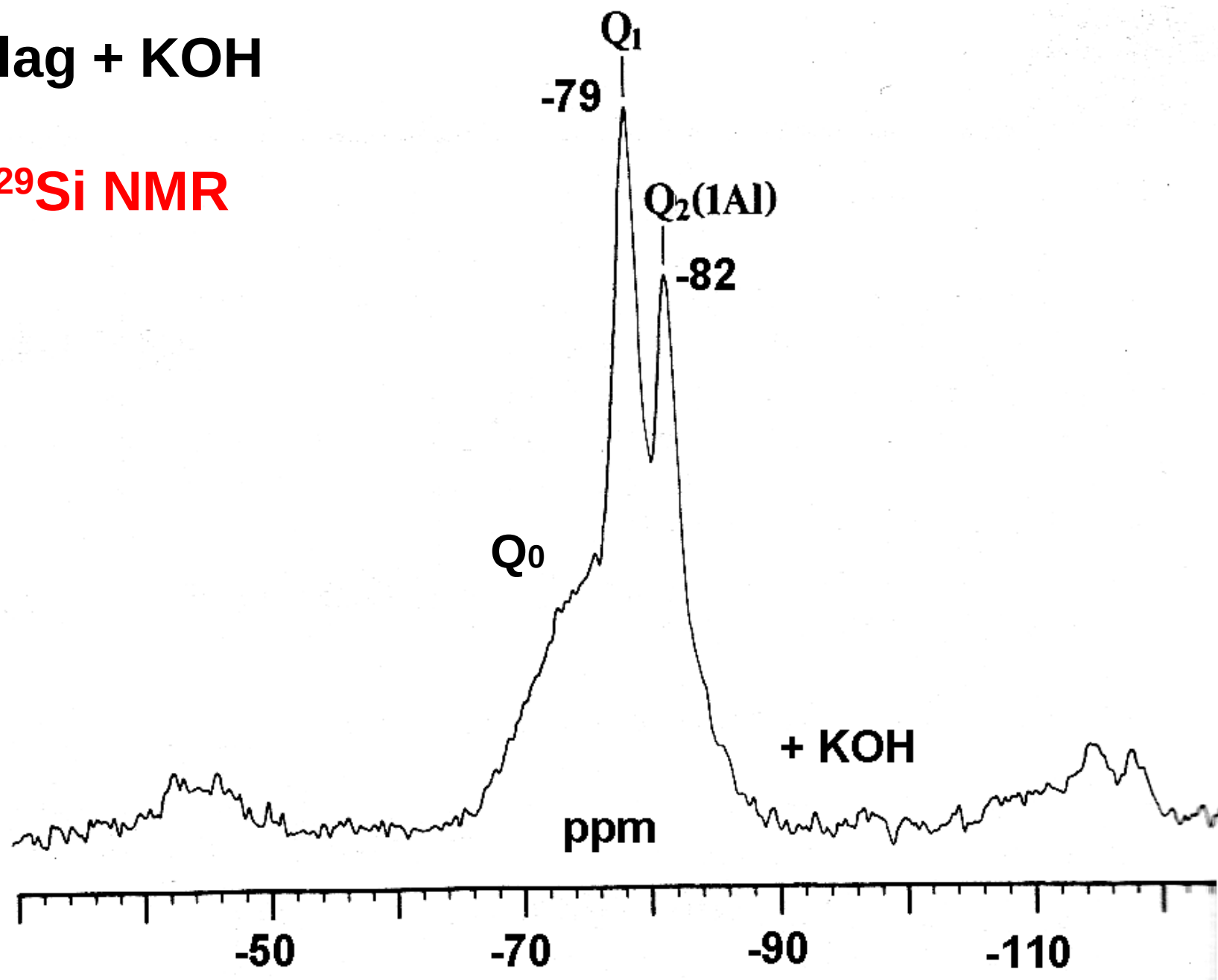


melilite

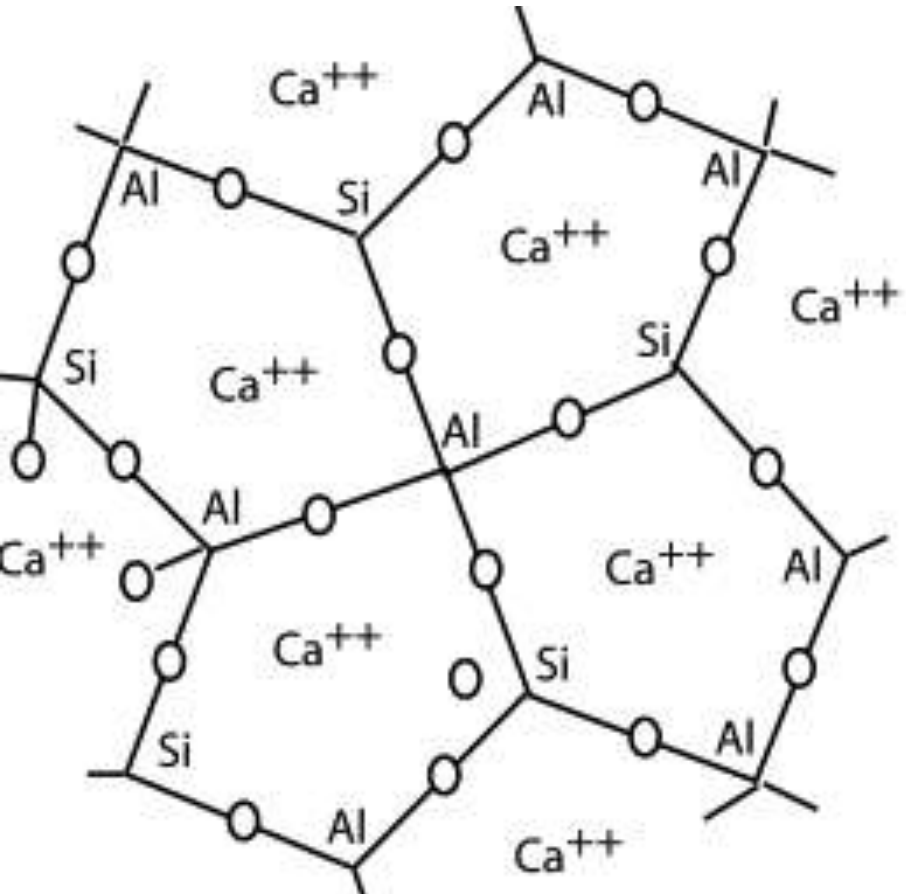


Slag + KOH

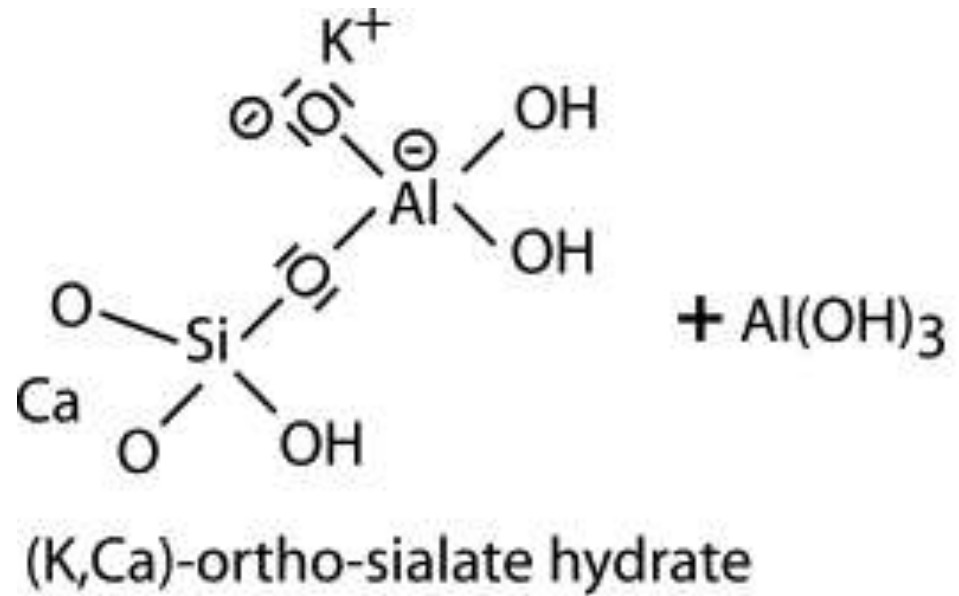
^{29}Si NMR



Alkalinization

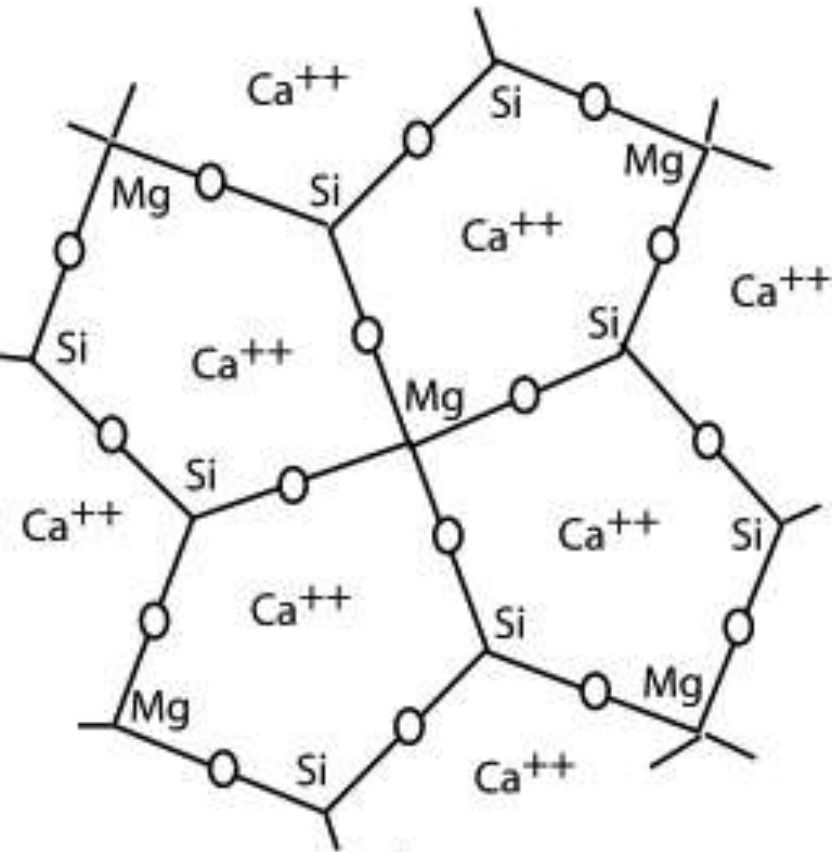


gehlenite

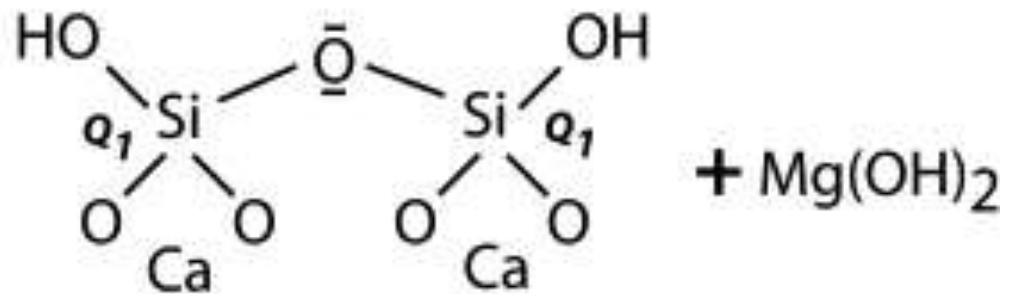


(K,Ca)-ortho-sialate hydrate

Alkalinization

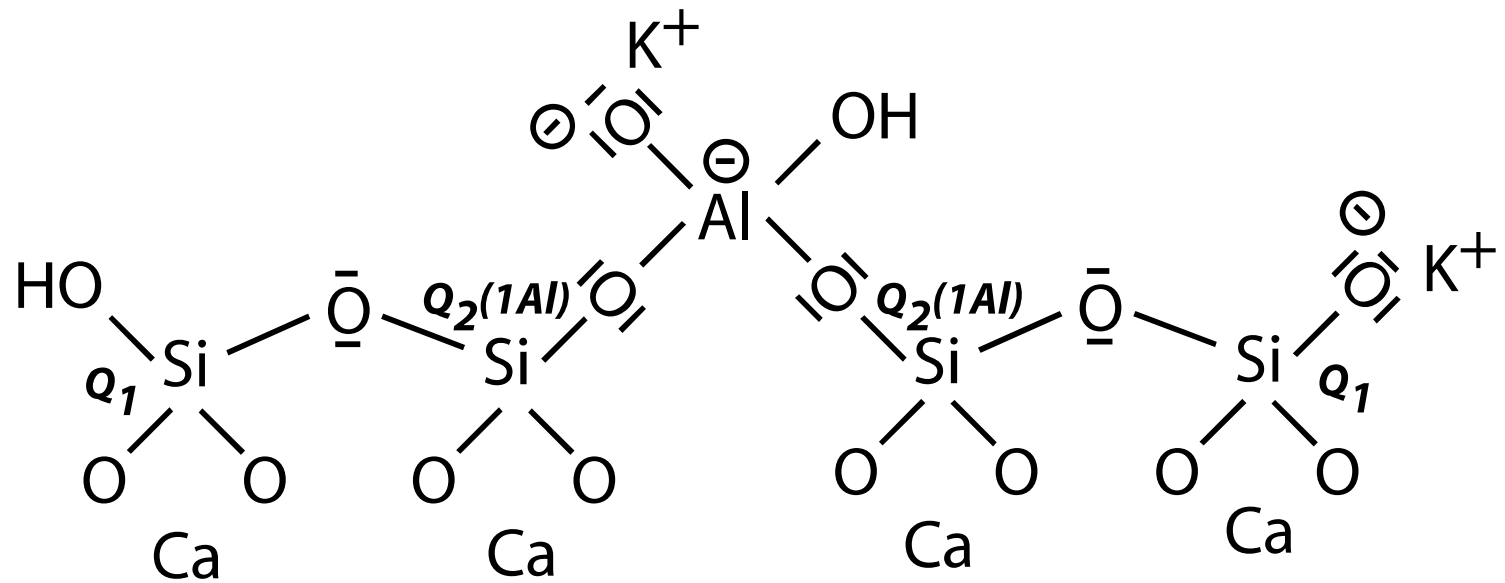


akermanite



