



4th Session

Geopolymer Cements



ANNAMALAI UNIVERSITY



Workshop

Geopolymer Cement and Concrete

07 December 2010

SEC 2010
 THE SEVENTH STRUCTURAL ENGINEERING CONVENTION
 PUBLIC LECTURE ON
 Why Pharaohs Built the Pyramids with Fake Stones
 By
Dr. JOSEPH DAVIDOVITS
 Geopolymer Institute
 SAINT-QUENTIN, FRANCE
 on 9-12-2010 at 6 pm
 AUMTEC HALL, FEAT, ANNAMALAI UNIVERSITY




Organised By

 DEPARTMENT OF CIVIL AND STRUCTURAL ENGINEERING
 ANNAMALAI UNIVERSITY
 ANNAMALAI NAGAR 608 002

**INTERNATIONAL WORKSHOP ON
 GEOPOLYMER CEMENT AND CONCRETE**
7th DECEMBER - 2010
 PRE-CONVENTION EVENT OF
 STRUCTURAL ENGINEERING CONVENTION - SEC 2010




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 DEPARTMENT OF CIVIL AND STRUCTURAL ENGINEERING
 ANNAMALAI UNIVERSITY
 ANNAMALAI NAGAR 608 002

SEC 2010
 THE SEVENTH STRUCTURAL ENGINEERING CONVENTION
MEGA BUILD EXPO
 08-12 DECEMBER, 2010
 TIME: 10AM - 8PM VENUE: KALAIARANGAM
 FEAT, ANNAMALAI UNIVERSITY



DEPARTMENT OF CIVIL AND STRUCTURAL ENGINEERING
 ANNAMALAI UNIVERSITY
 ANNAMALAI NAGAR 608 002

பதிவு
LTL
 8 P



Organised by
Dept. of Manufacturing Engineering
(DST/FST Level II & UOC-SAP assisted DRS Department)
Annamalai University
Dr. K. Nagarejan
Naga Roadmades & Tailoring
S.P. Kail Street
Chidambaram

WELCOMES YOU ALL

SEC 2010
THE SEVENTH STRUCTURAL ENGINEERING CONVENTION
AN INTERNATIONAL CONFERENCE
08-10 DECEMBER - 2010
Presented by

DEPARTMENT OF CIVIL AND STRUCTURAL ENGINEERING
ANNAMALAI UNIVERSITY ANNAMALAI NAGAR 608 002

INTERNATIONAL WORKSHOP ON
GEOPLYMER CEMENT AND CONCRETE
DECEMBER - 2010
PROFESSIONAL EVENT OF
STRUCTURAL ENGINEERING CONVENTION - SEC
DEPARTMENT OF CIVIL AND STRUCTURAL ENGINEERING
ANNAMALAI UNIVERSITY ANNAMALAI NAGAR 608 002





Imperative to find alternative to cement, says French expert

International workshop on 'Geopolymer cement and concrete' held

Special Correspondent

CUDDALORE: Going by the quantum of carbon-dioxide emission, the Portland cement industry is the highest polluting industry in the world. Therefore, more than the developed countries the developing countries that require enormous quantity of cement for infrastructure face acute pollution problem, according to Joseph Davidovits of Geopolymer Institute, France.

Hence, it has become imperative to find an alternative to cement, said Mr. Davidovits, popularly known as "Father of Geopolymer technology." He was participating as chief guest at an international workshop on "Geopolymer cement and concrete" organised by the Department of Civil and Structural Engineering of Annamalai University at Chidambaram on Tuesday.

He opined that India and France that had now signed many pacts on high-technology aspects could have focussed attention on geopolymer technology too because it could be equated to nanotechnology.

Mr. Davidovits, who has coined the term 'geopolymer,' said that although geopolymer technology was considered new it had ancient roots and had been used in the construction of the pyramids at Giza in Egypt.

The production of one tonne of Portland cement generated one tonne of carbon-dioxide. According to statistics, 1.8 billion tonnes of



Annamalai University Vice Chancellor M.Ramanathan handing over the proceedings of the international workshop on "Geopolymer cement and concrete" to Joseph Davidovits of Geopolymer Institute, France, at Chidambaram on Tuesday.

- PHOTO: C VENKATACHALAPATHY

cement were produced in the world in 2000 and it accounted for 1.8 billion tonnes of carbon-dioxide.

In developing countries, particularly China, India and Brazil, there was exponential increase in cement production.

Any further economic development in these countries would strongly depend upon creation of more infrastruc-

ture and production of more cement. On the contrary, cement production remained constant in the Western countries, particularly in the U.S. and European Union.

The production of one tonne of geopolymer cement would require 3.5 times less energy than that of Portland cement. Therefore, besides deriving cost benefit the geopolymer cement application

would also safeguard environment, Mr. Davidovits added. B.Vijaya Rangan of Curtin University of Technology, Perth, Australia, called for transferring the laboratory work on geopolymer to large-scale applications.

M. Ramanathan, Vice-Chancellor of Annamalai University, said that according to statistics 120 million tonnes of coal were burnt in

380 thermal stations in the country during 2006-2007 that generated 108 million tonnes of fly ash.

Hardly 30 million tonnes of fly ash were utilised in the cement and brick industries and the remaining was dumped in ash pond. Using the fly ash in a purposeful manner would also spare vast stretches of land and address the pollution problem, Dr.

Ramanathan added.

P.Paramasivam of National University of Singapore, Singapore, B.Palaniappan, Dean, Faculty of Engineering and Technology, Annamalai University, C.Antony Jeyasehar, Head, Department of Civil and Structural Engineering and chairman of organising committee and S.Thiruganasambandam, secretary, spoke.

Geopolymer

inorganic macromolecules

Geopolymer inorganic macromolecules

Portland CSH

Geopolymer inorganic macromolecules

Portland CSH
geopolymer NaASH

Ca-based Geopolymer cement

**Ca-based
Geopolymer cement
chemistry =**

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

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

1. alkalination: alumino-silicates + alkali

**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)

Geopolymerization *in alkaline milieu*

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- 3. Inter-reaction of oligo-sialates/oligo-siloxo**

Geopolymerization *in alkaline milieu*

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- 3. Inter-reaction of oligo-sialates/oligo-siloxo**
- 4. Polycondensation into poly(sialates)**

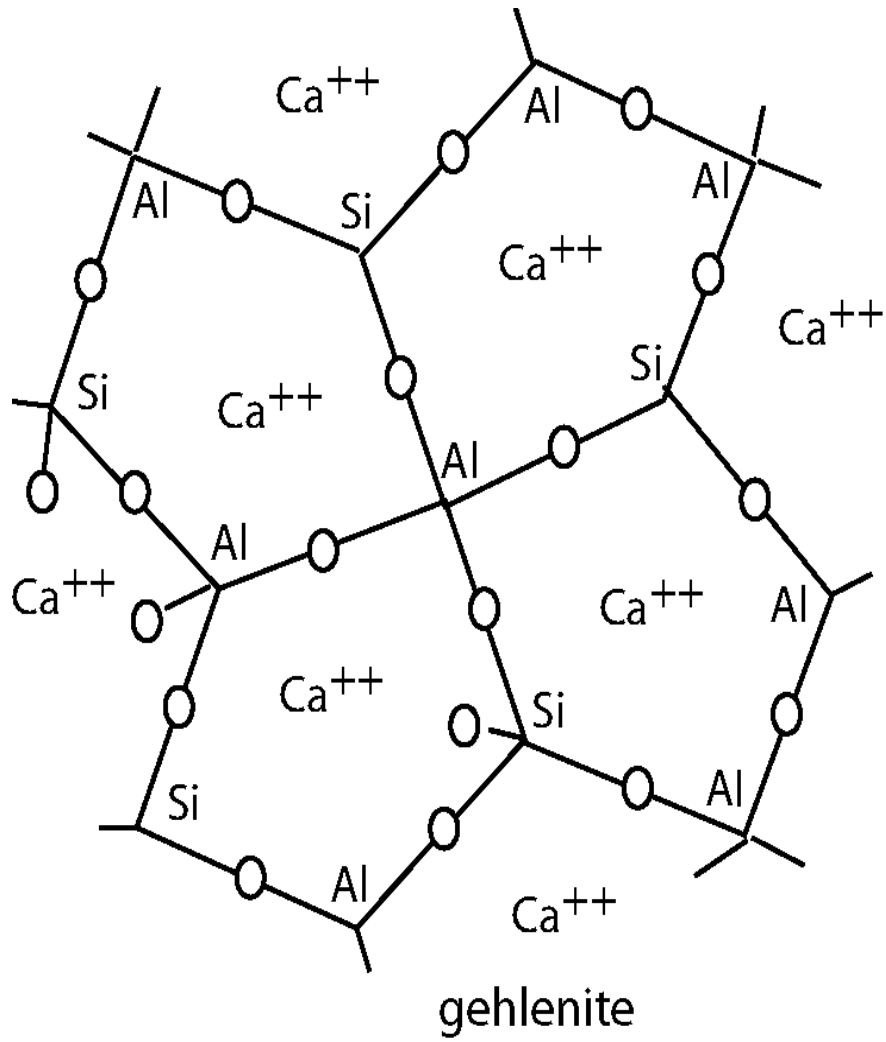
Geopolymerization *in alkaline milieu*

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- 5. Reticulation, networking**

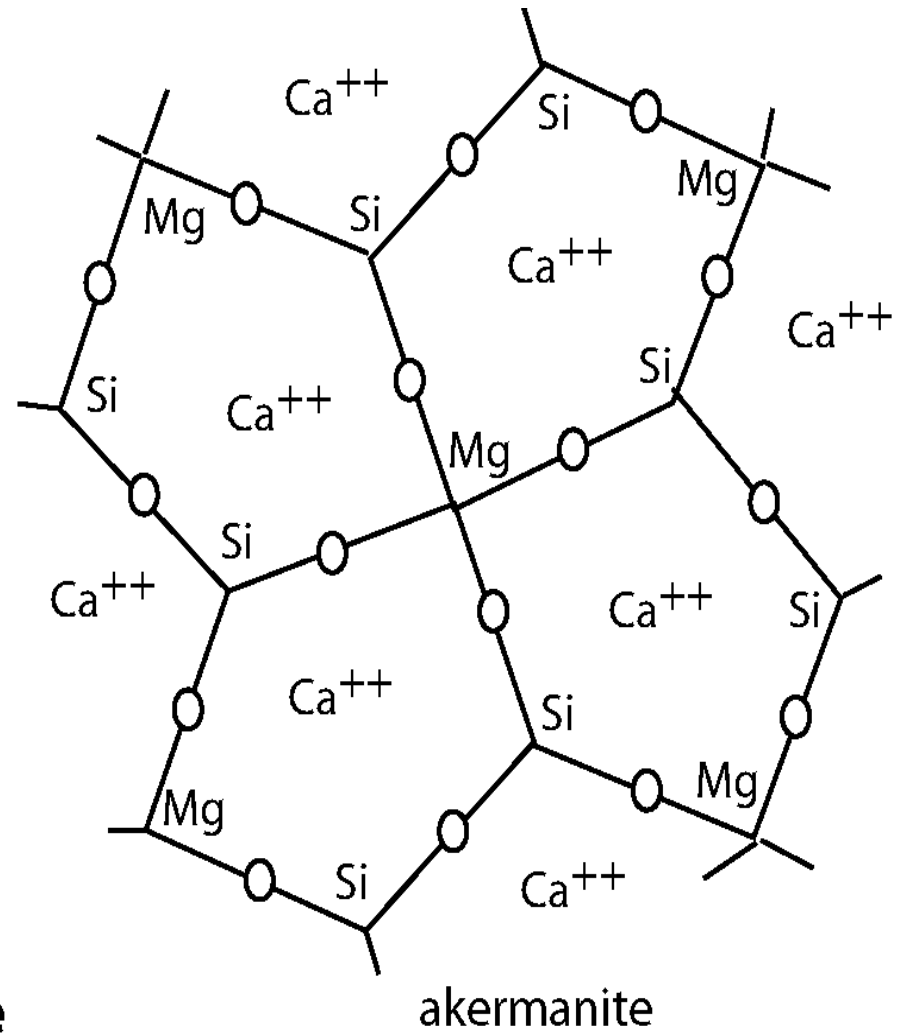
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- 3. Inter-reaction of oligo-sialates/oligo-siloxo**
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- 5. Reticulation, networking**
- 6. Geopolymer solidification**