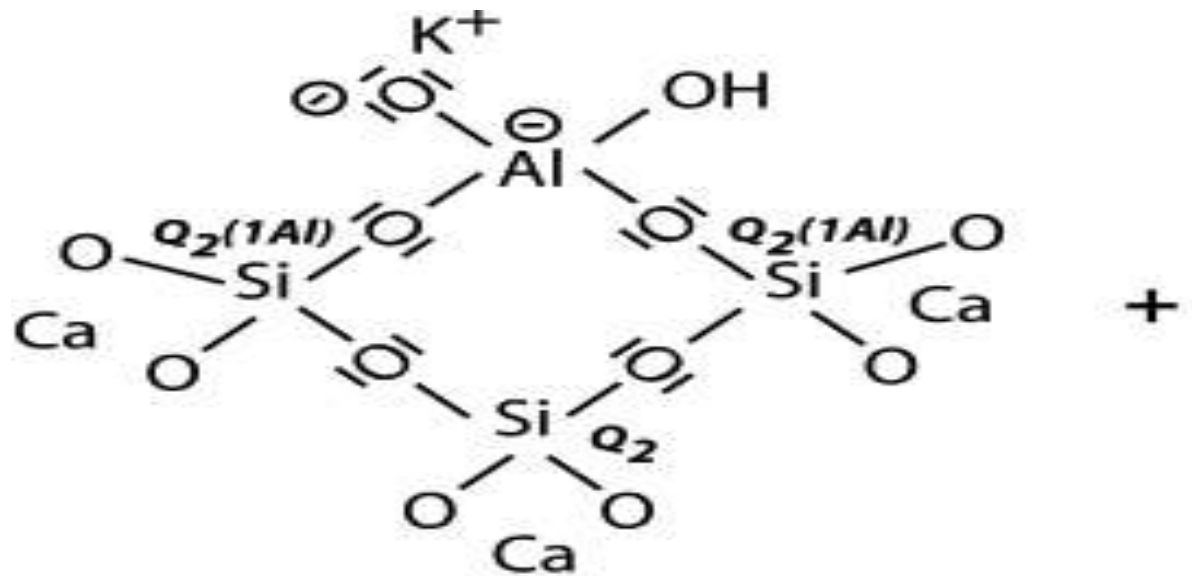
Ca-di-siloxonate hydrate

CSH



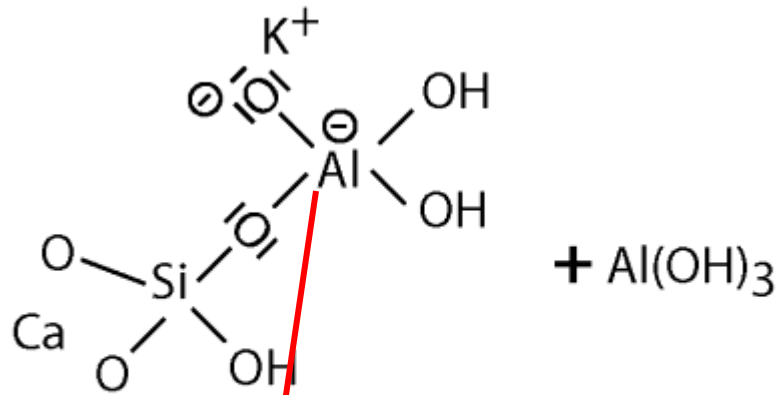
tobermorite with Al substitution

Si Q₂ unit



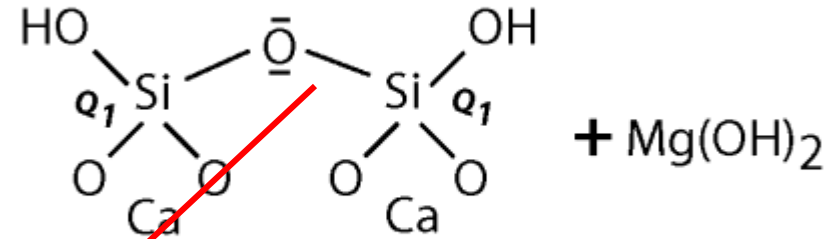
(K,Ca)-cyclo-ortho(sialate-disiloxo)

gehlenite

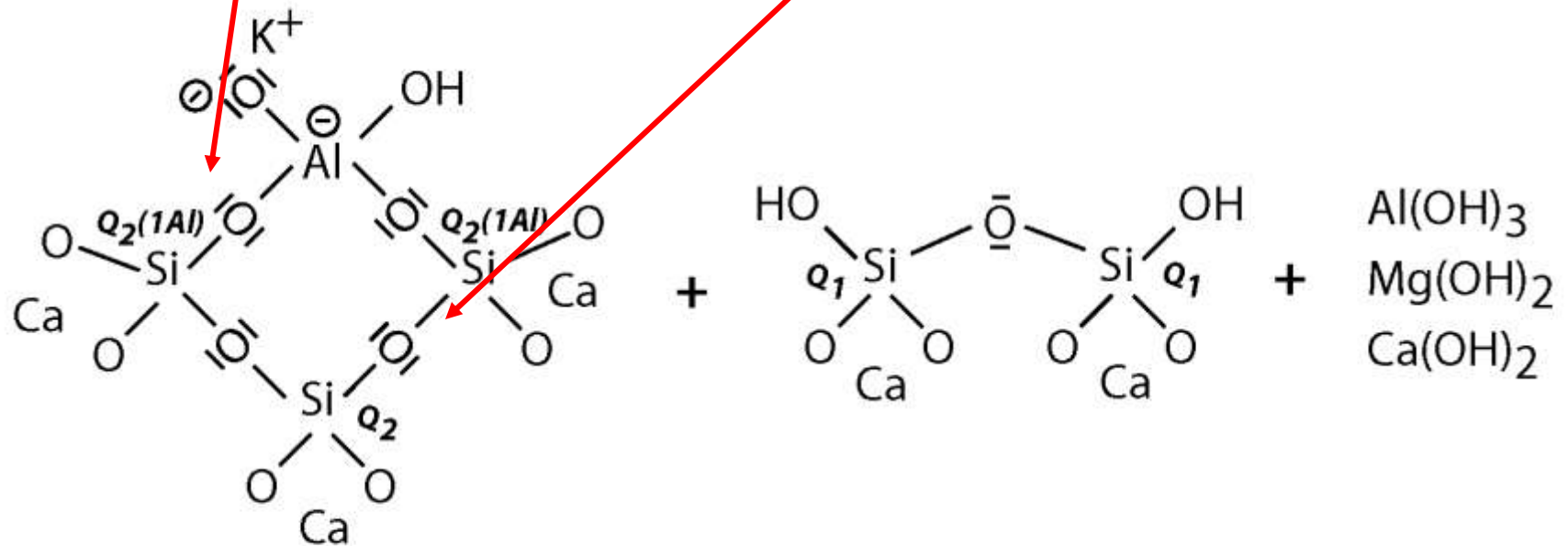


(K,Ca)-ortho-sialate hydrate

akermanite



Ca-di-siloxonate hydrate



(K,Ca)-cyclo-ortho(sialate-disiloxo)

Ca-di-siloxonate hydrate

1) MK-750 / slag - based

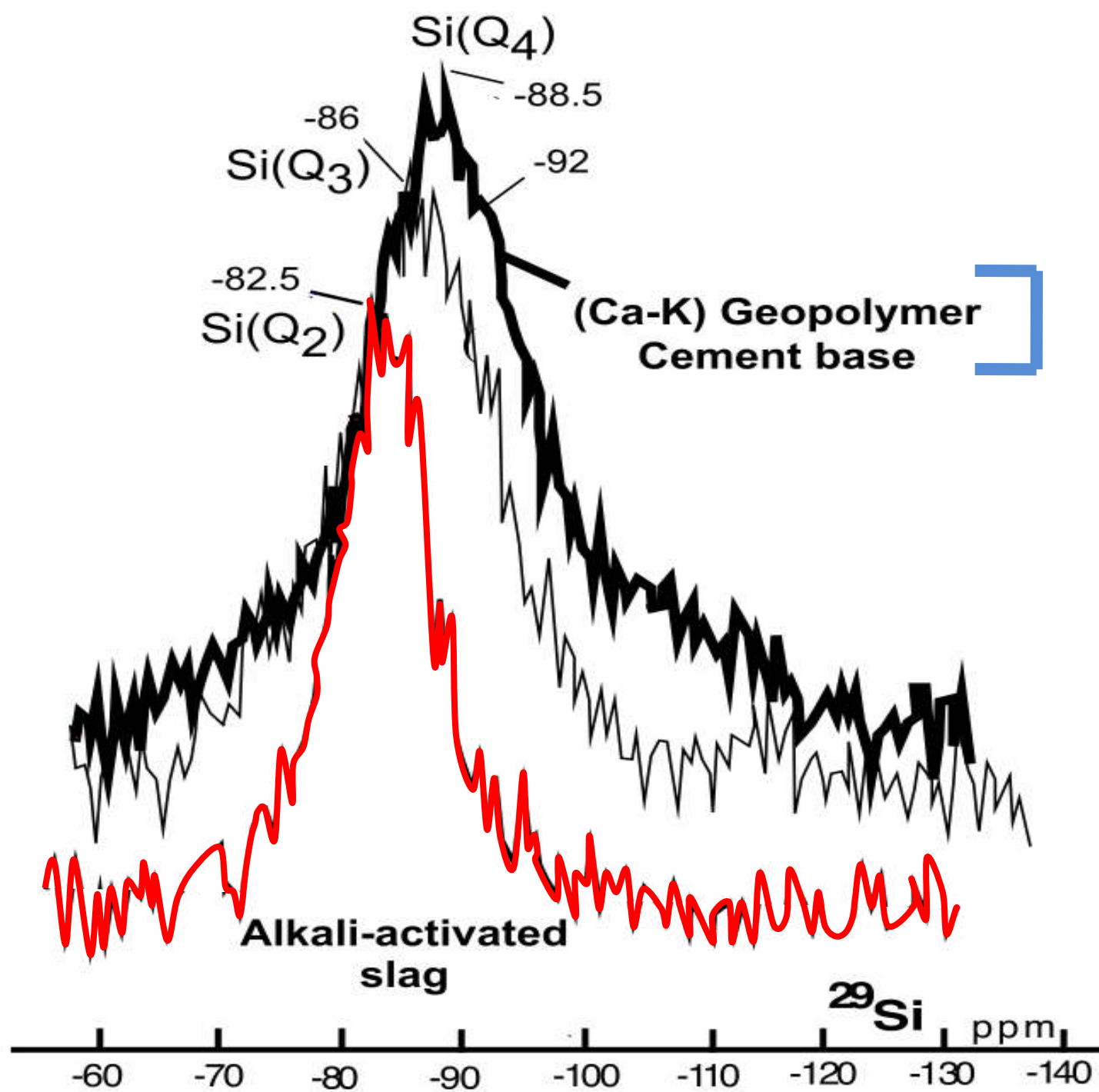
2) Rock / slag-based

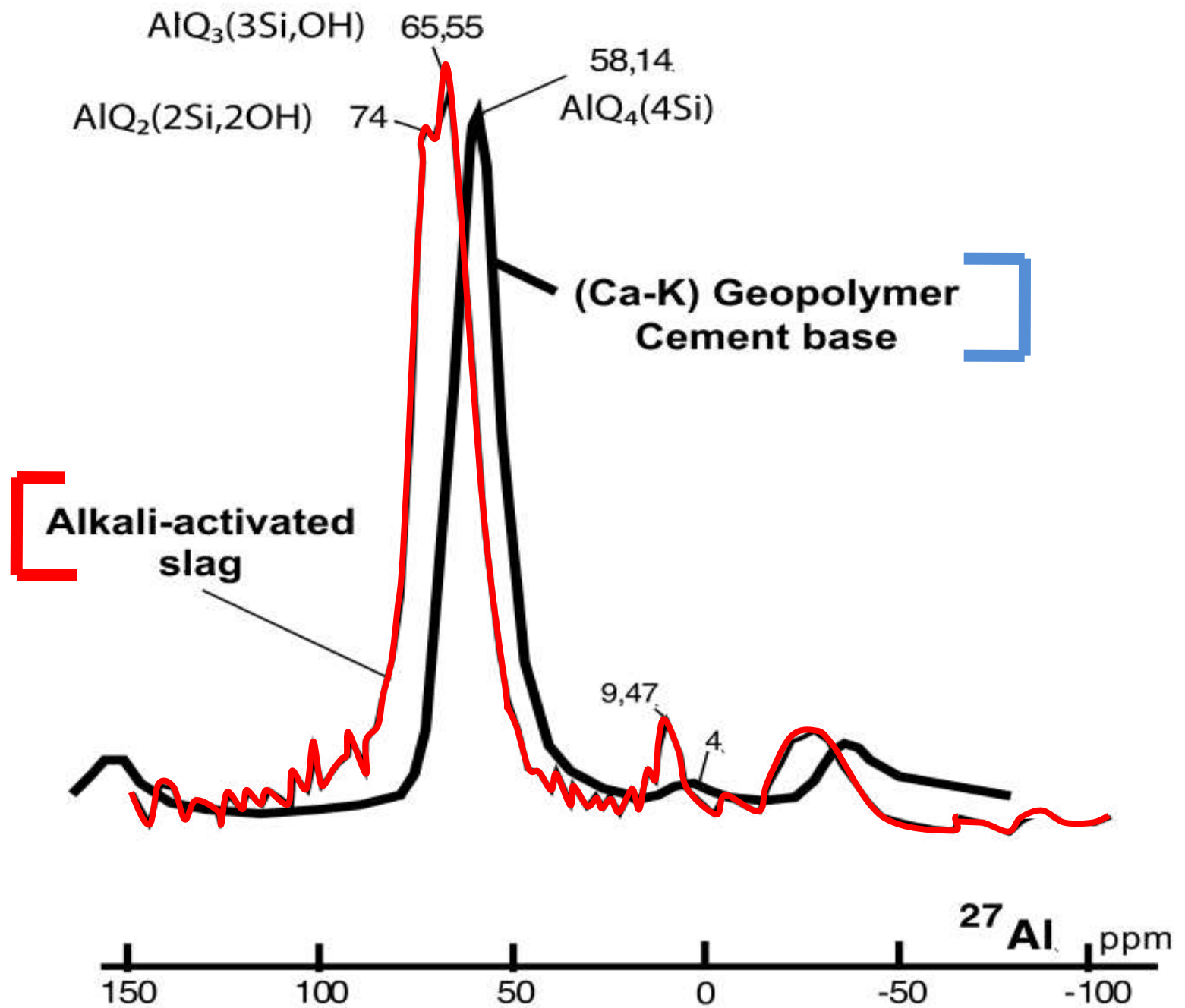
3) Fly ash / slag-based

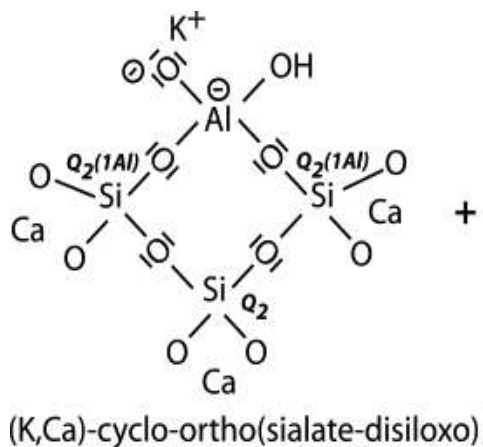
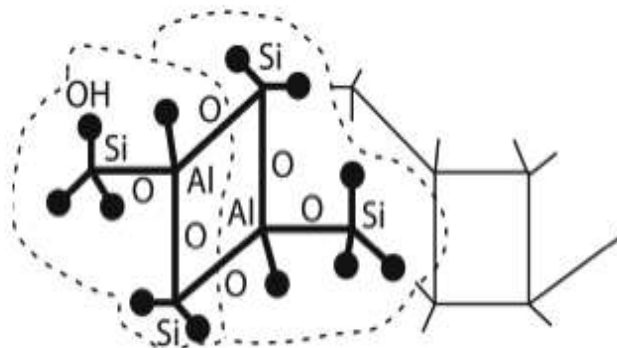
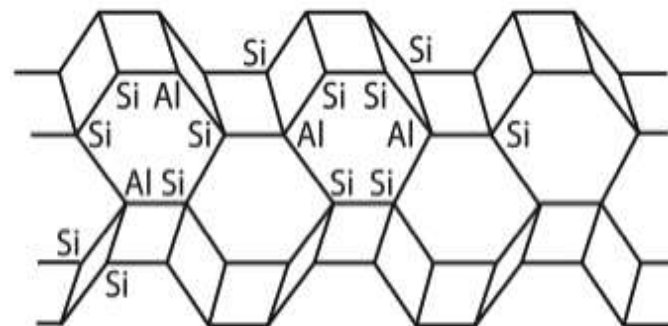
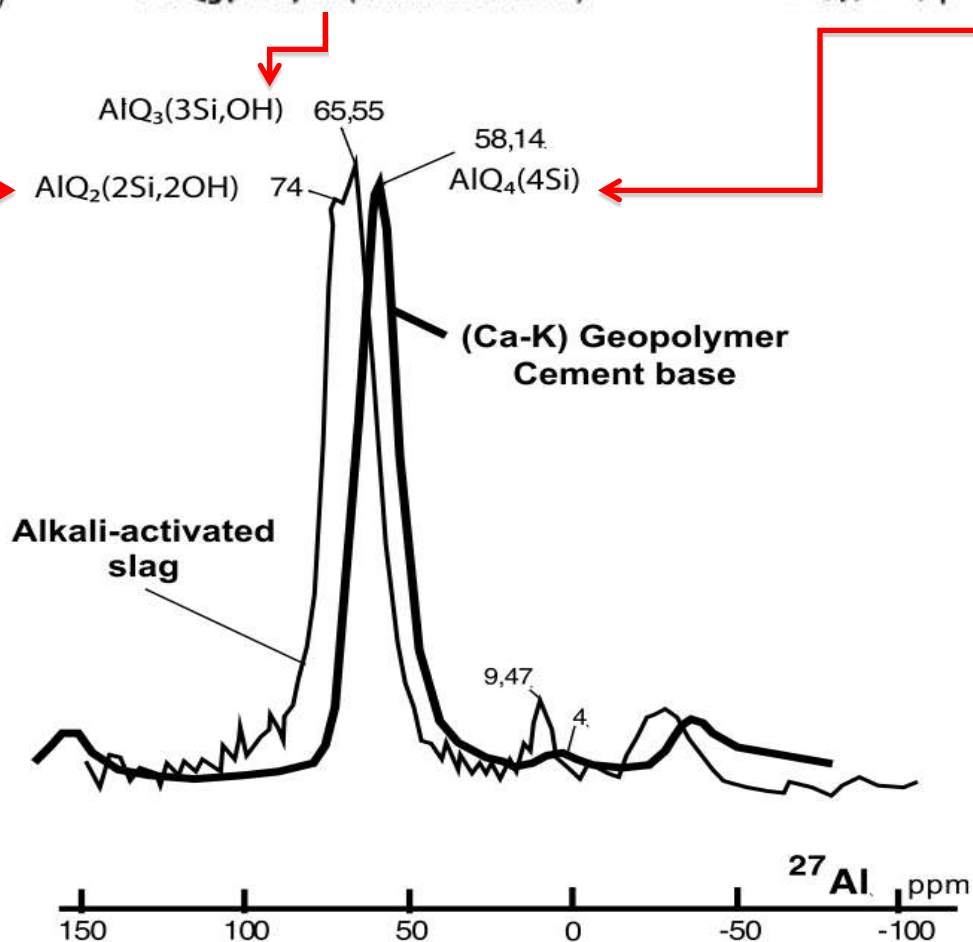
(1)

Geopolymerization

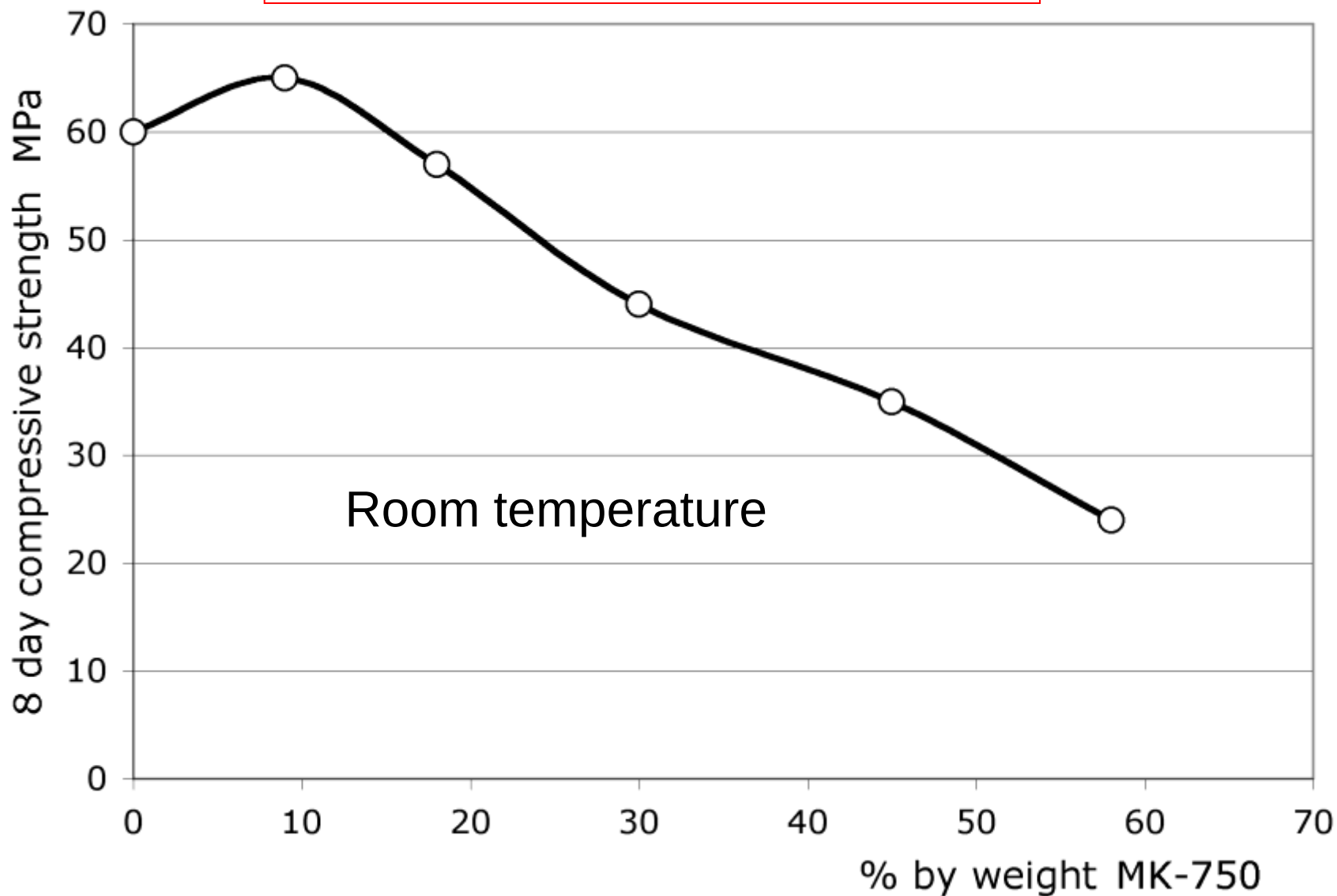
MK-750 + slag







8 day strength / % MK-750



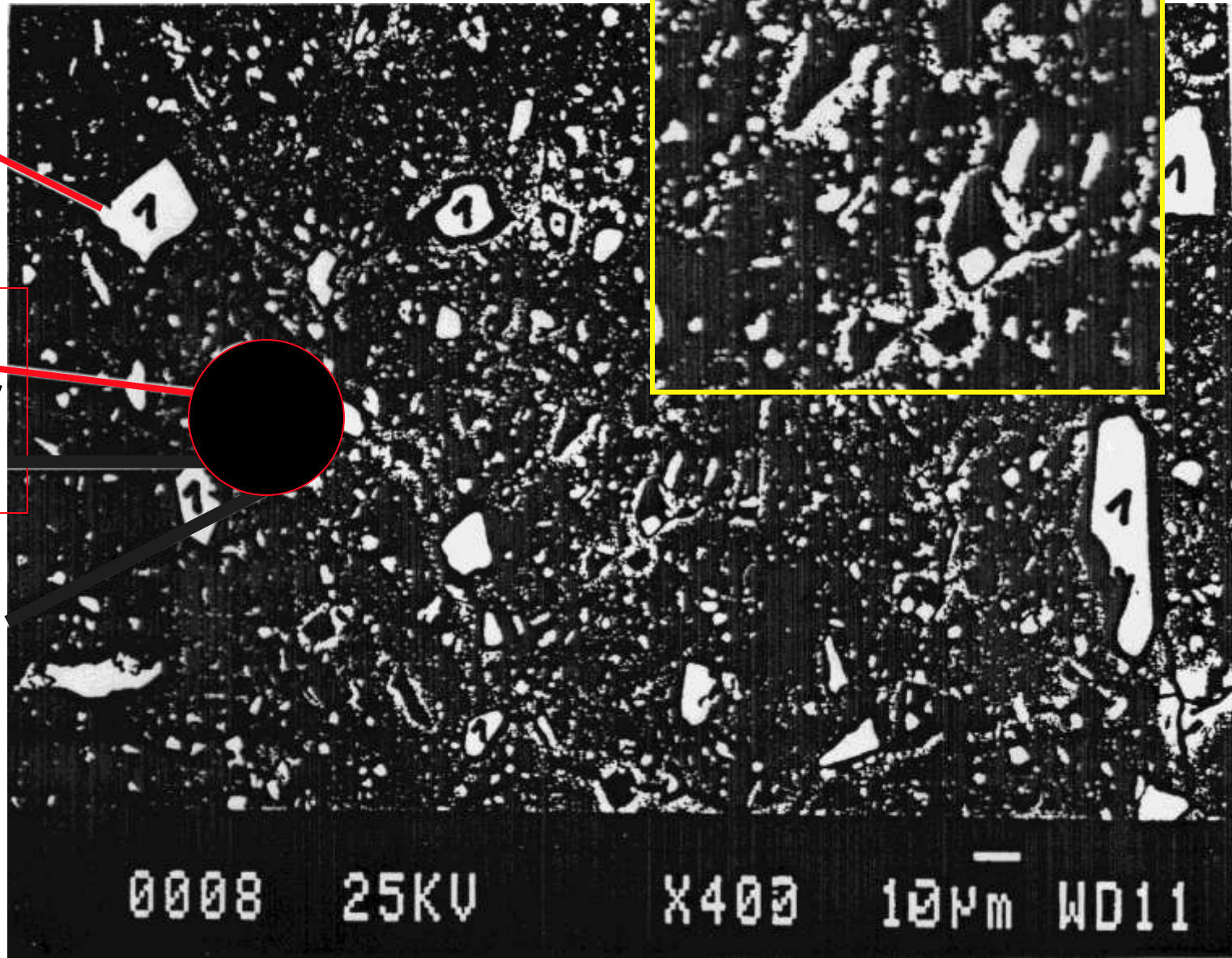
The Choice

- ☐ **high strength with bad physico-chemical properties**
- ☐ **medium strength with high durability**