Blast furnace slag

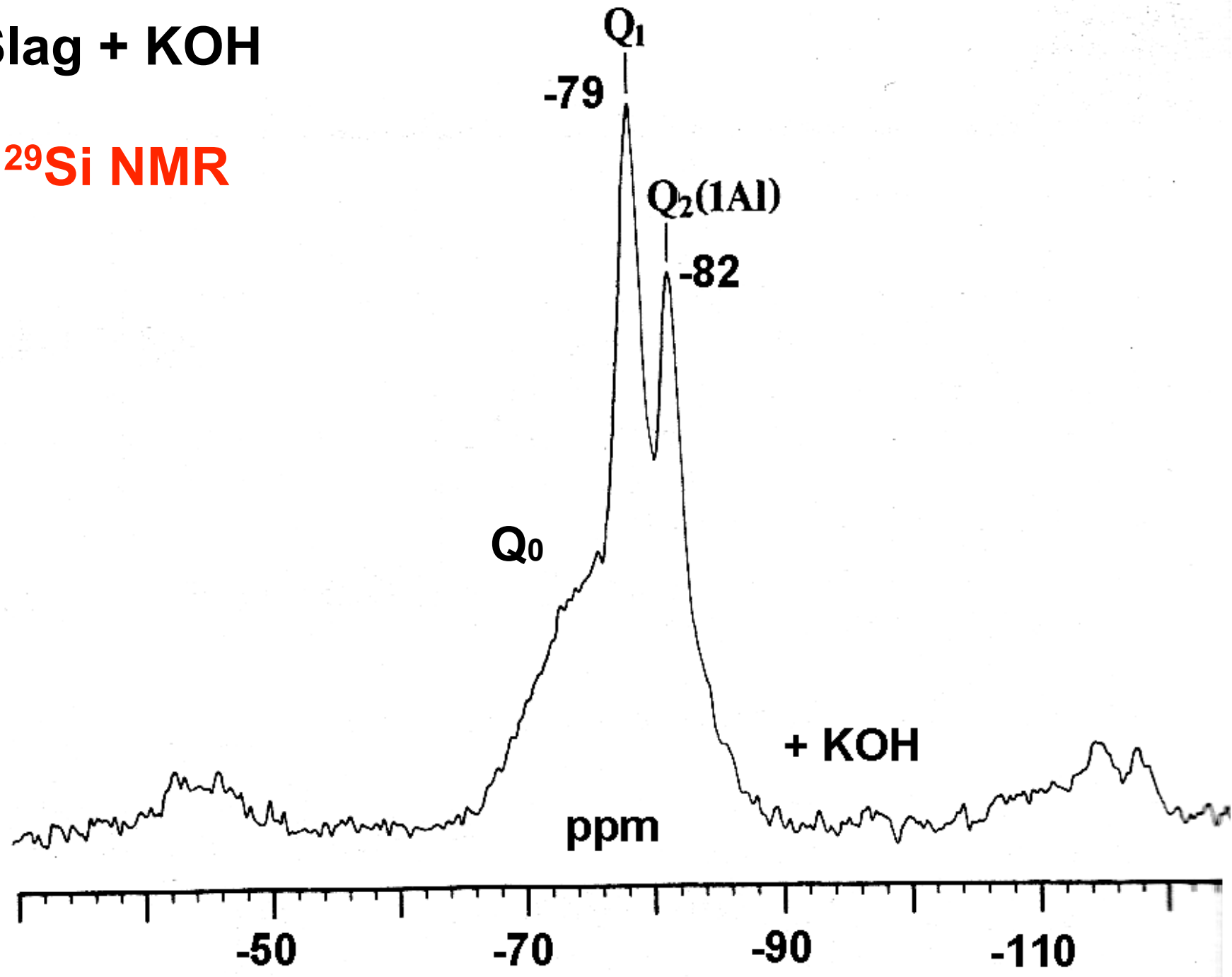


melilite

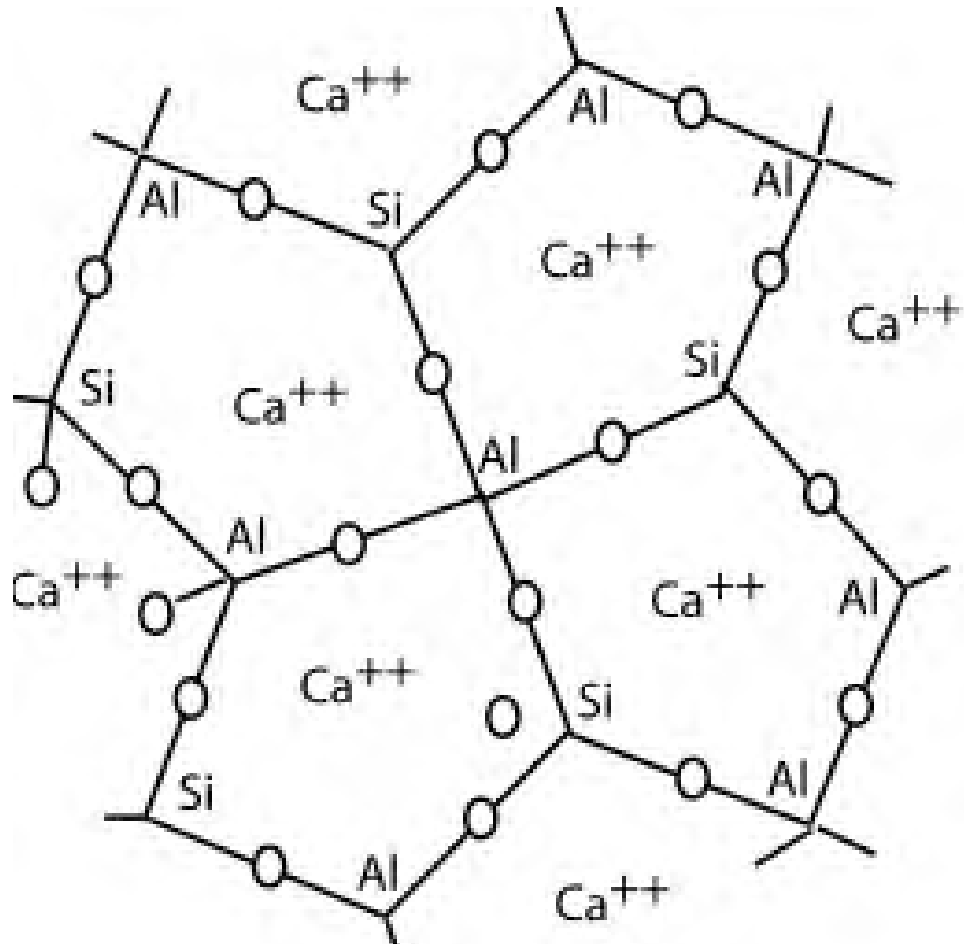


Slag + KOH

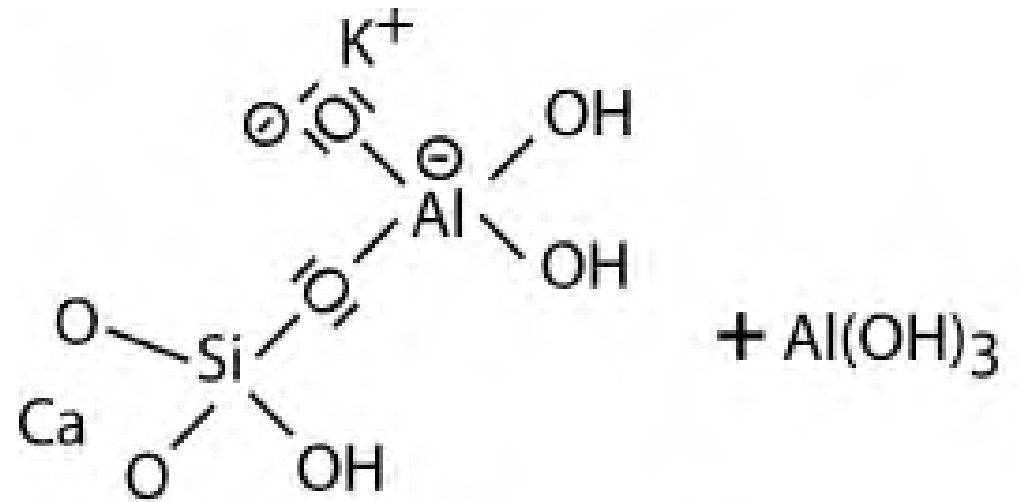
^{29}Si NMR



Alkalinization

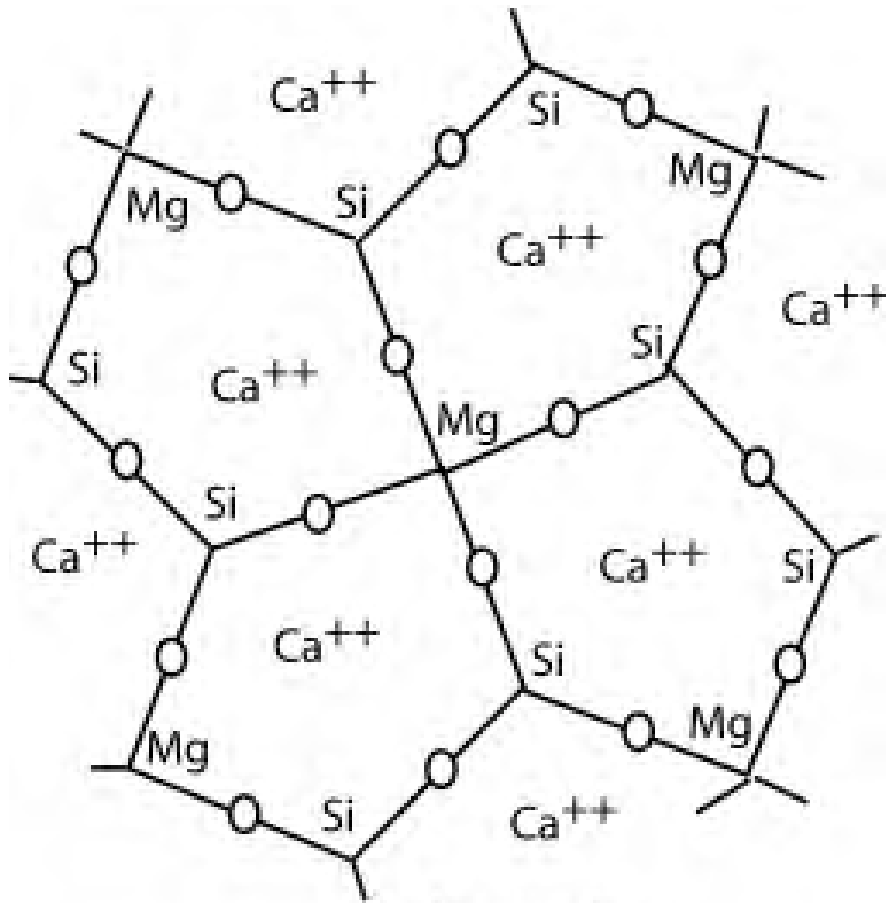


gehlenite

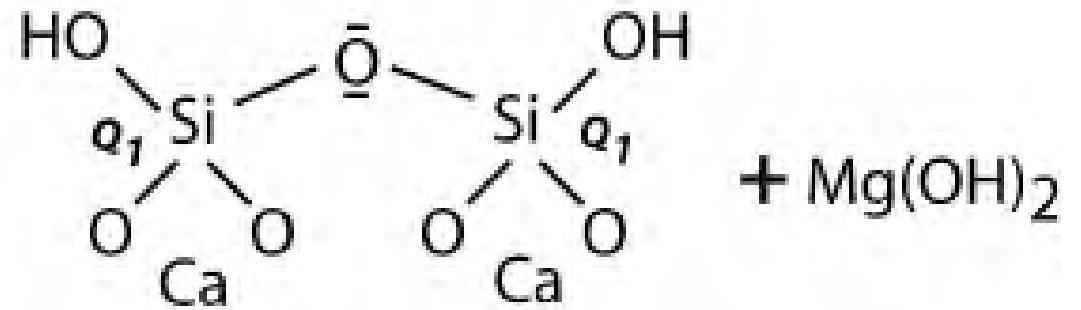


(K,Ca)-ortho-sialate hydrate

Alkalinization



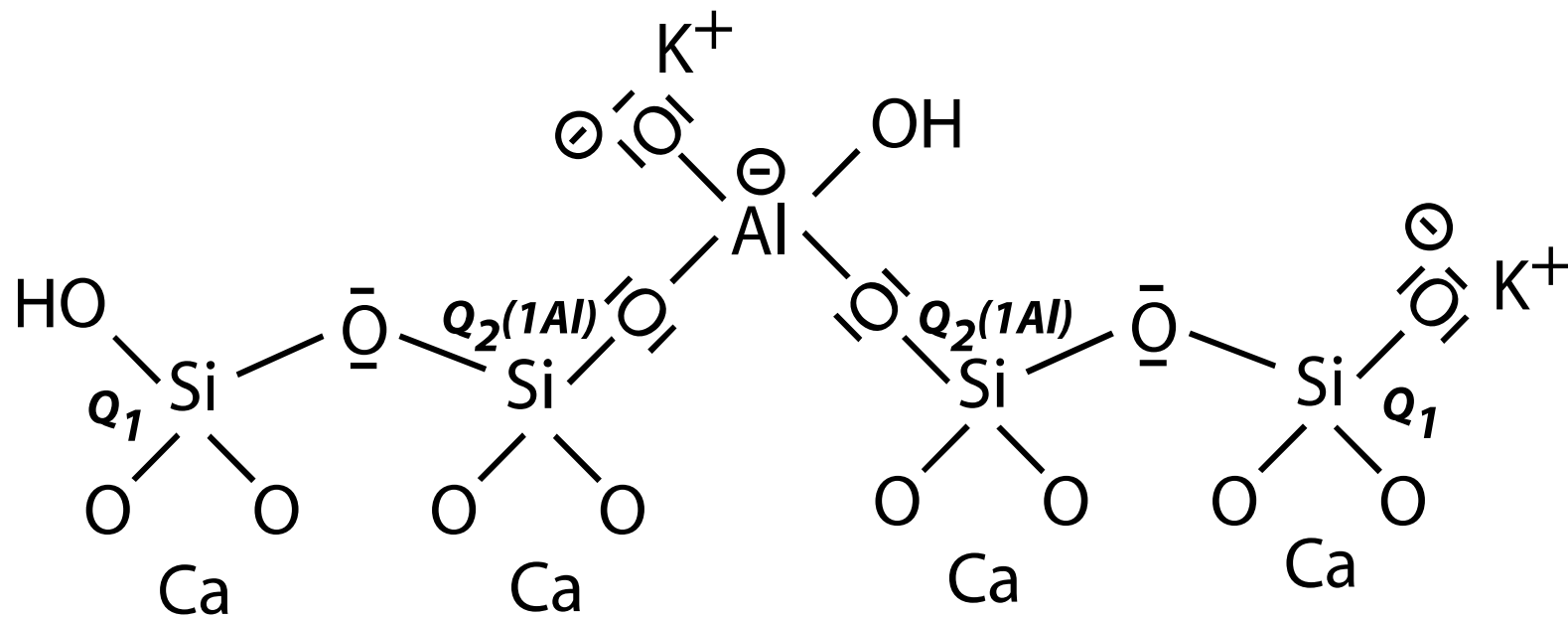