E-Microprobe analysis

Si, Ca,
Al, Mg
Slag

Si, Al, Ca, K,
*Geopolymer
matrix*



atomic ratios

Si:Al 1.65

K:Al 0.48   Si:K 3.43

Ca:Al 0.65   Si:Ca 2.53

electronic micro beam analysis

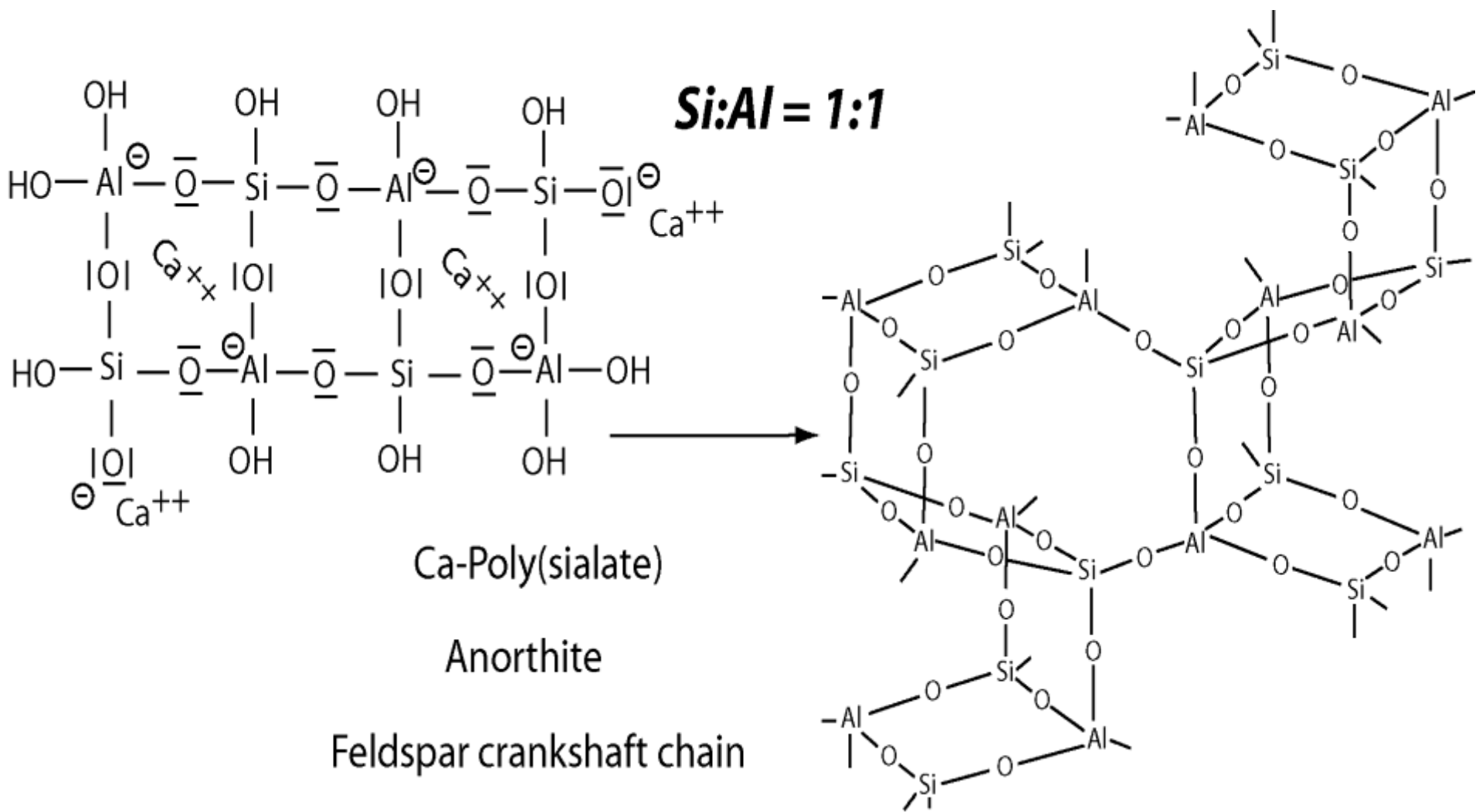
Si:Al 1.655 (1.317 to 1.832)

K:Al 0.442 (0.192 to 0.614)   Si:K 3.73

Ca:Al 0.679 (0.388 to 0.870)   Si:Ca 2.43

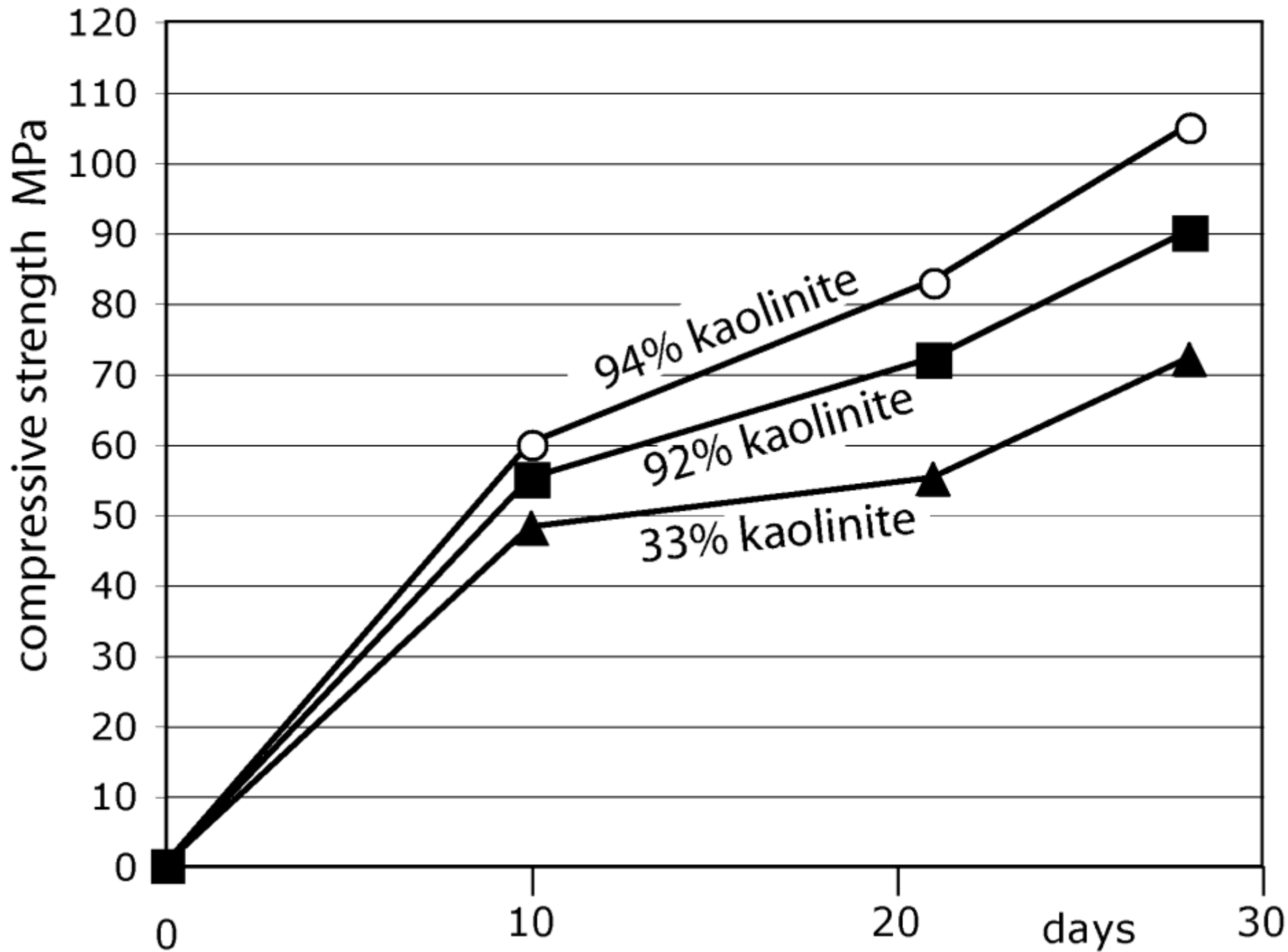
geopolymeric matrix may be a solid solution of

- ✓ - 1.67[K-poly(sialate)], kalsilite, hydrate
+ 0.41[Ca-poly(di-sialate)], anorthite hydrate;
- ✓ - 0.33[K-poly(sialate-disiloxo)], orthoclase hydrate,
+ 0.08[Ca-poly(di-sialate)], anorthite hydrate;
- ✓ - 0.5[Ca-di-siloxonate] (CSH) + CAH ...



**MK-750 / slag-based
geopolymer cement**

Practical experience



Basic MK-750/slag mix:

- a) calcined kaolinitic clay.....80
- b) slag (15-25 microns) 20
- c) K silicate sol.
(MR = 1,40), H₂O:53%.....20
- d) water.....2

Ambient temperature hardening

45 MPa at 7 days

70 MPa at 28 days.

Si:Al = 2:1

(K,Ca)-(Si-O-Al-O-Si-O-)

(K,Ca)-poly(sialate-siloxo)



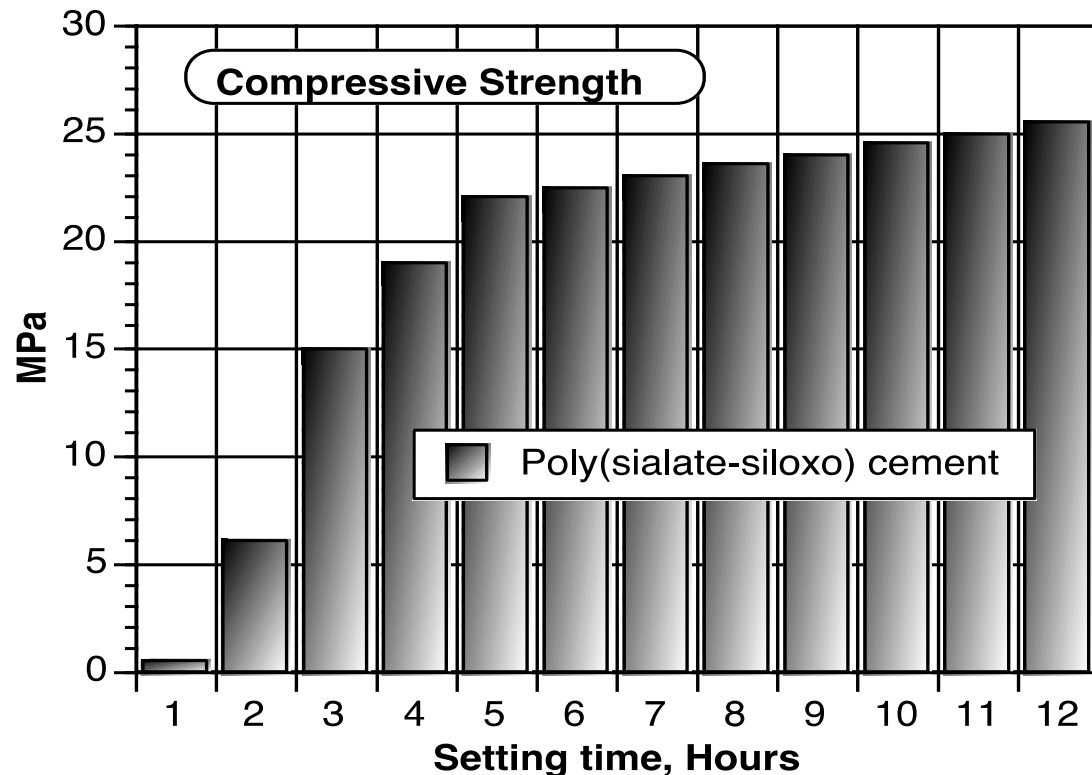
Geopolymer Cement

Early high-strength mineral polymer

US 4.509.985: 22/02/1984

PYRAMENT Inc., Lone Star Ind. Inc.

Joseph Davidovits, James L. Sawyer



1988: PYRAMENT Blended Cement

Portland 75

geopolymer precursors.....25

Lone Star/PYRAMENT cement

1988-1997



Los Angeles: a crew begins placing concrete.

New York: a Boeing departs

1 hour
Strong enough
to walk on

4 hours
Strong enough
to drive on

6 hours
Ready for the weight
of a commercial jet

23 years later

Message to Professor Joseph Davidovits,

I recently purchased your latest book *Geopolymer Chemistry & Applications* and have read a number of your papers and learned that I have you to thank for *PYRAMENT* Cement. My first experience using *PYRAMENT* was about 23 years ago when we were the first to use it to replace damaged concrete on runways and taxiways at the Atlanta airport. We used it until it was no longer available and have never found a material quite as good.

You might be interested to know that a major aircraft runway intersection at Charleston Air Force Base, in South Carolina, was replaced with a concrete mix using *PYRAMENT* Cement about twenty years ago. I just learned that they are going to remove and replace one of the runways but the intersection made out of *PYRAMENT* is still in such good condition that they are leaving it in place. A nice tribute to your invention!

.....

Further information on the Charleston Air Force Base Project...It was Completed in 1989 and the contractor was Summers Concrete Contracting, from Hahira, Georgia. In 1991, a full runway was replaced at Barksdale Air Force Base, Louisiana, by the same contractor, using concrete made with PYRAMENT cement. Twenty years later, that runway is still being used by US Air Force B52 bomber aircraft. Please use this information as you wish.