akermanite



Ca-di-siloxonate hydrate

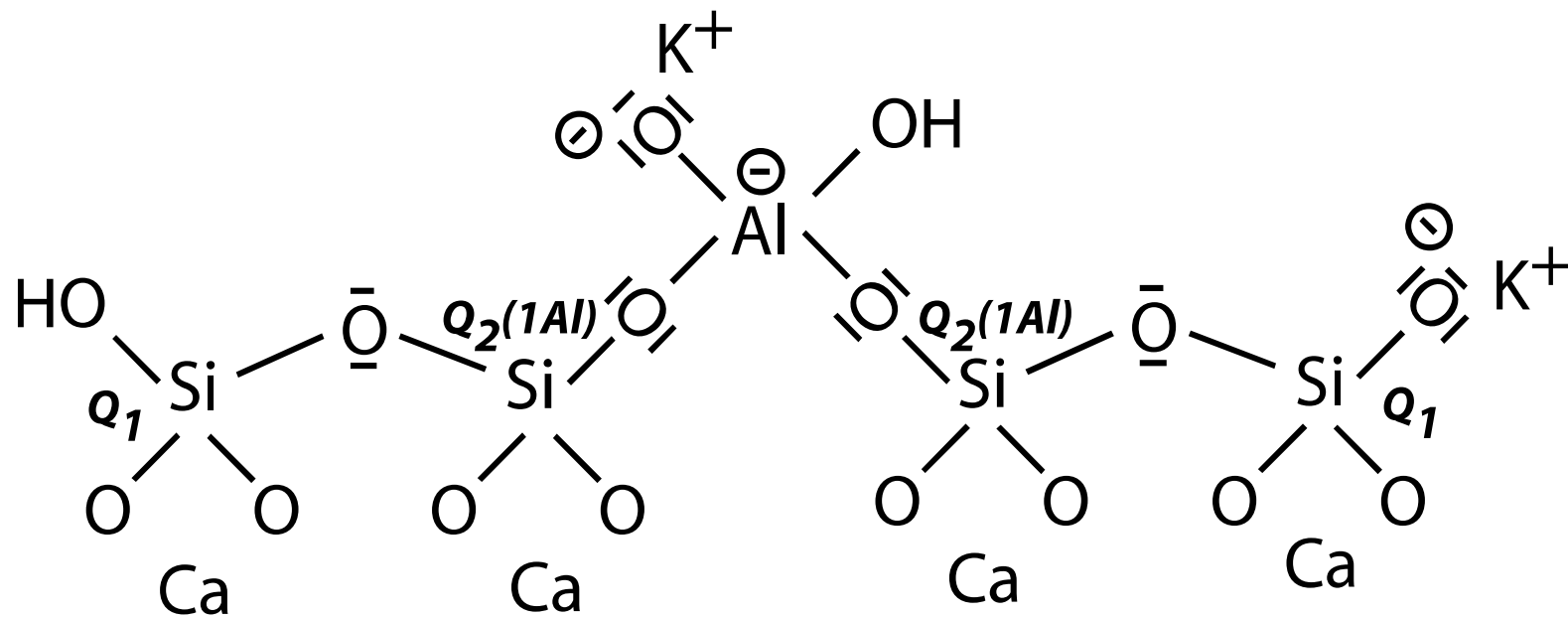
CSH

Si Q2 unit



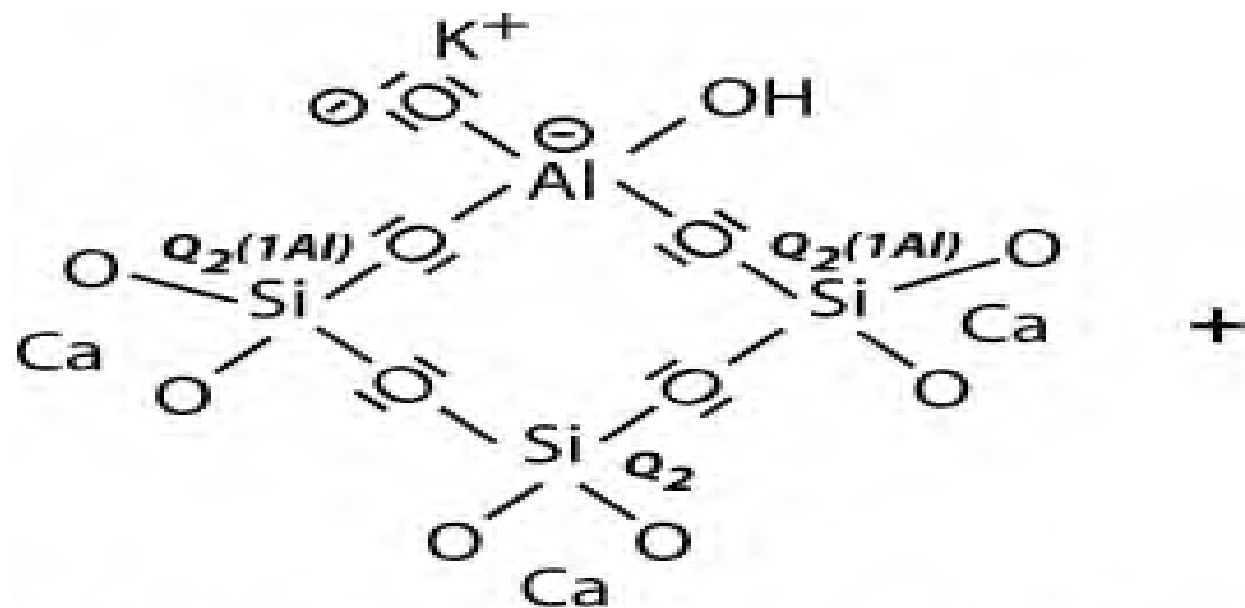
tobermorite with Al substitution

Si Q2 unit



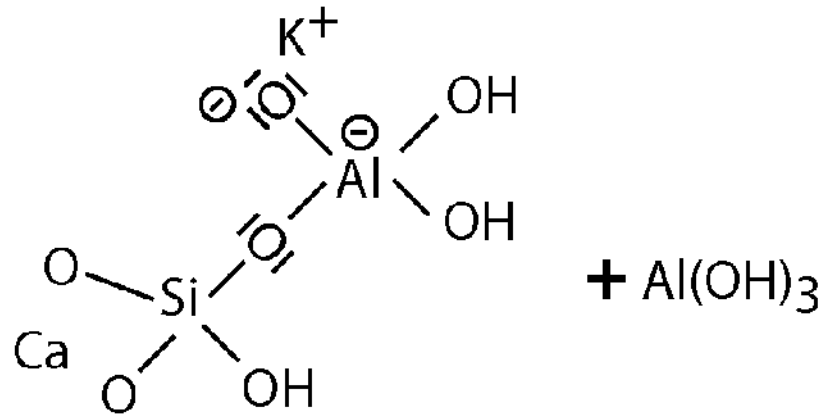
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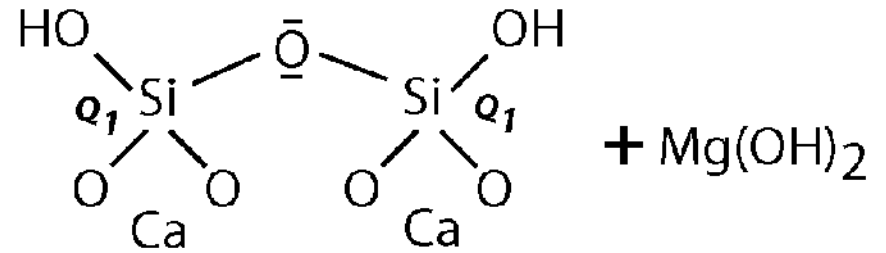
(K,Ca)-cyclo-ortho(sialate-disiloxo)