David L. Barton, Chairman, Prime Resins, Inc., www.primeresins.com

(2)

**Rock / slag - based
geopolymer cement**



Si:Al = 3:1

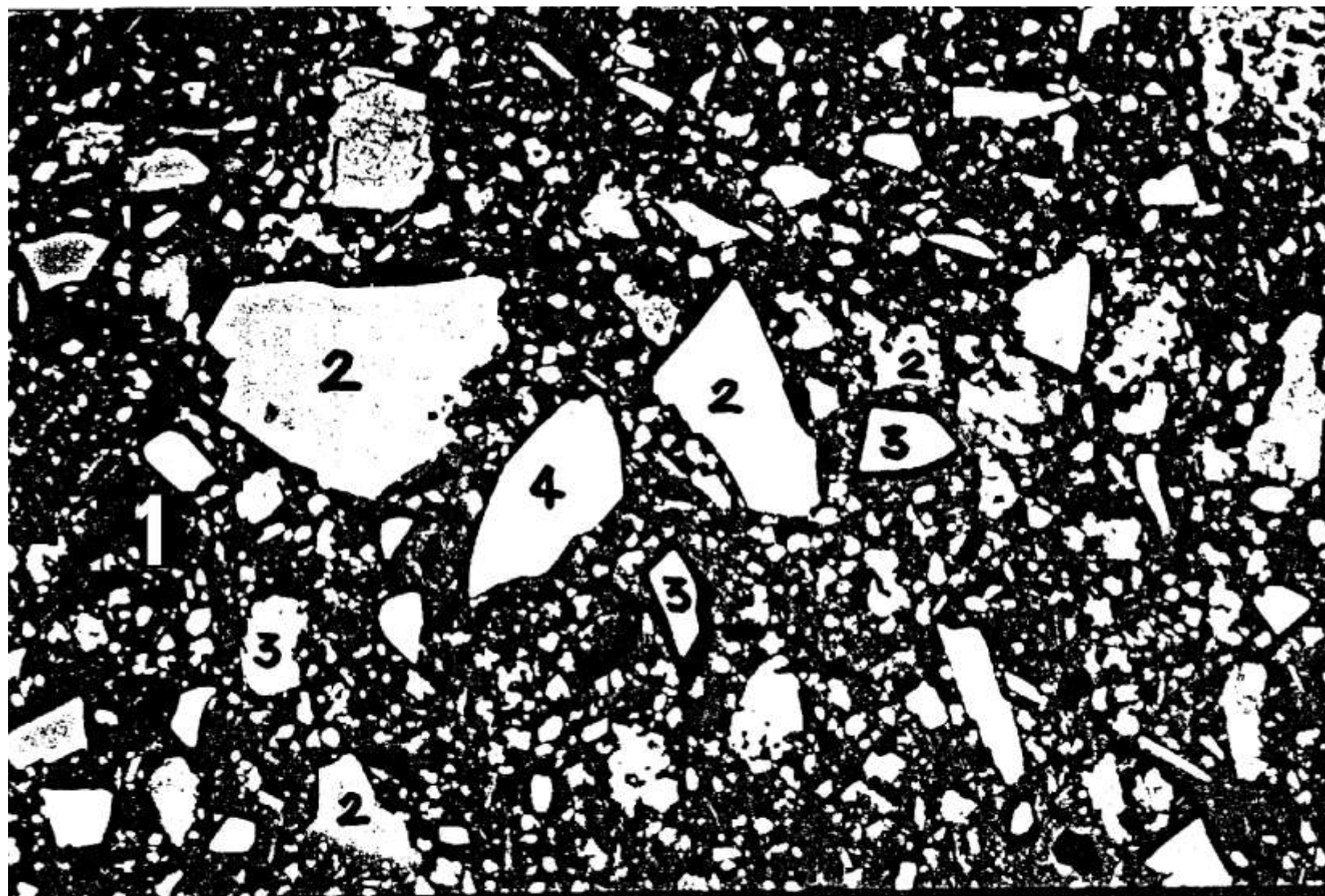
Poly(sialate-disiloxo) geopolymeric cement

❖ Based on geological raw-materials

Compressive Strength at 28 days (room temperature hardening) :

European raw materials: up to 140 MPa

Qatari raw materials: up to 150 MPa



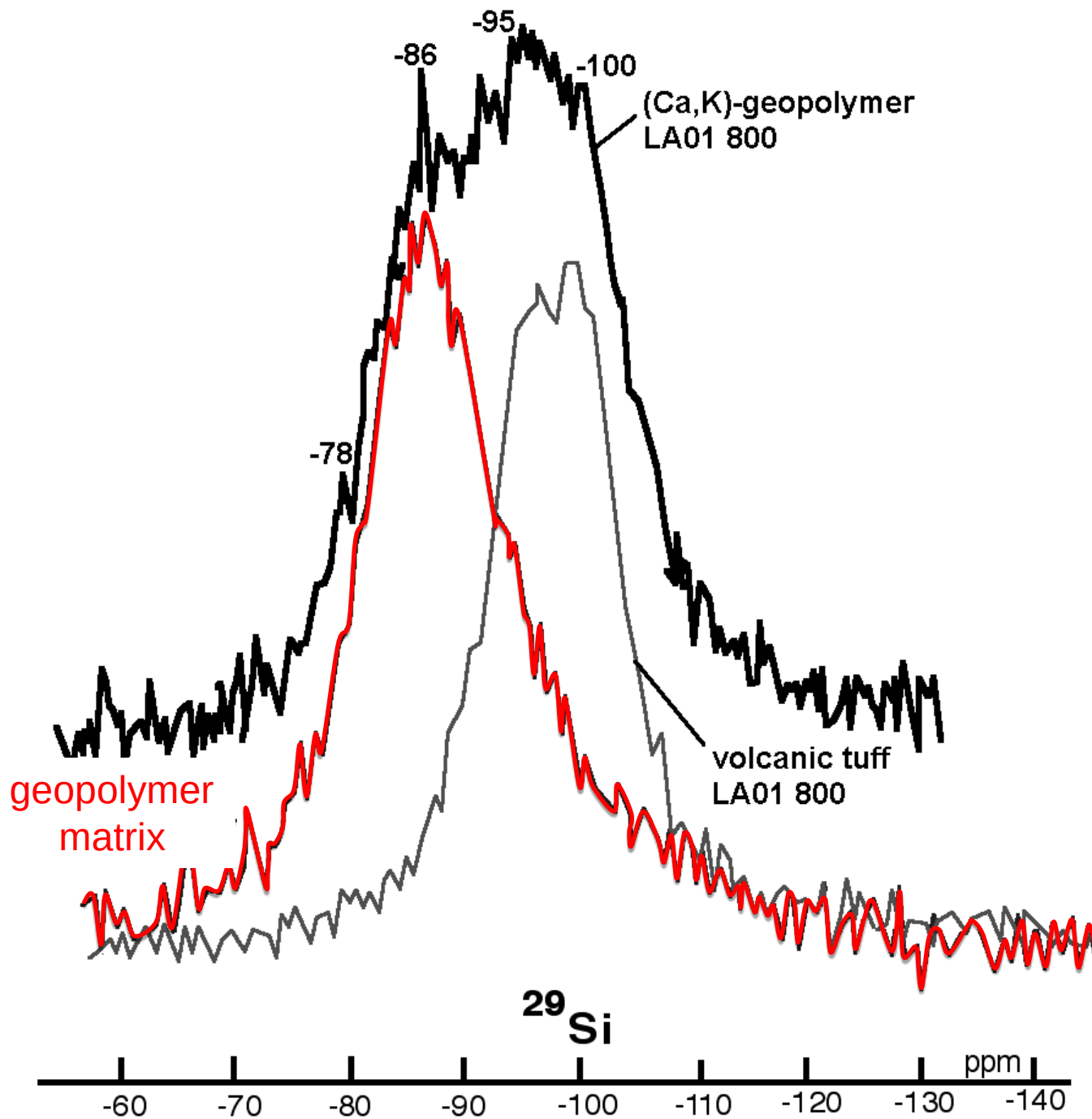
0007

25KV

X400

10µm

WD11



Coal-waste tailing

Coal-waste tailing

- 25% plagioclase (feldspar),
- 30% quartz,
- 10% amphibole,
- 27% kaolinite,
- 3-5% coal and
- 6% of other elements.

calcined at 750° C for 3 hours,
ground to 15-25 microns.

Remains of coal supply part of needed energy

Coal-waste tailing mixture:

- a) coal-mining waste 80
- b) slag (15-25 microns) 20
- c) K silicate sol.
(MR = 1,40), H₂O:53%.....20
- d) water.....20

Ambient temperature hardening

30 MPa at 7 days

75 MPa at 28 days.

Special coal-mining tailings

Coal-waste tailing, calcined by Nature



**Coal-waste
tailing,
calcined
by Nature**

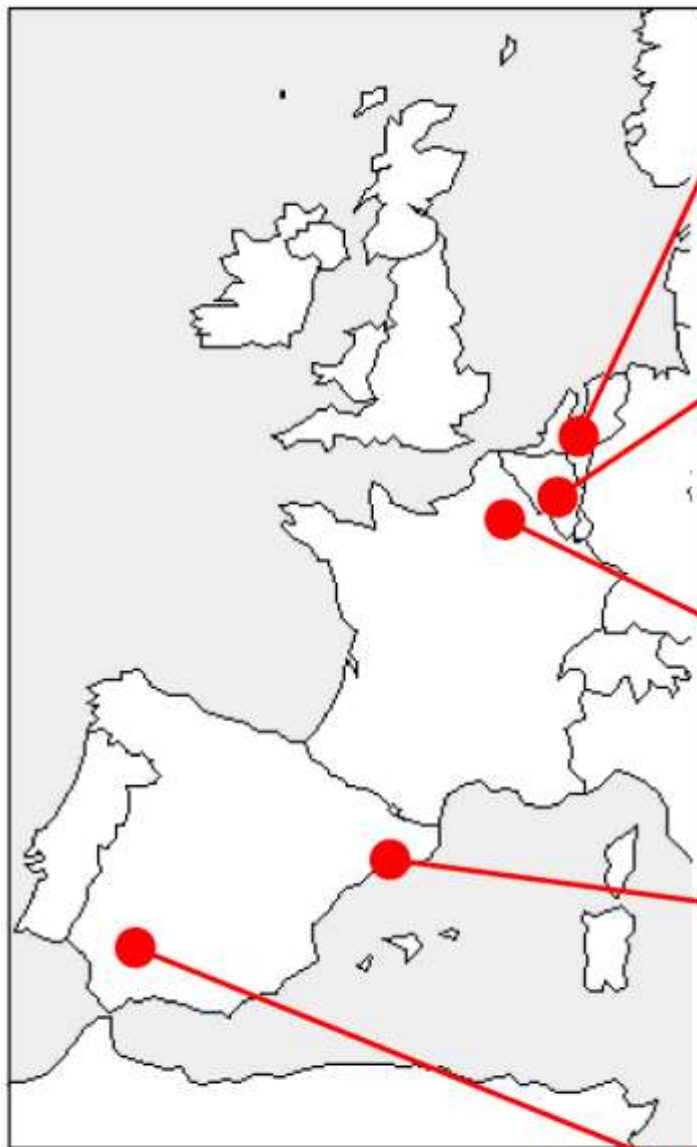


(3)

**Fly ash / slag - based
geopolymer cement**



GEOASH



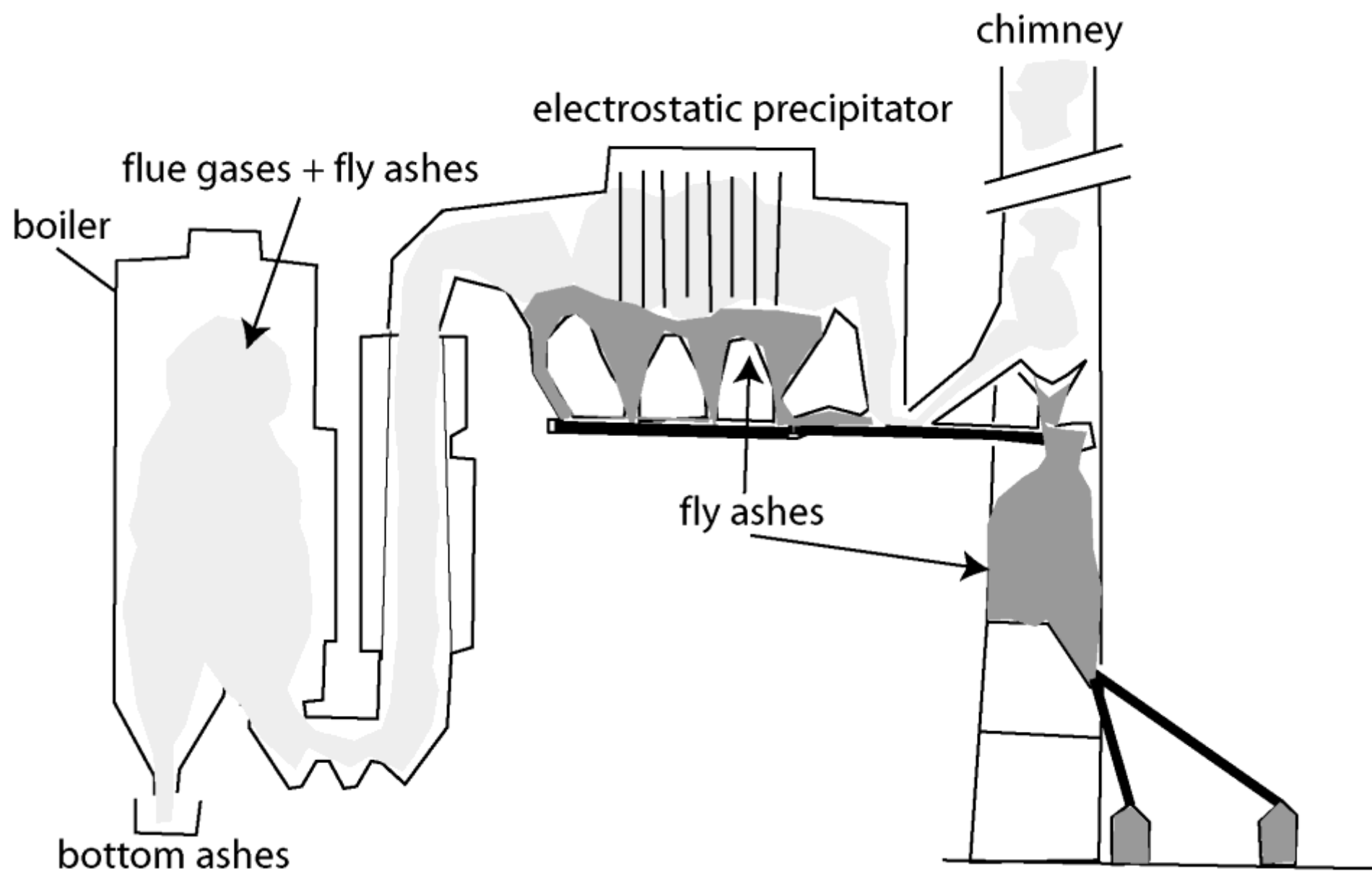
Nederlands
Delft University of Technology
TU Delft, DELFT