gehlenite



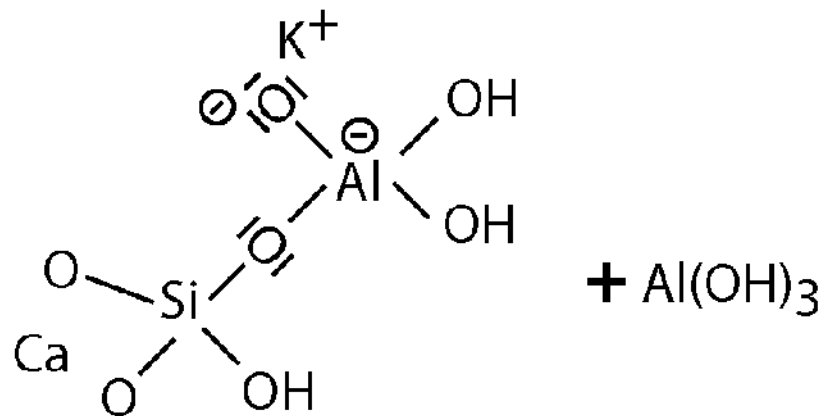
(K,Ca)-ortho-sialate hydrate

akermanite



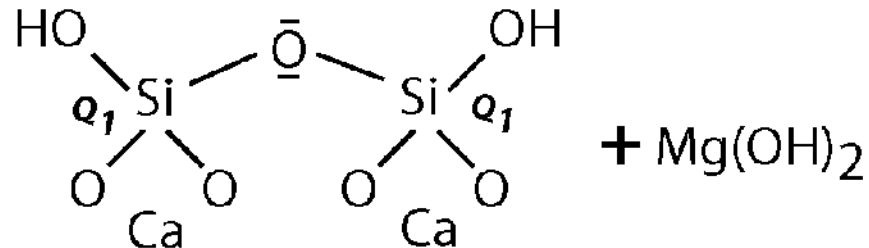
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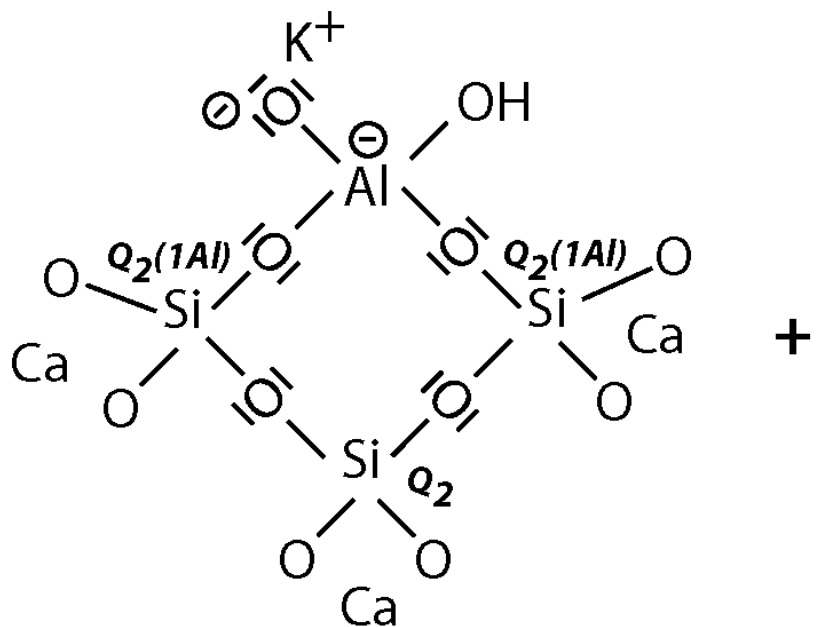


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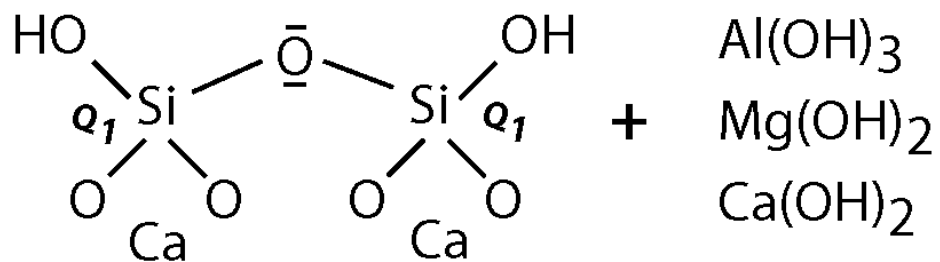
akermanite



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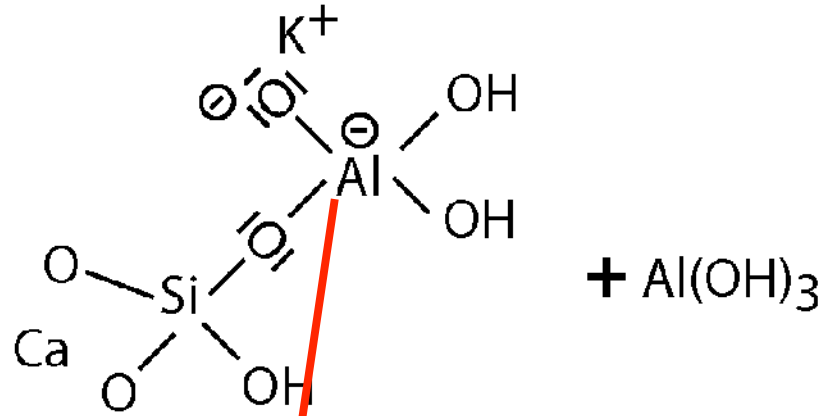


(K,Ca)-cyclo-ortho(sialate-disiloxo)



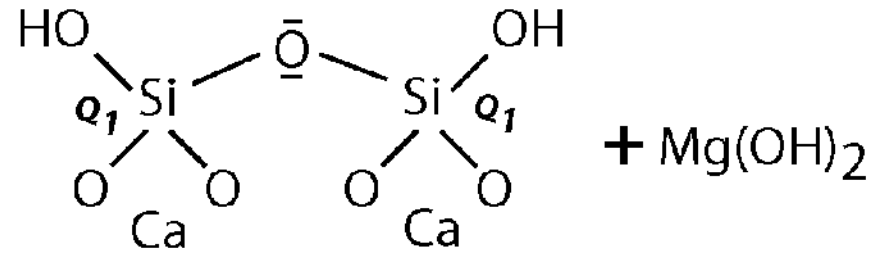
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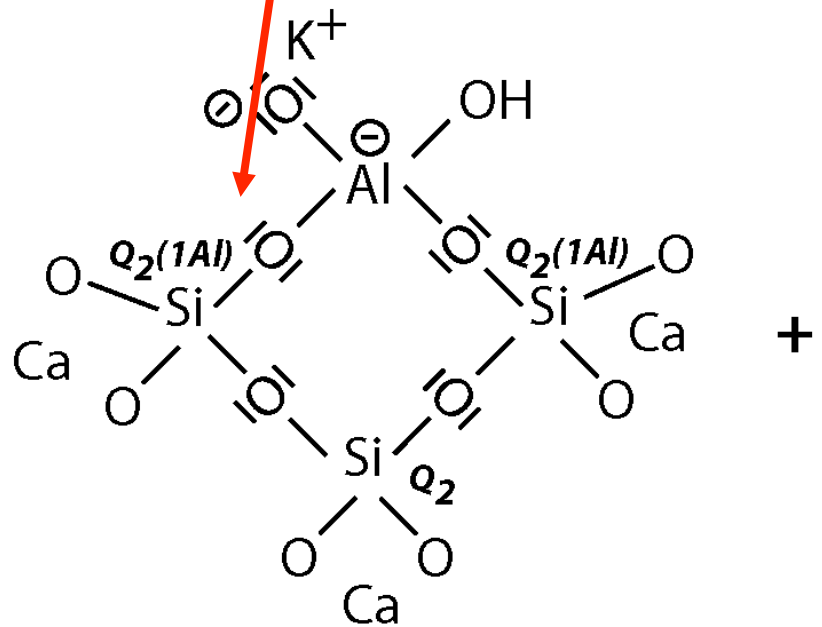


(K,Ca)-ortho-sialate hydrate

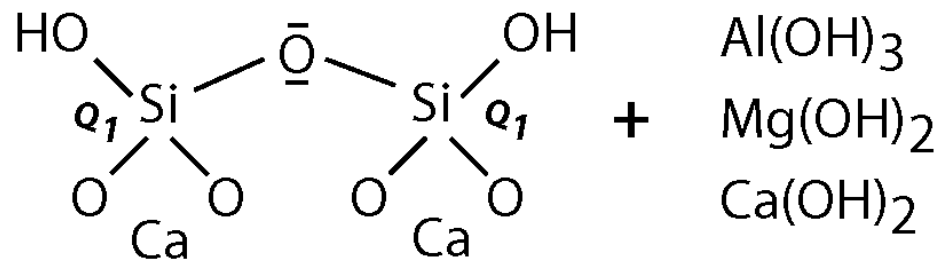
akermanite



Ca-di-siloxonate hydrate

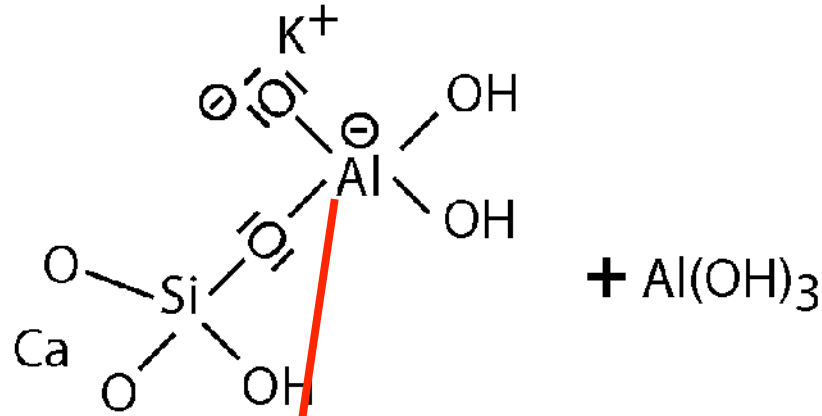


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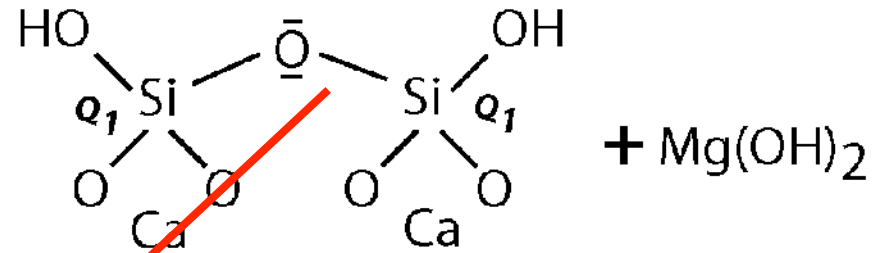
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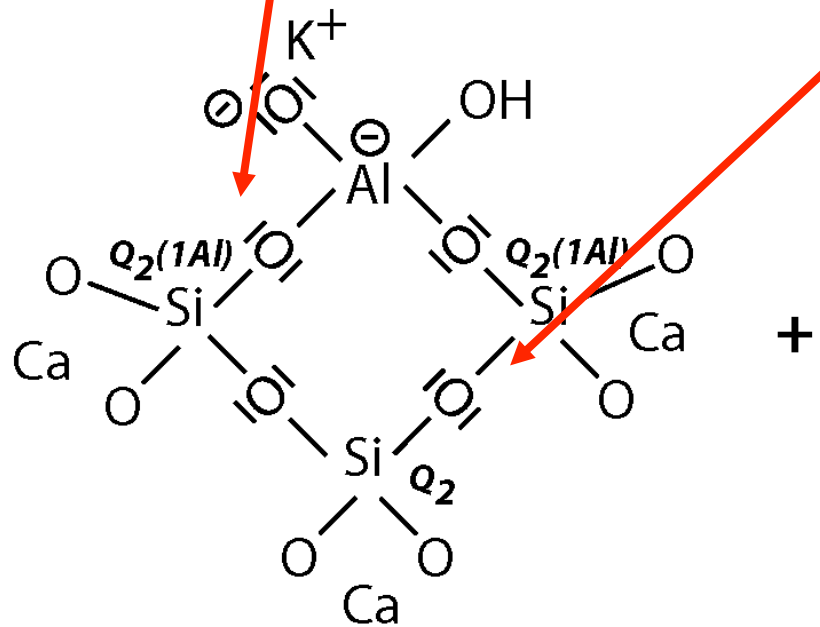