Belgium
Institut Scientifique
de Service Public
ISSEP, LIÈGE

France
Cordi-Géopolymère
SAINT-QUENTIN

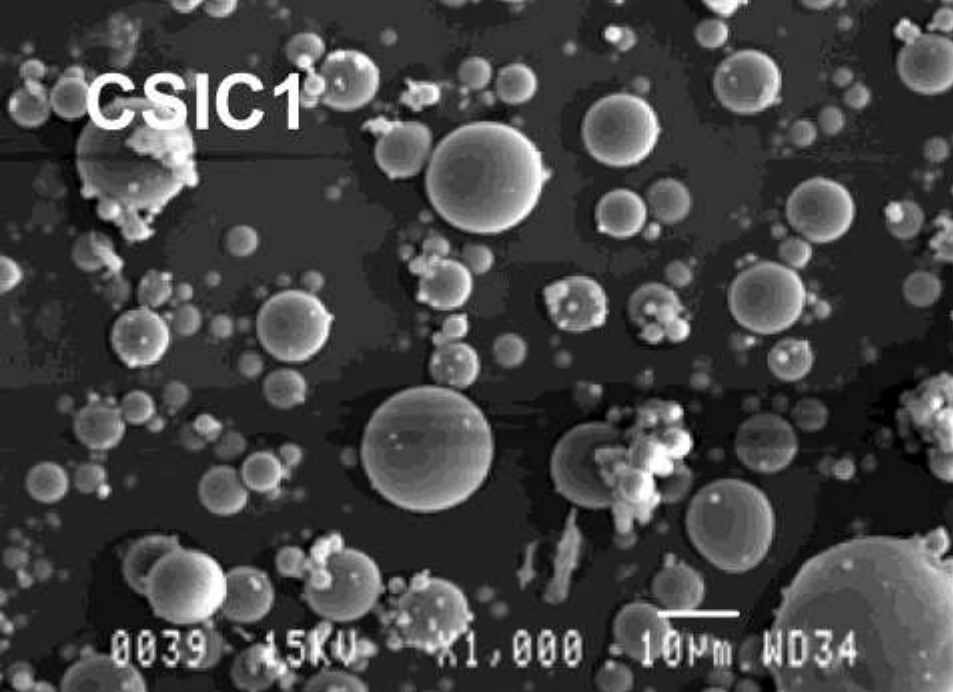
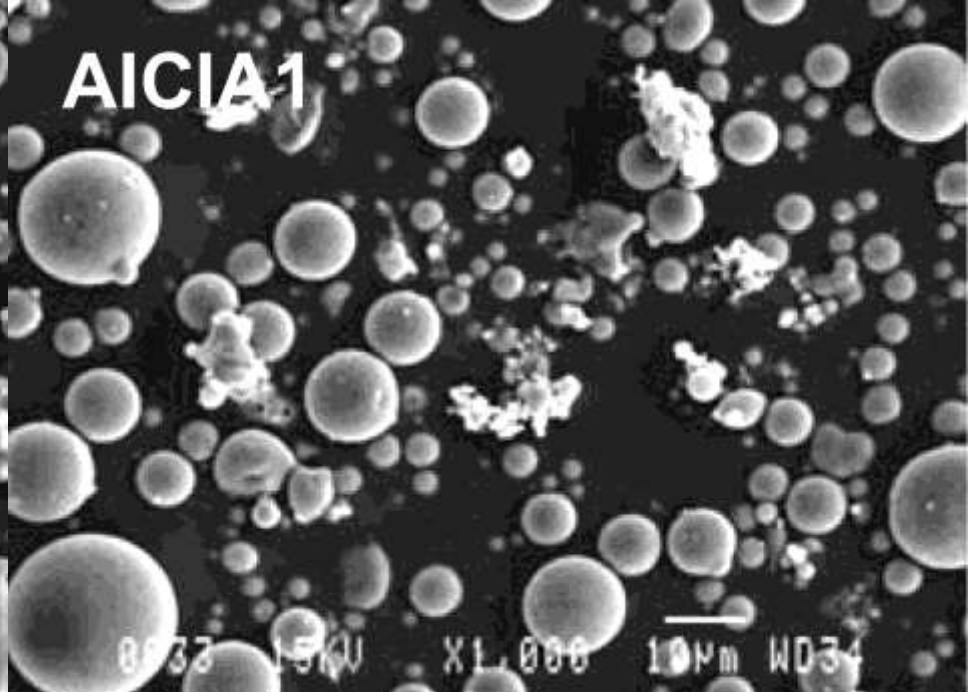
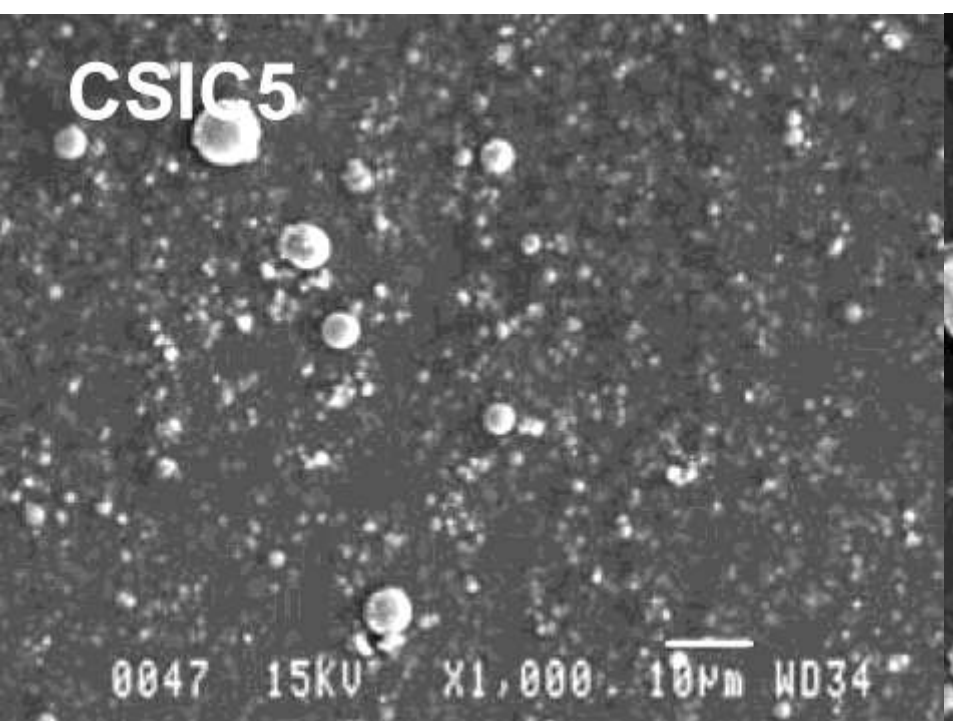
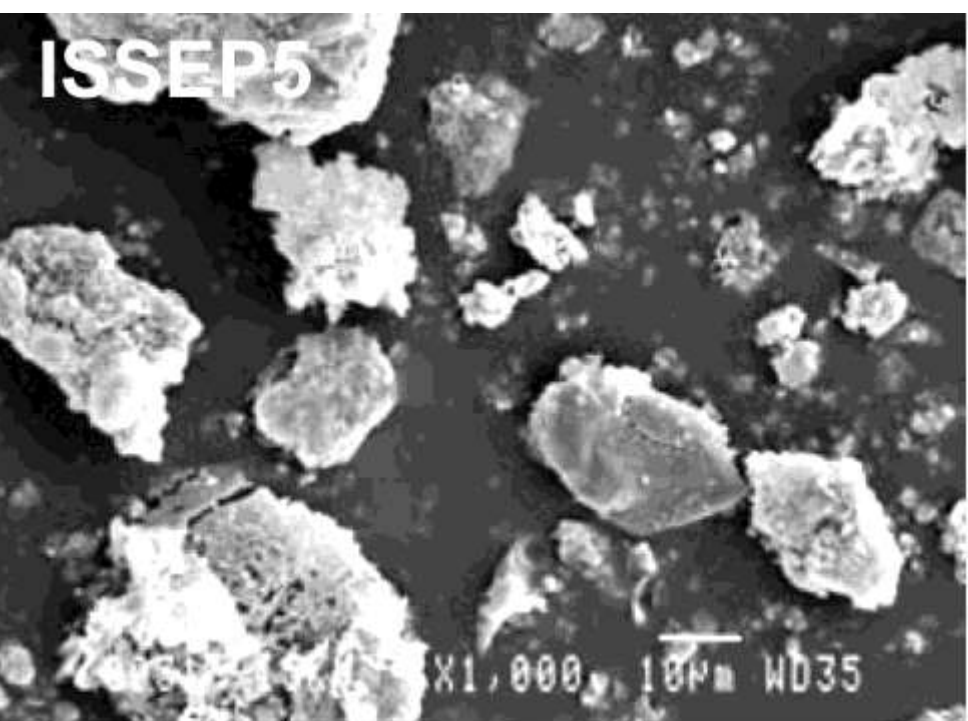
Spain
Consejo Superior de
Investigaciones
Scientificas, BARCELONE

Spain
Ass. Cooperacion Ind. Andalucia
SÈVILLE



Combustion technologies and operating temperatures

Technology	Temperature
fluidized-bed	850° C
pulverized coal combustion 1	1250° C
pulverized coal combustion 2	1500° C
Coal gasification IGCC	1800° C



COAL FLY-ASH GEOPOLYMERIZATION

**Hardening at Room-Temperature
Based on
(K,Ca)-poly(sialate-siloxo) matrix**

Conventional method: alkali-activation dissolution and zeolite formation

- 0.3-0.4 L/kg, NaOH 12M,
- 24h room temperature ageing,
- curing at 80°C for 48h.

User-hostile

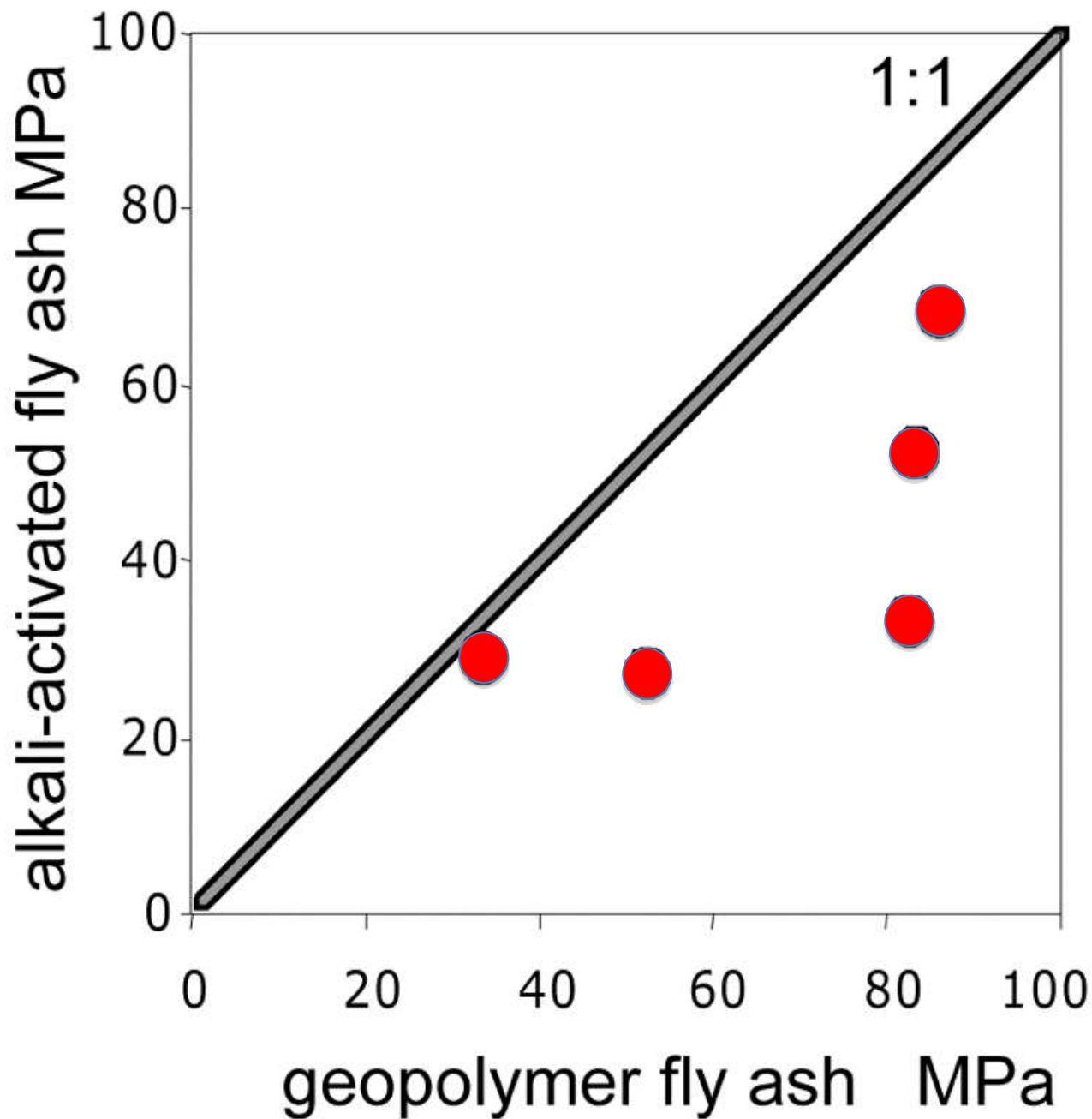
Geopolymeric method:

room temperature hardening polycondensation

- fly ash.....50 to 85
- K-silicate solution $\text{SiO}_2:\text{K}_2\text{O} > 1.4$ 10
- blast furnace slag.....15
- water.....5