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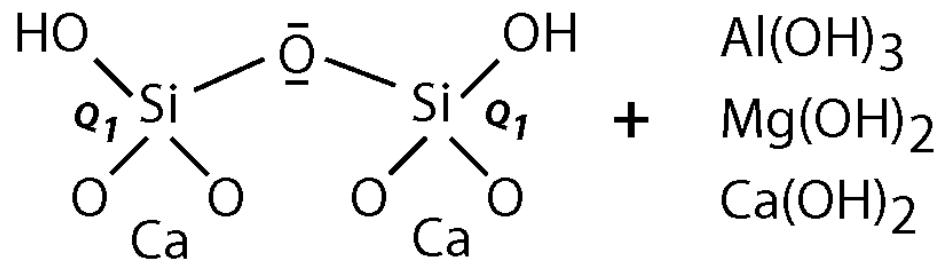
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Ca-di-siloxonate hydrate



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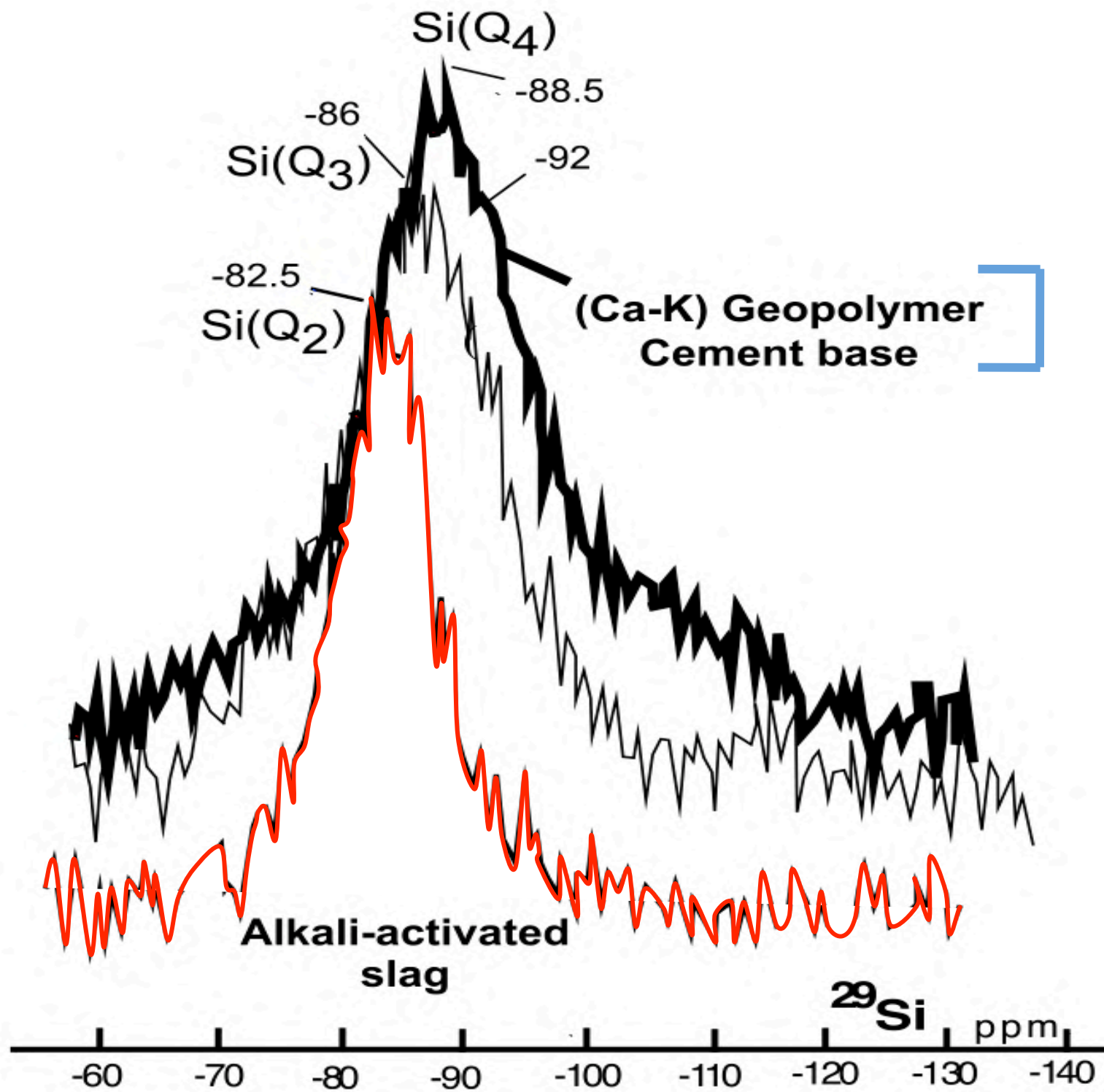
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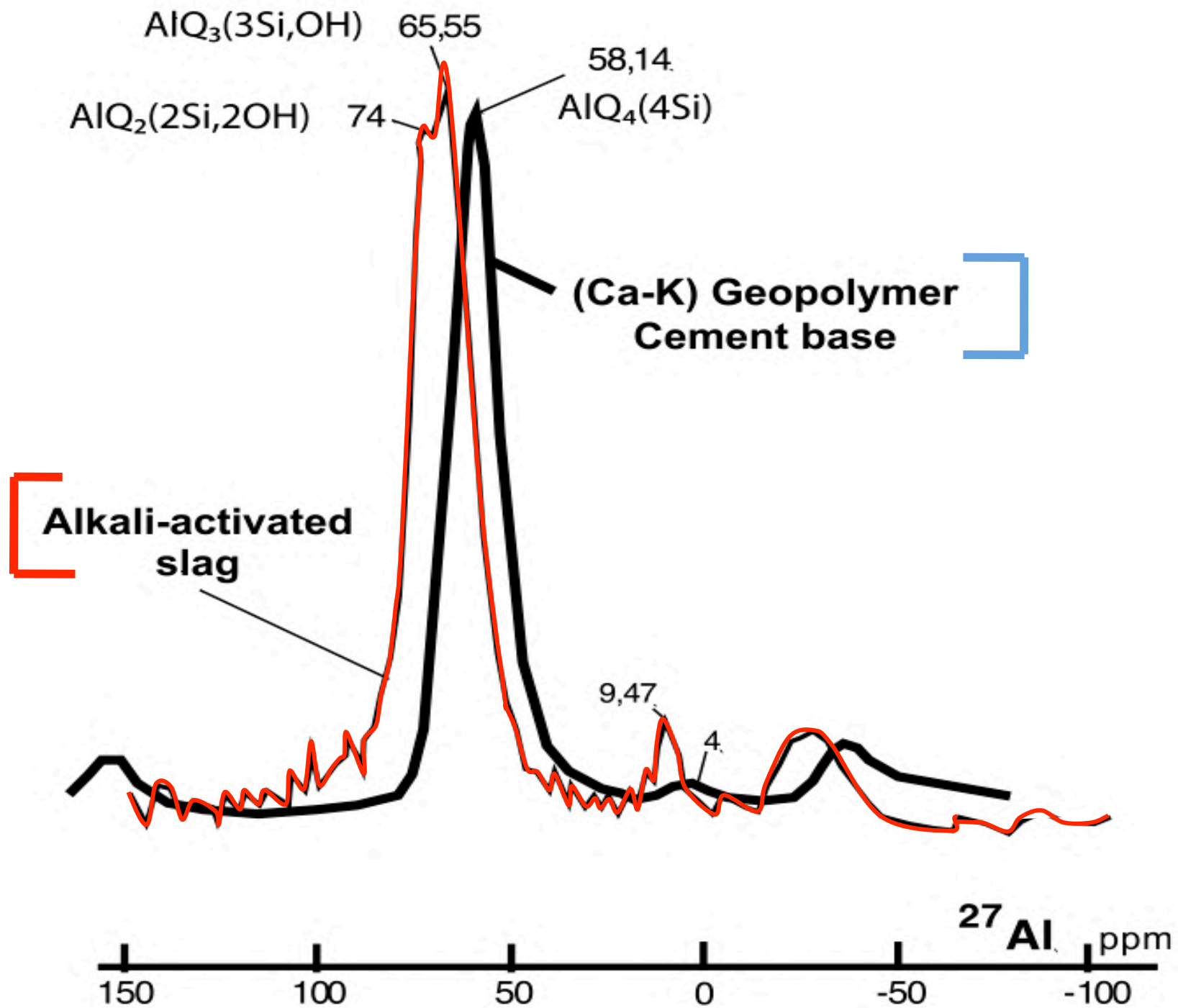
- 1) MK-750 / slag - based**
- 2) Rock / slag-based**
- 3) Fly ash / slag-based**

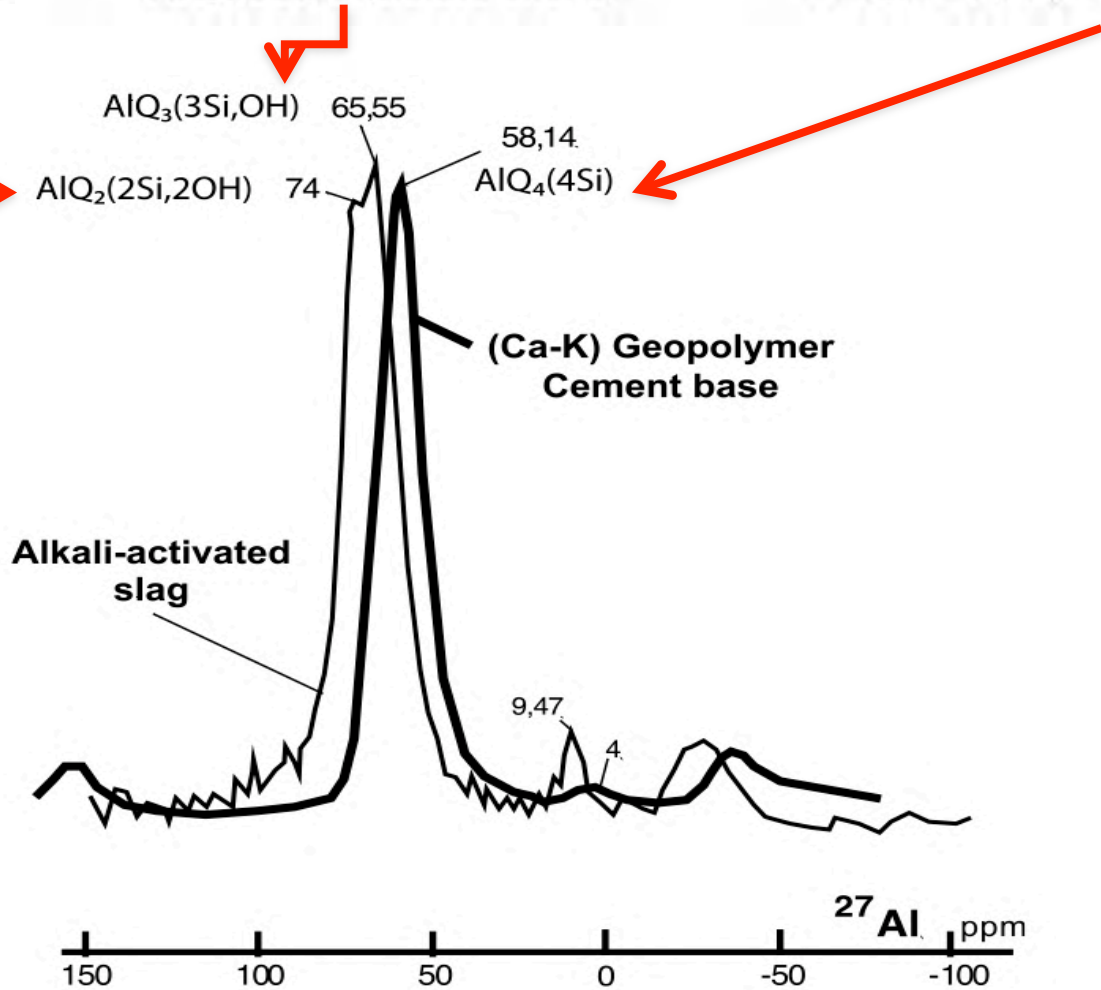
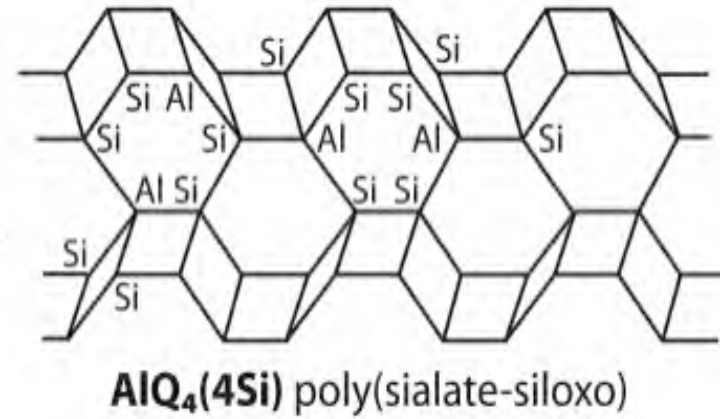
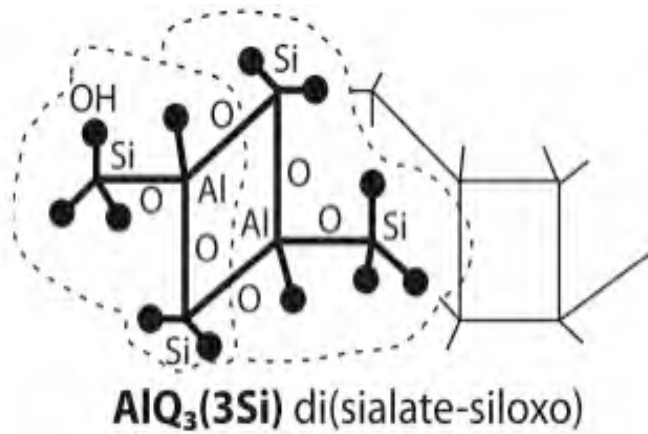
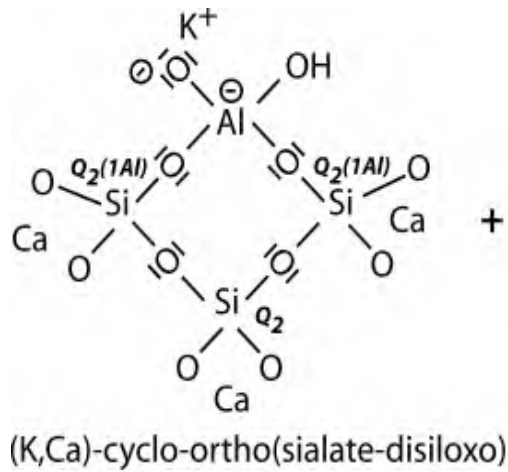
(1)

Geopolymerization

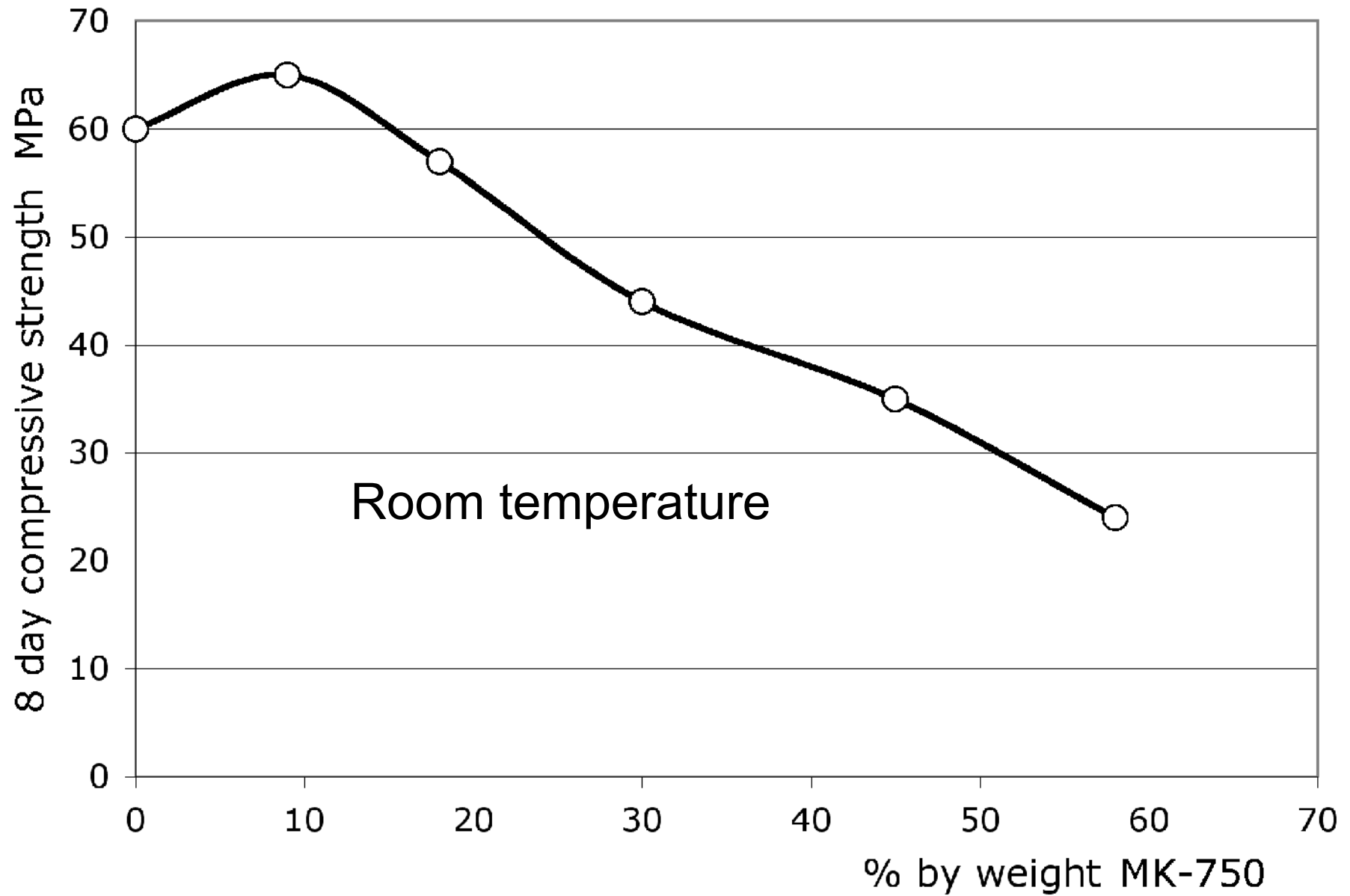
MK-750 + slag







8 day strength / % MK-750



The Choice

The Choice

- high strength with bad physico-chemical properties**

The Choice

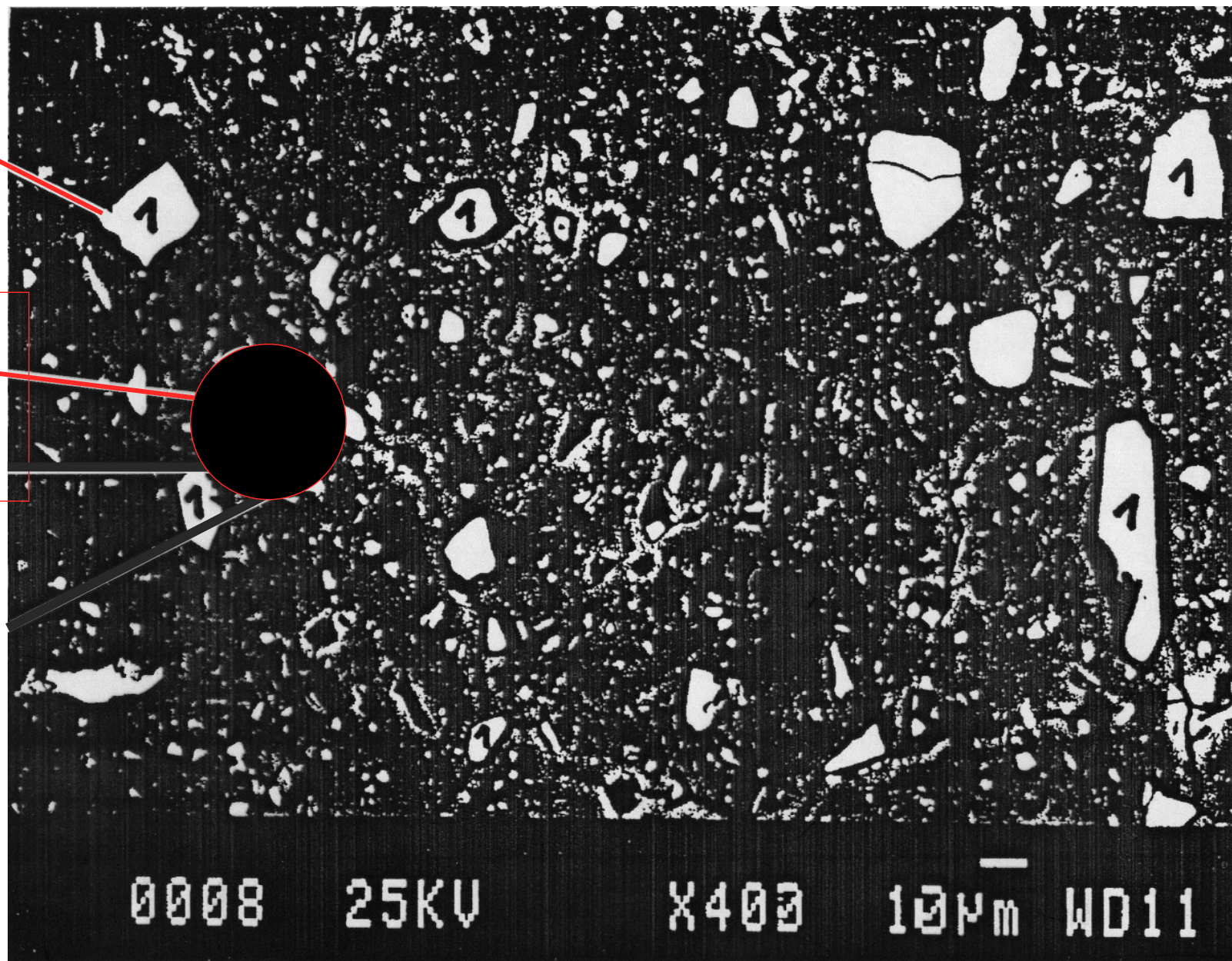
- high strength with bad physico-chemical properties**
- medium strength with high durability**