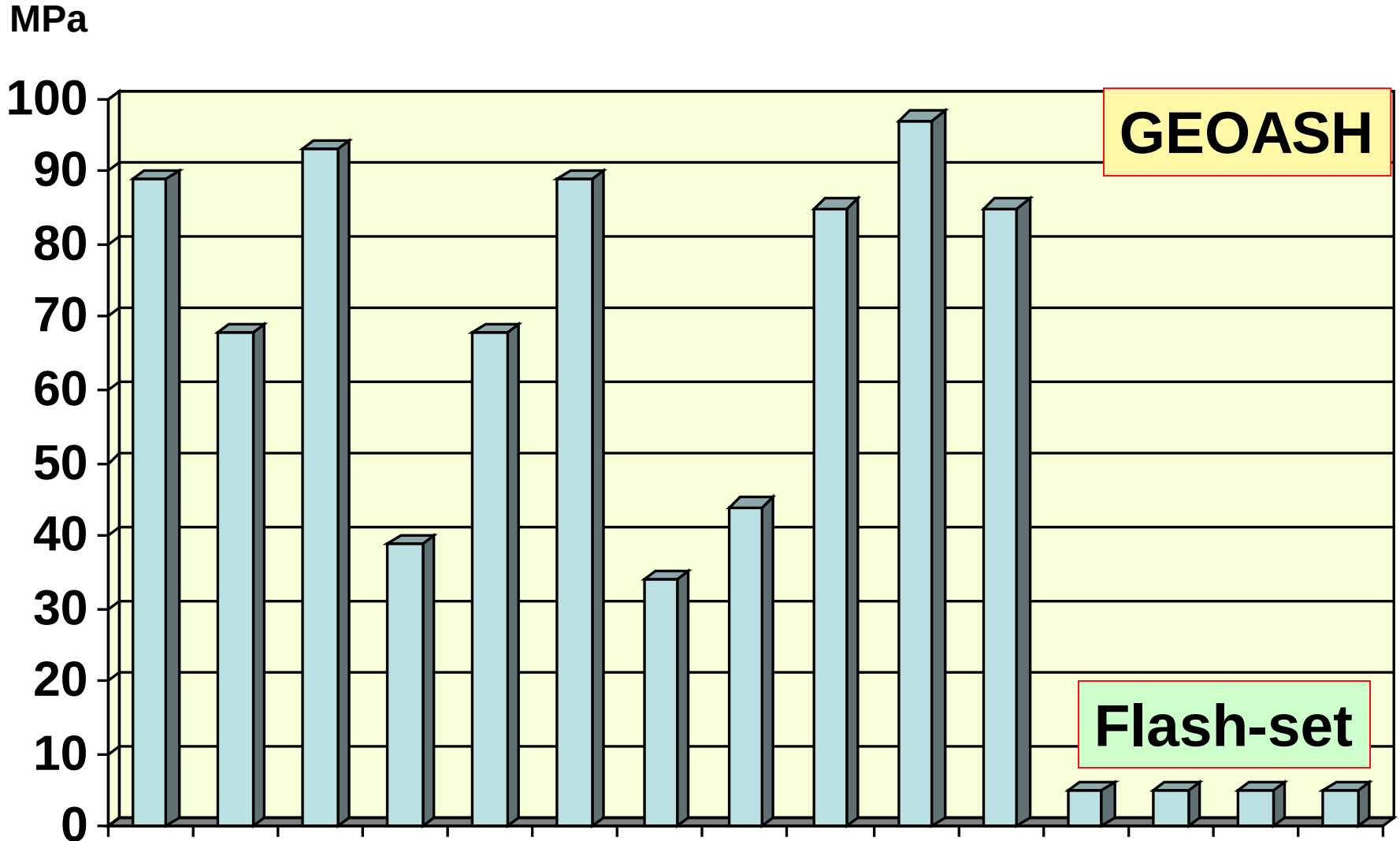
User-friendly.

**28 day
compressive
strength**



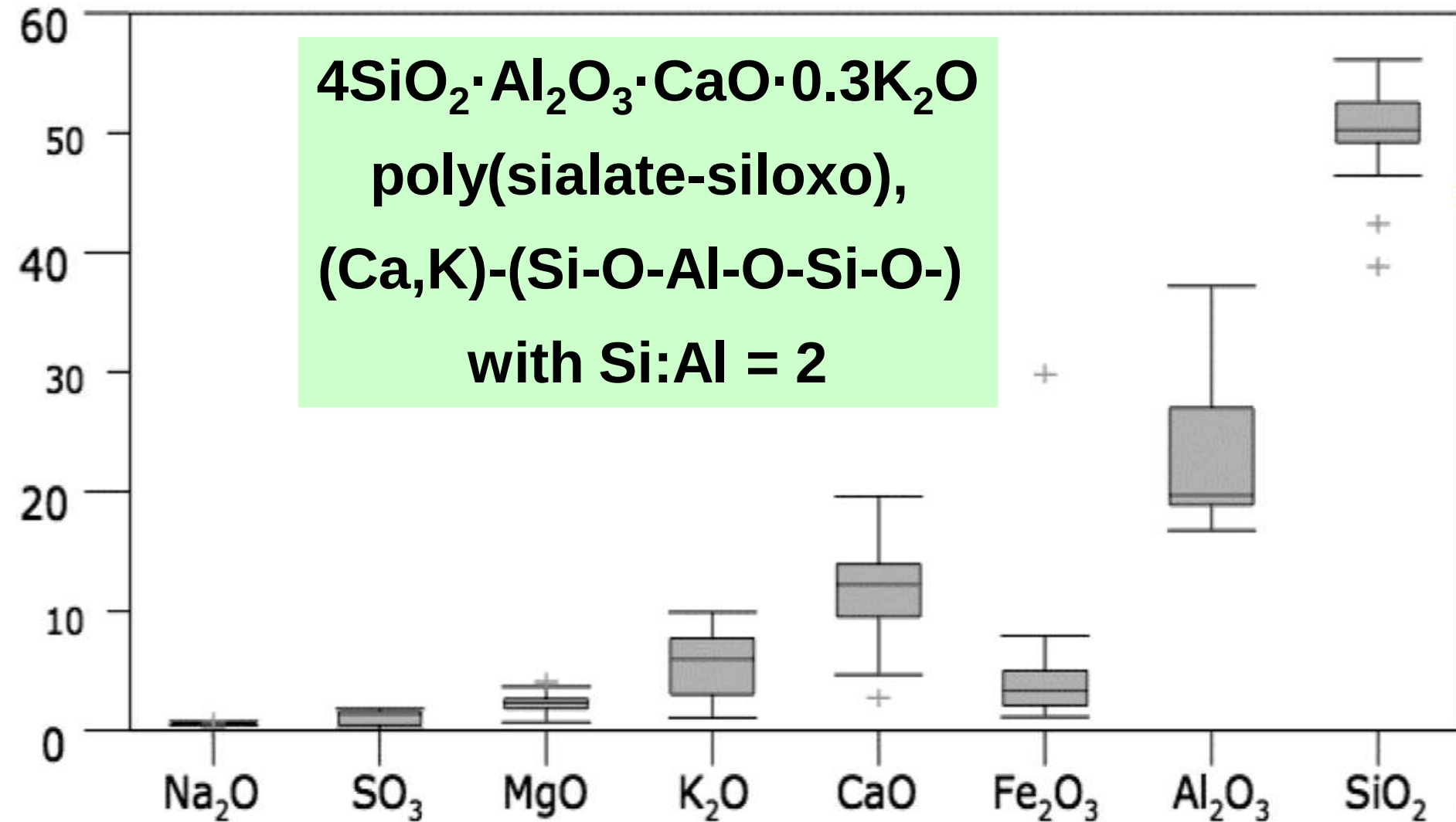
Hardening at ROOM TEMP.

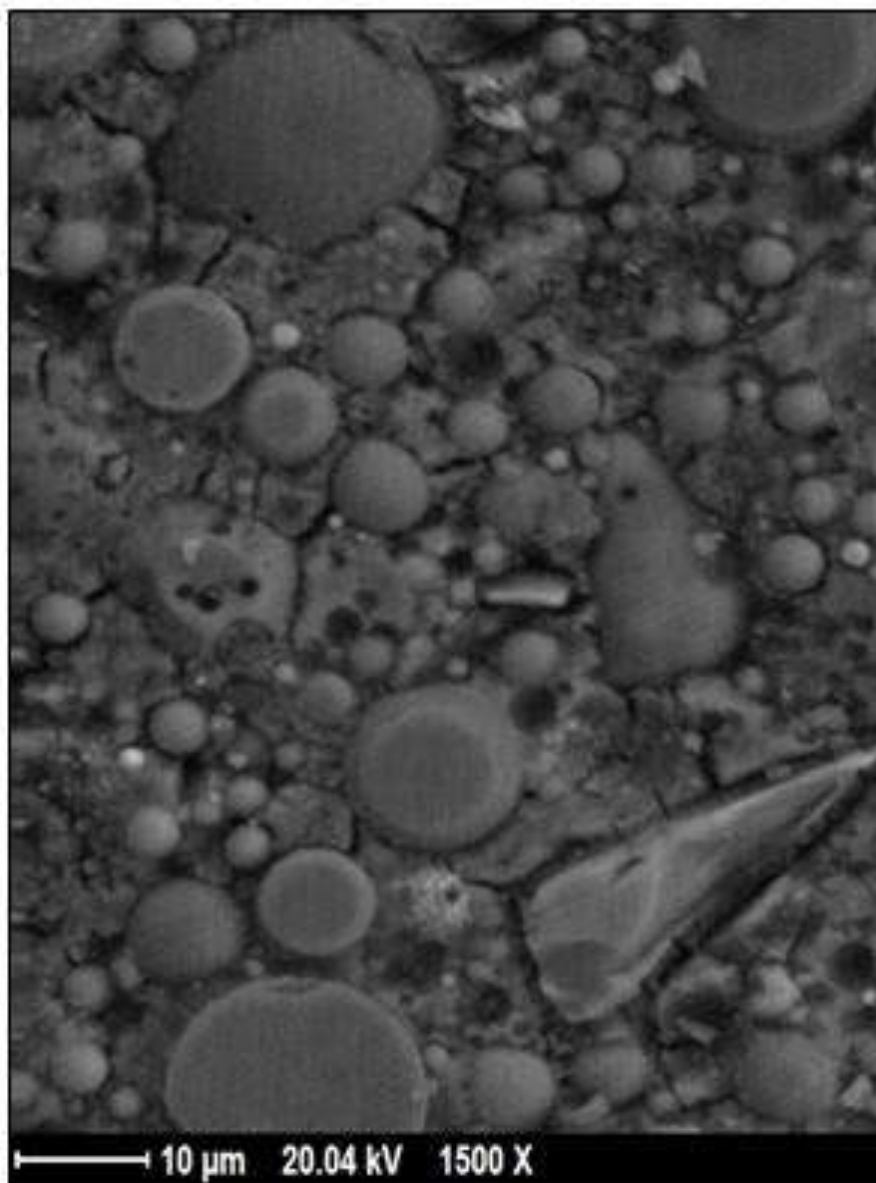
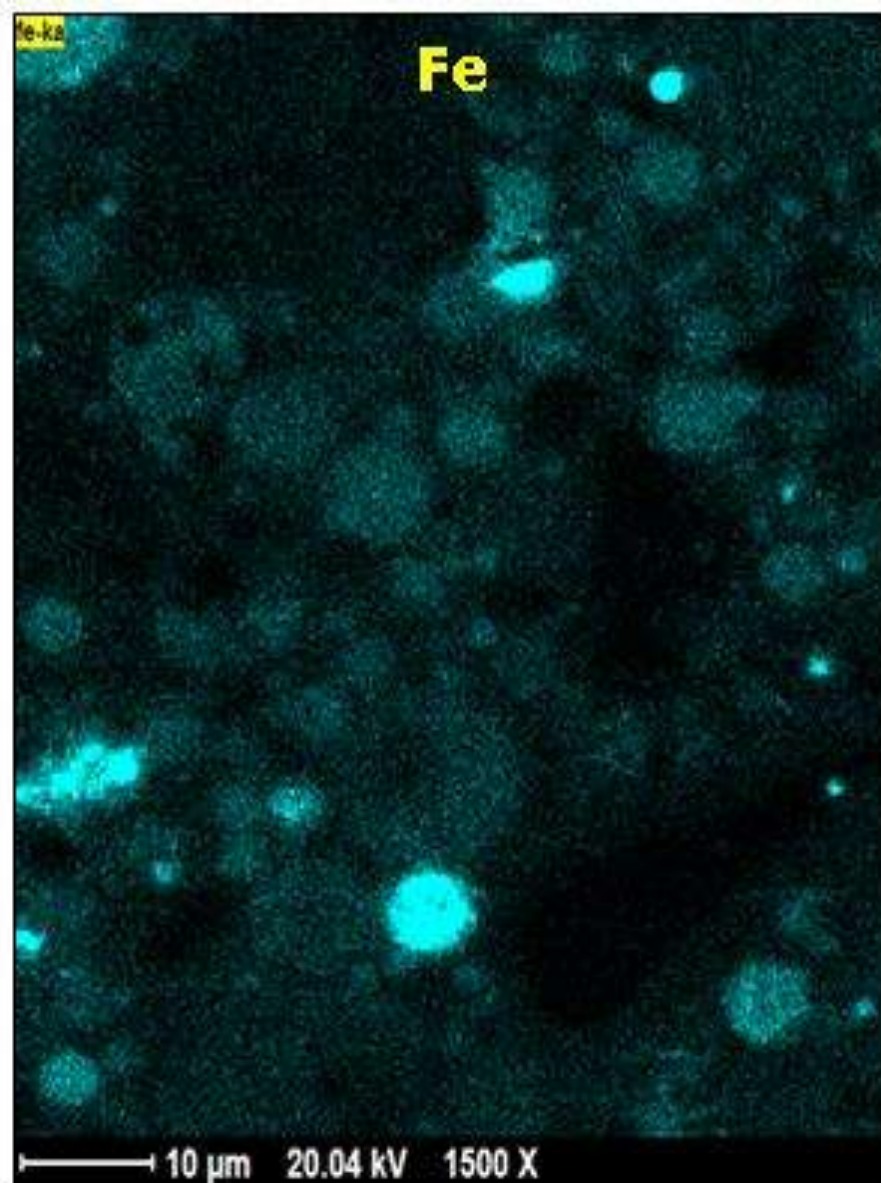
28 day compressive strength