E-Microprobe analysis

E-Microprobe analysis

Si, Ca,
Al, Mg
Slag

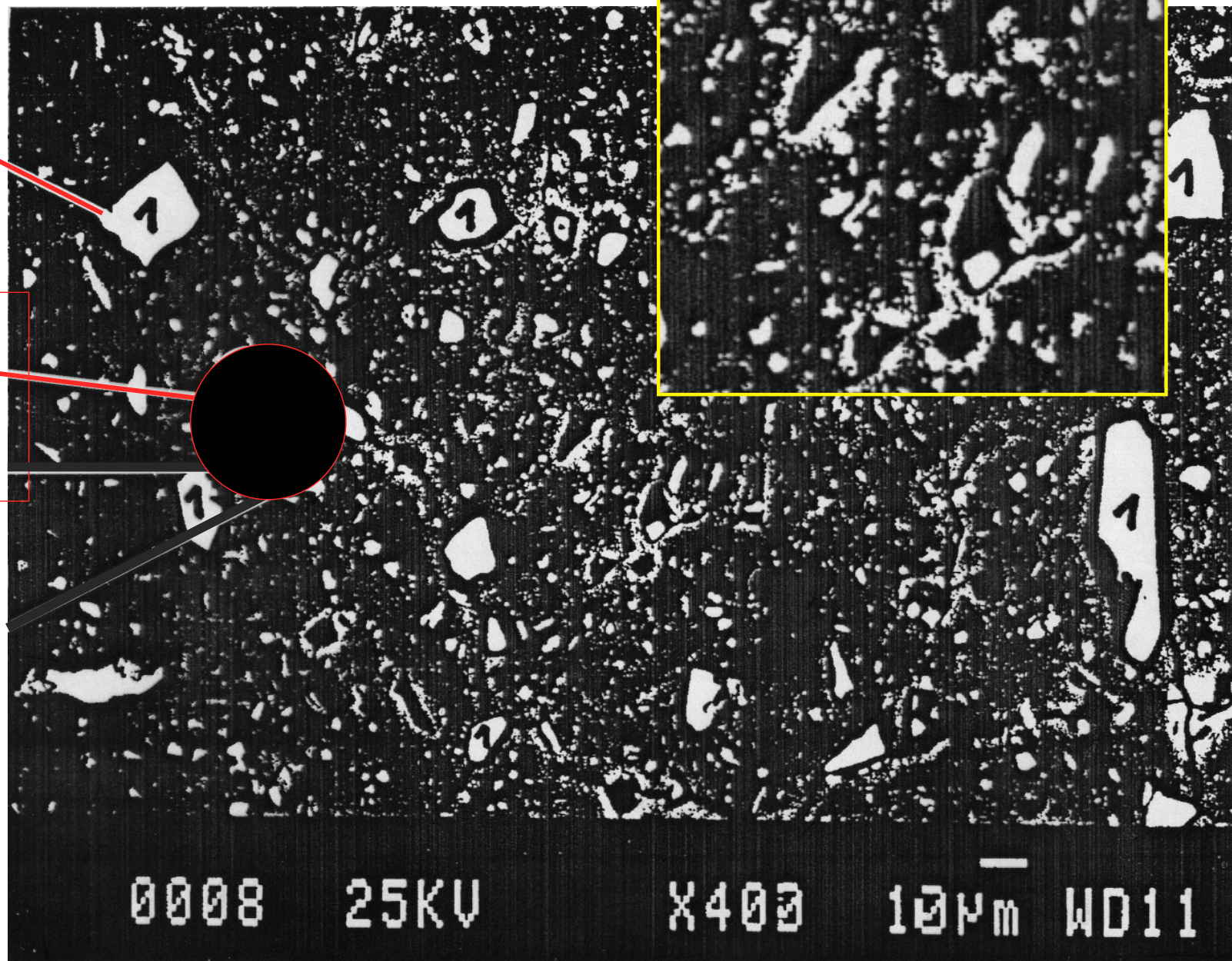
Si, Al, Ca, K,
*Geopolymer
matrix*



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

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✓ - **0.33[K-poly(sialate-disiloxo)], orthoclase hydrate,**

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+ 0.41[Ca-poly(di-sialate)], anorthite hydrate;

✓ - 0.33[K-poly(sialate-disiloxo)], orthoclase hydrate,

+ 0.08[Ca-poly(di-sialate)], anorthite hydrate;

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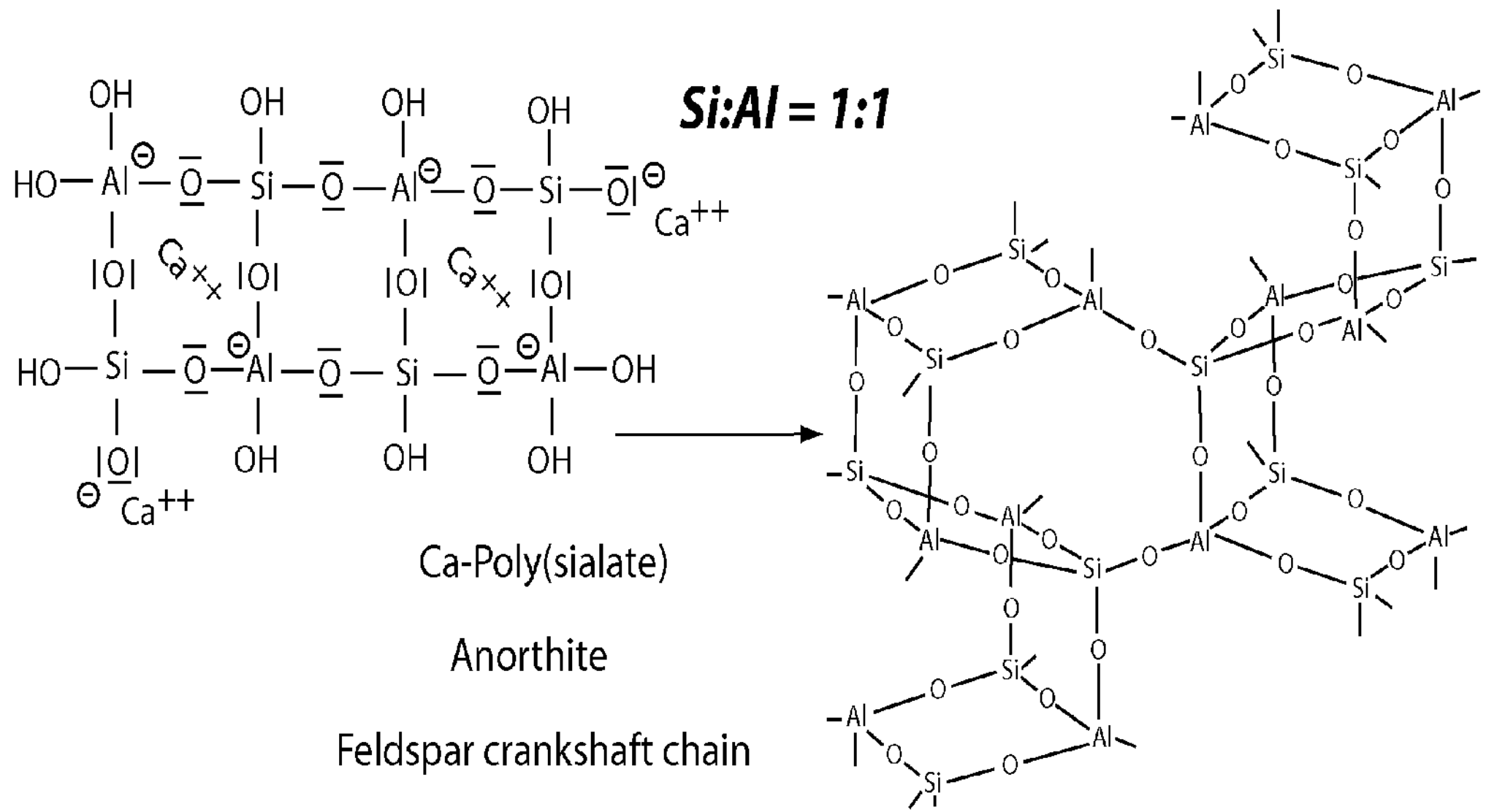
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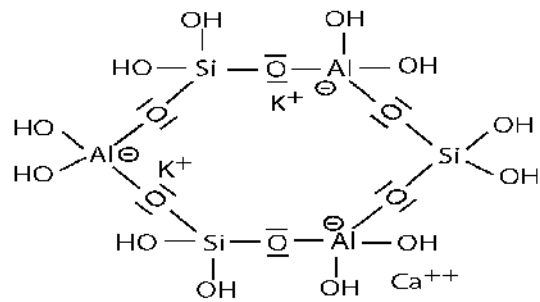
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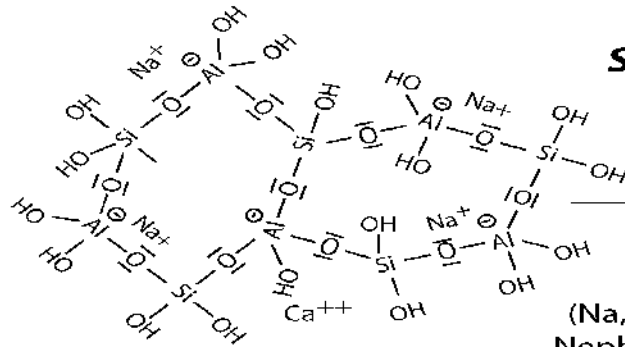
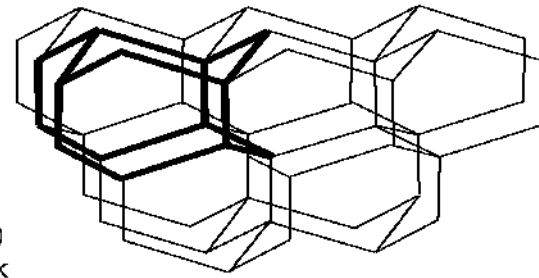
✓ - 0.5[Ca-di-siloxonate] (CSH) + CAH ...





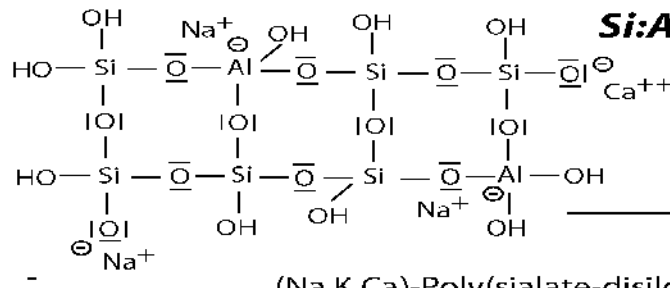
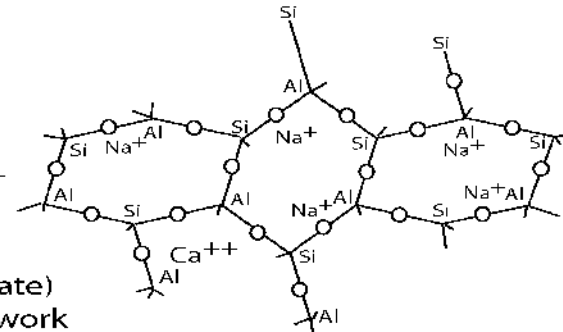
Si:Al = 1:1

(K,Ca)-Poly(sialate)
Kalsilite framework



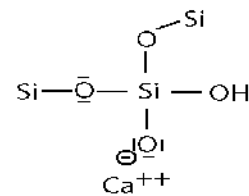
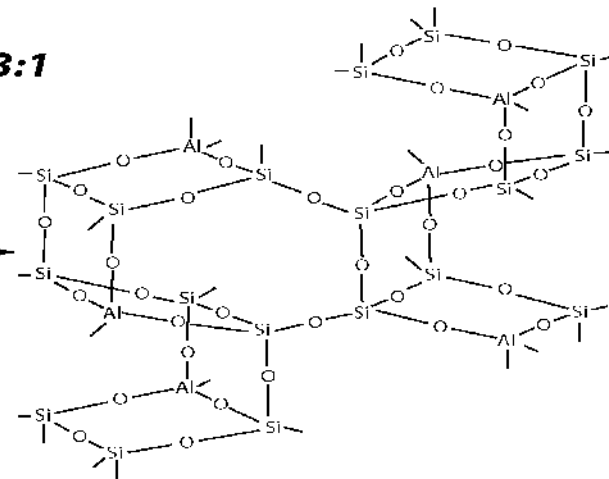
Si:Al = 1:1

(Na,Ca)-Poly(sialate)
Nepheline framework

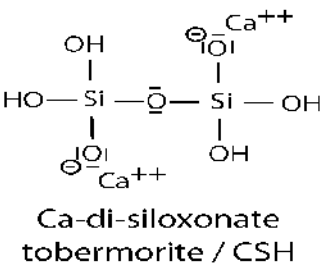


Si:Al = 3:1

(Na,K,Ca)-Poly(sialate-disiloxo)
Albite, Orthoclase, Sanidine
Feldspar crankshaft chain