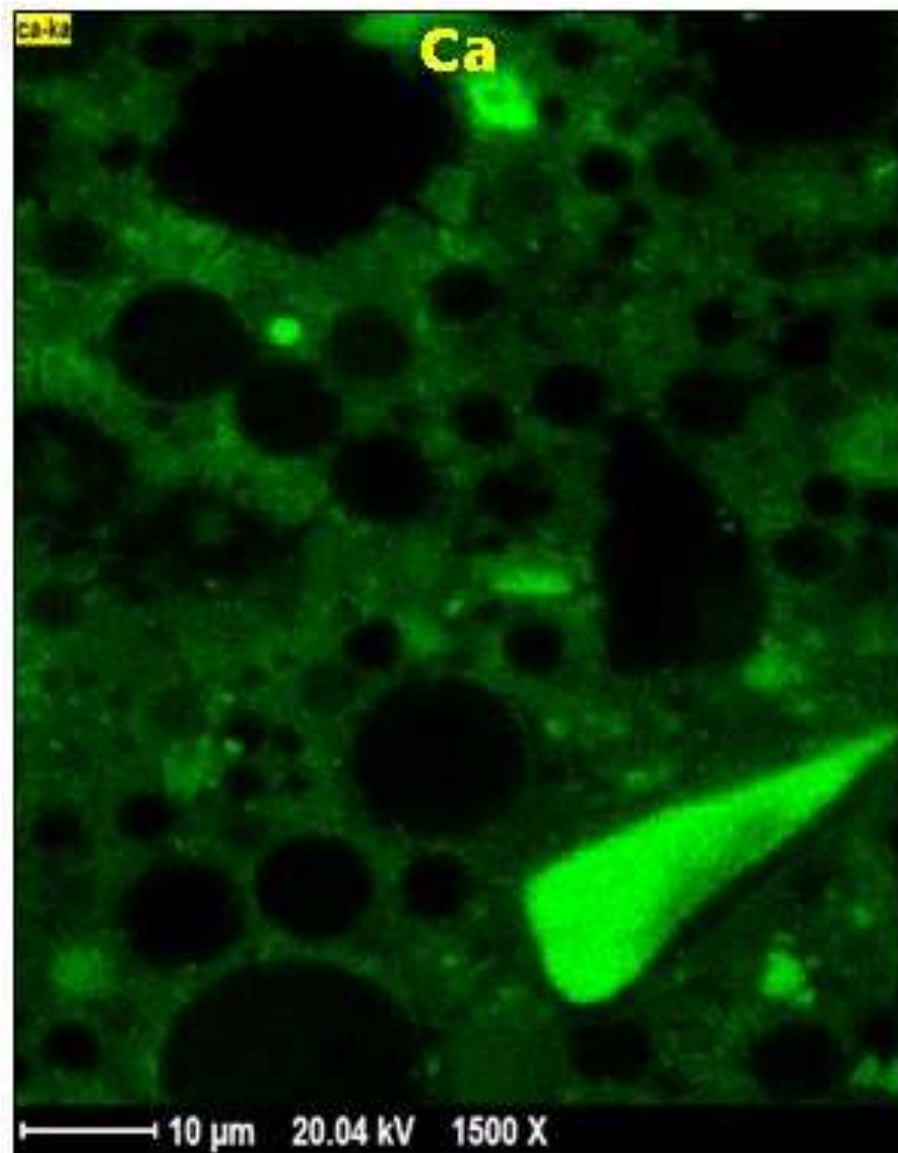
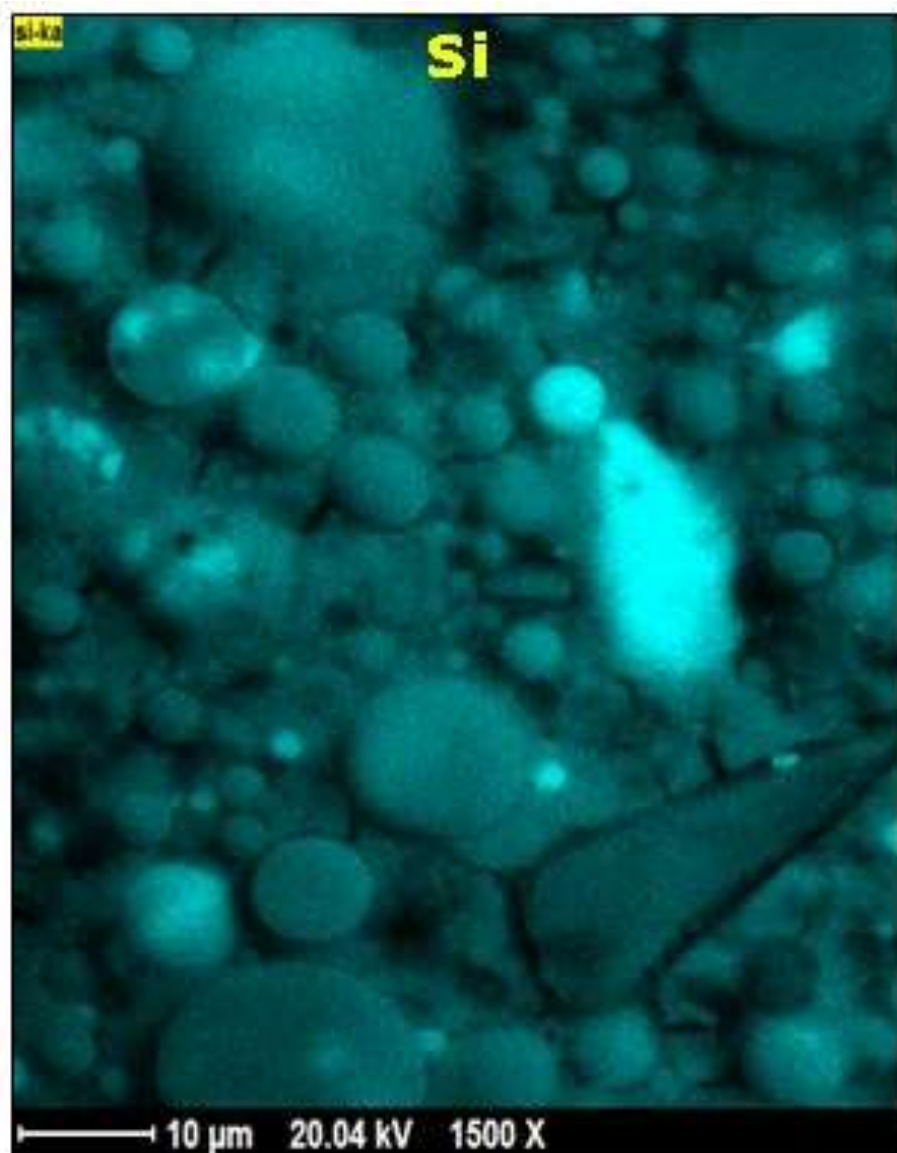


Ca-based geopolymer fly ash matrix composition

$4\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{CaO} \cdot 0.3\text{K}_2\text{O}$
poly(sialate-siloxo),
(Ca,K)-(Si-O-Al-O-Si-O-)
with Si:Al = 2







(4)

**Radio-active waste management
with
MK-750 / slag-based geopolymer
cement**

Method for obtaining a geopolymeric binder allowing to stabilize, solidify and consolidate toxic or waste materials.

FR 2.666.253: **04/09/1990**

CORDI-Géopolymère, Joseph Davidovits



1994-1997

European Research Project:

***GEOpolymer Cement for Innocuous
Stabilization of Toxic EleMents***



Partners: European Commission, CORDI-Géopolymère

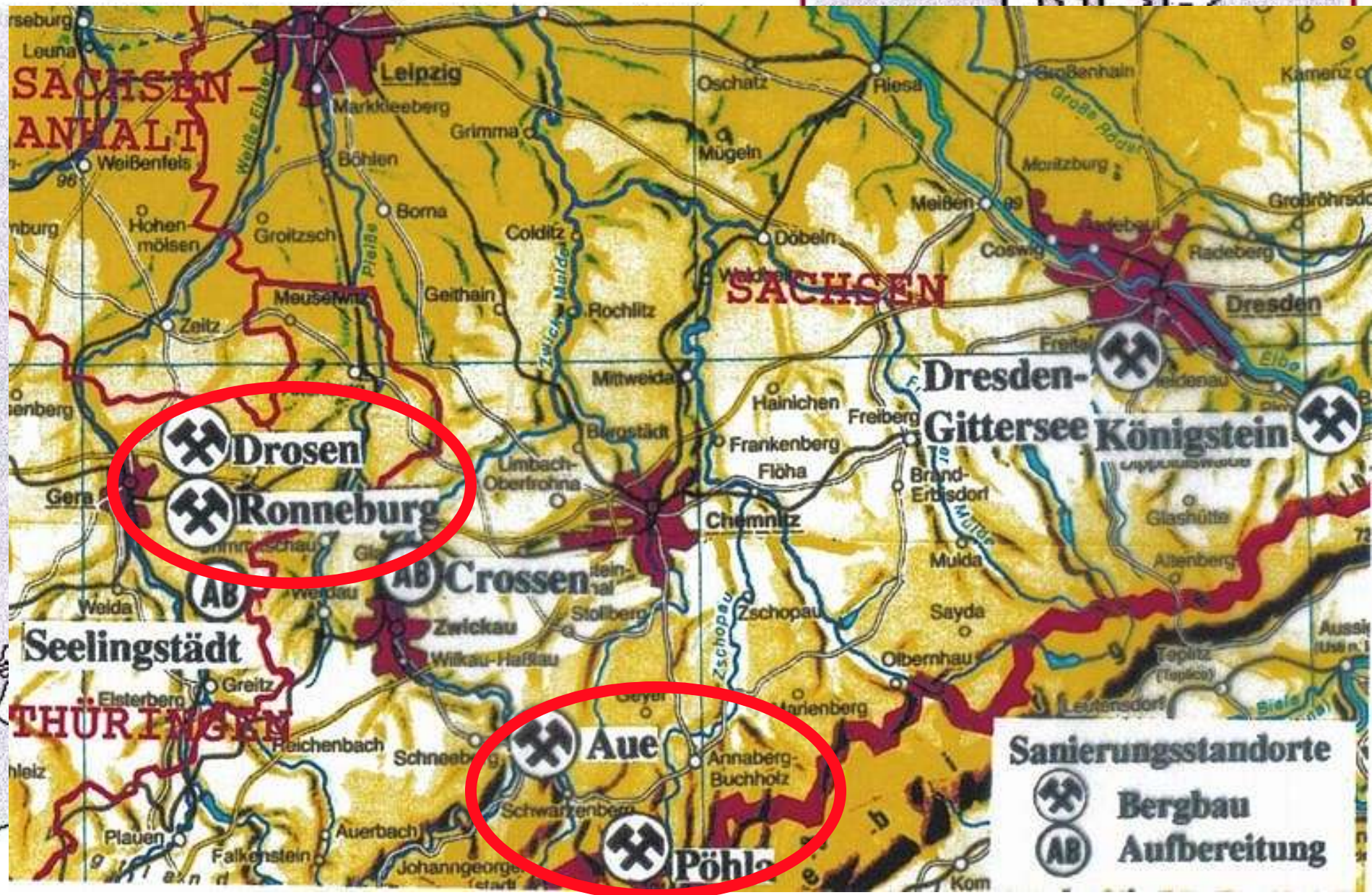
Geology: B.R.G.M. (France), Univ. Barcelona (Spain), Univ. Cagliari (Italy)

Industry: Laviosa (Italy), Heidelberger Cement (Germany),
Cementi Buzzi (Italy), Wismut GmbH (Germany)

1998-2000: Project with WISMUT (Germany),
Uranium mine tailings

Partners: BPS Engineering, Wismut GmbH.







Engineering, Germany



WISMUTH, Germany

DROSEN

**Safe encapsulation of
sludge from decantation
pond (hydrocarbon +
radioactive + Arsenic +
heavy metals)**



**AUE, mine water, 450 m³/h treatment plant,
3.5 - 4 tons sludge per day**



Geopolymer-waste mix cast in the big-bag



20 big-bags : 30 tonnes



Simple disposal area



**From Low-Tech
to High-Tech Development
of USER-FRIENDLY systems**

➤ pH



CORROSIVE



IRRITANT



User- hostile Systems



**User- friendly
Systems**

Corrosive and irritant chemicals



Hostile

CaO (quick lime)

NaOH

KOH

Sodium metasilicate

$\text{SiO}_2:\text{Na}_2\text{O} = 1$

Any soluble silicate

MR $\text{SiO}_2:\text{M}_2\text{O} < 1.45$

Friendly



$\text{Ca}(\text{OH})_2$

Portland cement

Iron slag

**Slurry soluble
silicate/kaolin**

MR $1.25 < \text{SiO}_2:\text{M}_2\text{O} < 1.45$

Any soluble silicate

MR $\text{SiO}_2:\text{M}_2\text{O} > 1.45$

Joseph DAVIDOVITS

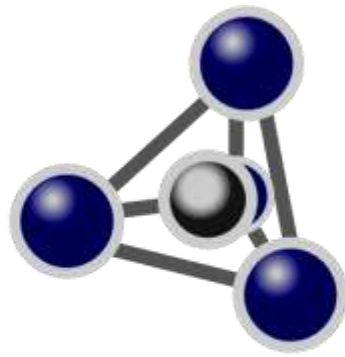
GEOPOLYMER

Chemistry & Applications



GEOPOLYMÈRE
www.geopolymer.org

GEOPOLYMER



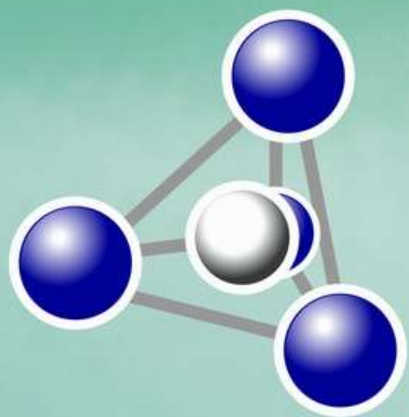
GEOPOLYMERCAMP

3rd Geopolymer Camp

July 4-6, 2011

Saint-Quentin, France

www.geopolymer.org/camp



INSTITUT

GÉOPOLYMÈRE

www.geopolymer.org