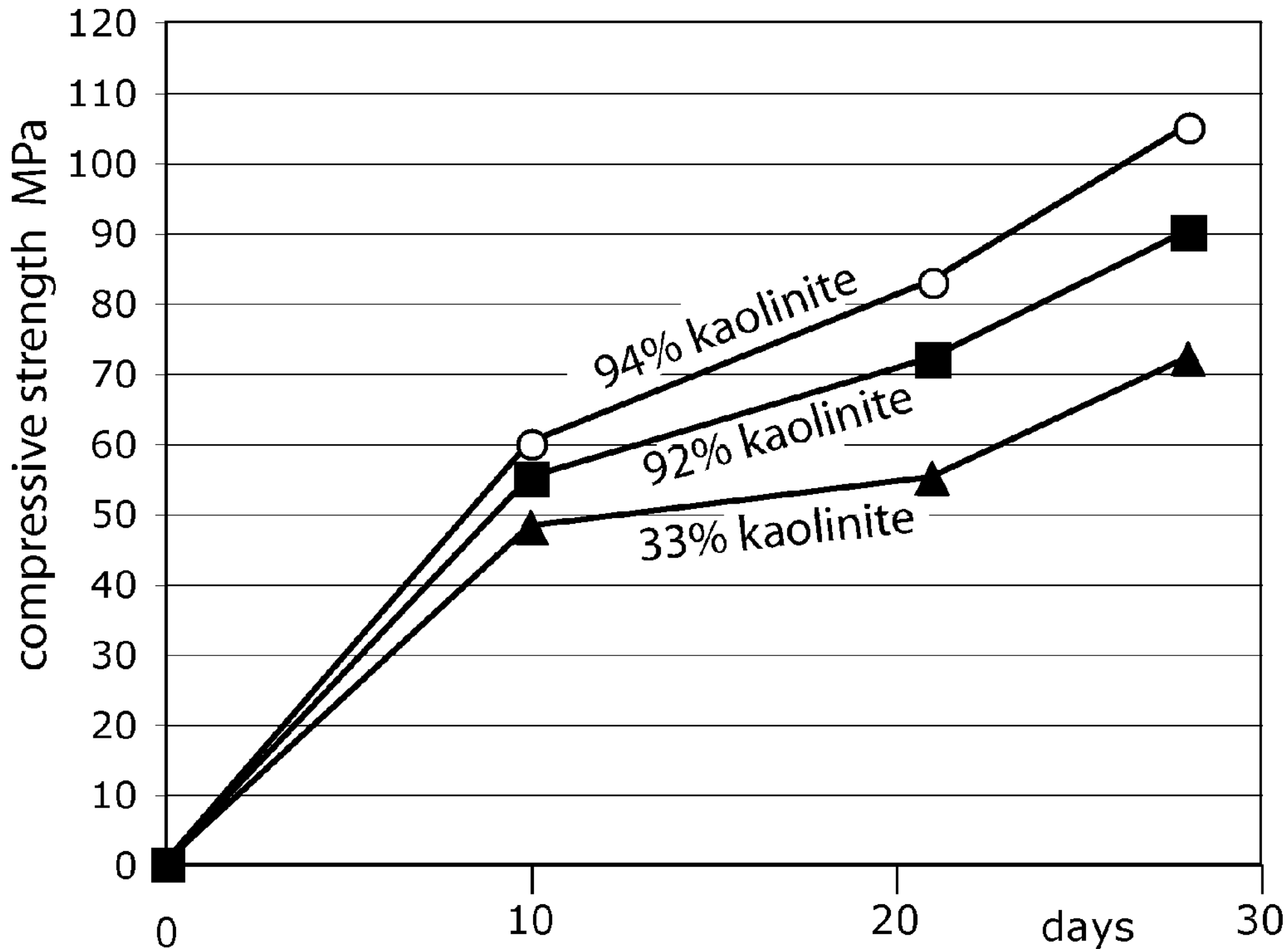


Si:Al = 1:0



**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.

(2)

**Rock / slag - based
geopolymer cement**





Si:Al = 3:1
Poly(sialate-disiloxo) geopolymeric cement



Si:Al = 3:1

Poly(sialate-disiloxo) geopolymeric cement

Based on geological raw-materials



Si:Al = 3:1

Poly(sialate-disiloxo) geopolymeric cement

Based on geological raw-materials

Compressive Strength at 28 days (room temperature hardening) :



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



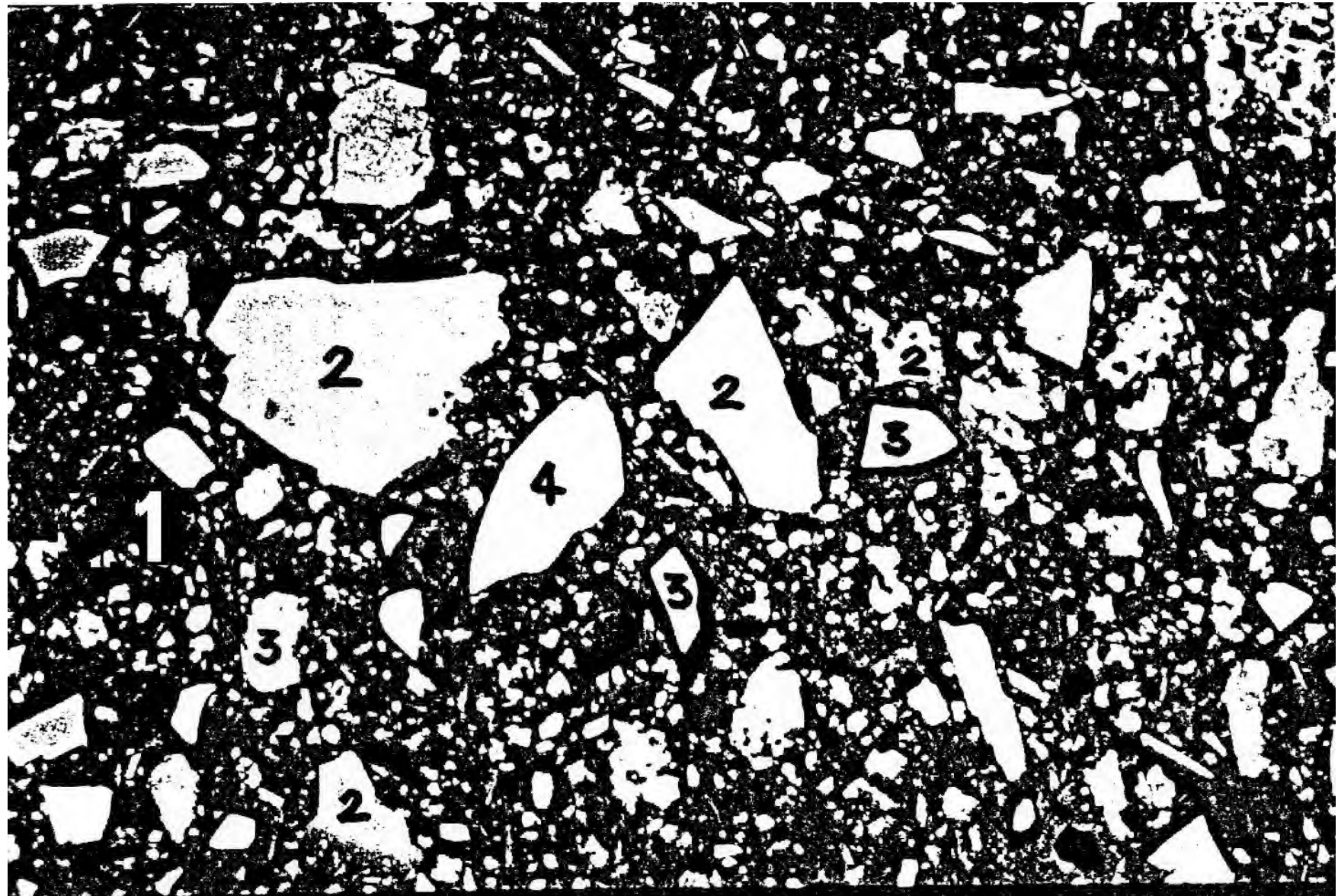
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Poly(sialate-disiloxo) geopolymeric cement

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**



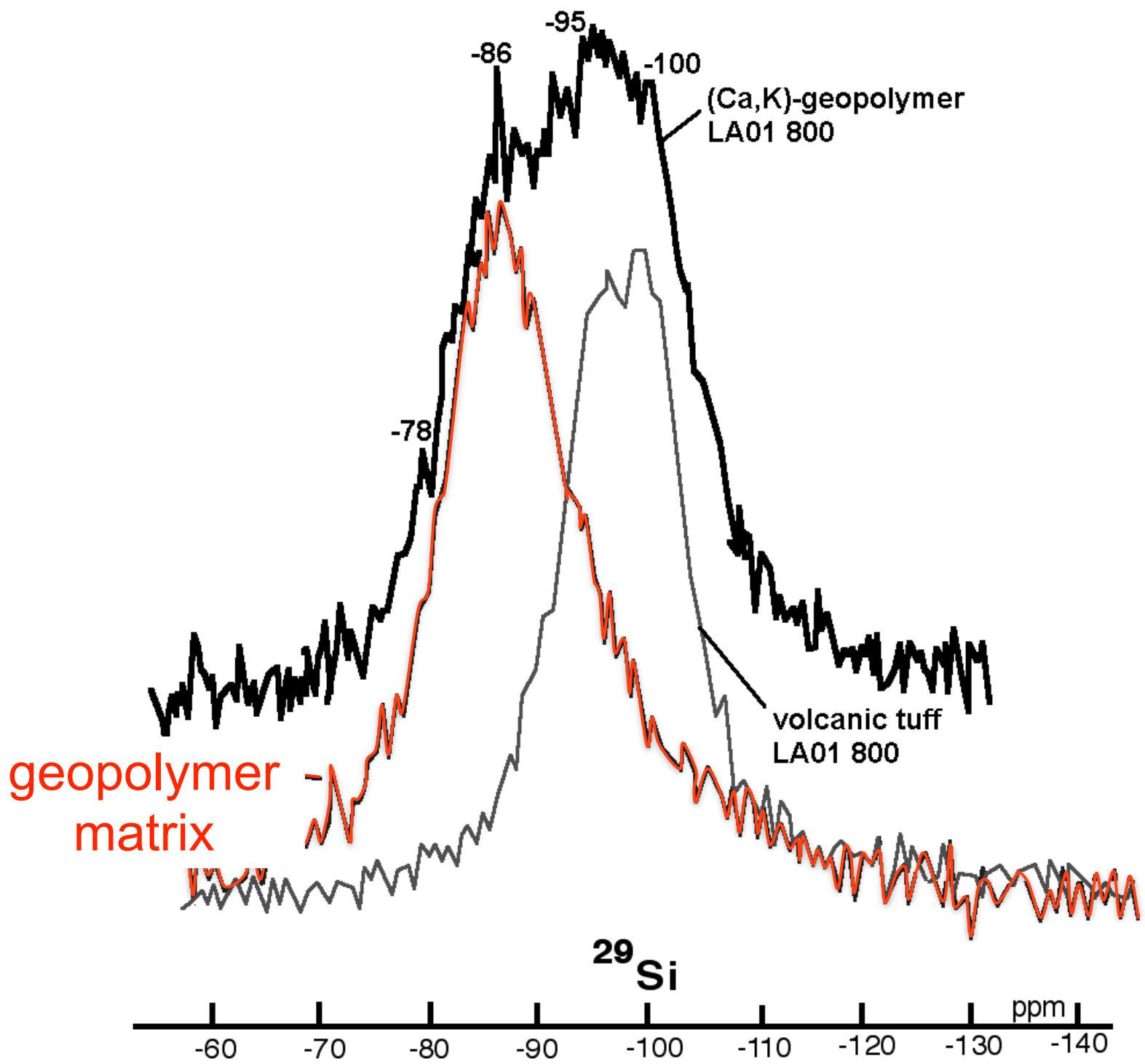
0007

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.

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

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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 waste80
- 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**



DÉVELOPPEMENT DURABLE DU BÂTIMENT

Publié le 30 septembre 2010

LAFARGE ÉLABORE UN CIMENT À EMPREINTE DE CO² FORTEMENT RÉDUITE

Ce nouveau produit, un clinker, qui sert à fabriquer le ciment, entrant lui-même dans la liste des constituants du béton, a un taux réduit d'environ 30% de calcaire. Grâce à une augmentation de Gypse, argile ou bouxite, les chercheurs de Lafarge affirment que la réduction des émissions de CO² atteint 25%. De plus, en réduisant la

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Patent filed in 2004, granted and issued in 2010; pilot plant funding through European Union

At the Geopolymer Camp 2010

At the Geopolymer Camp 2010

GEOPOLYMER BASED CONCRETES : ENVIRONMENTAL IMPACTS OF CURRENT RESEARCH TRENDS

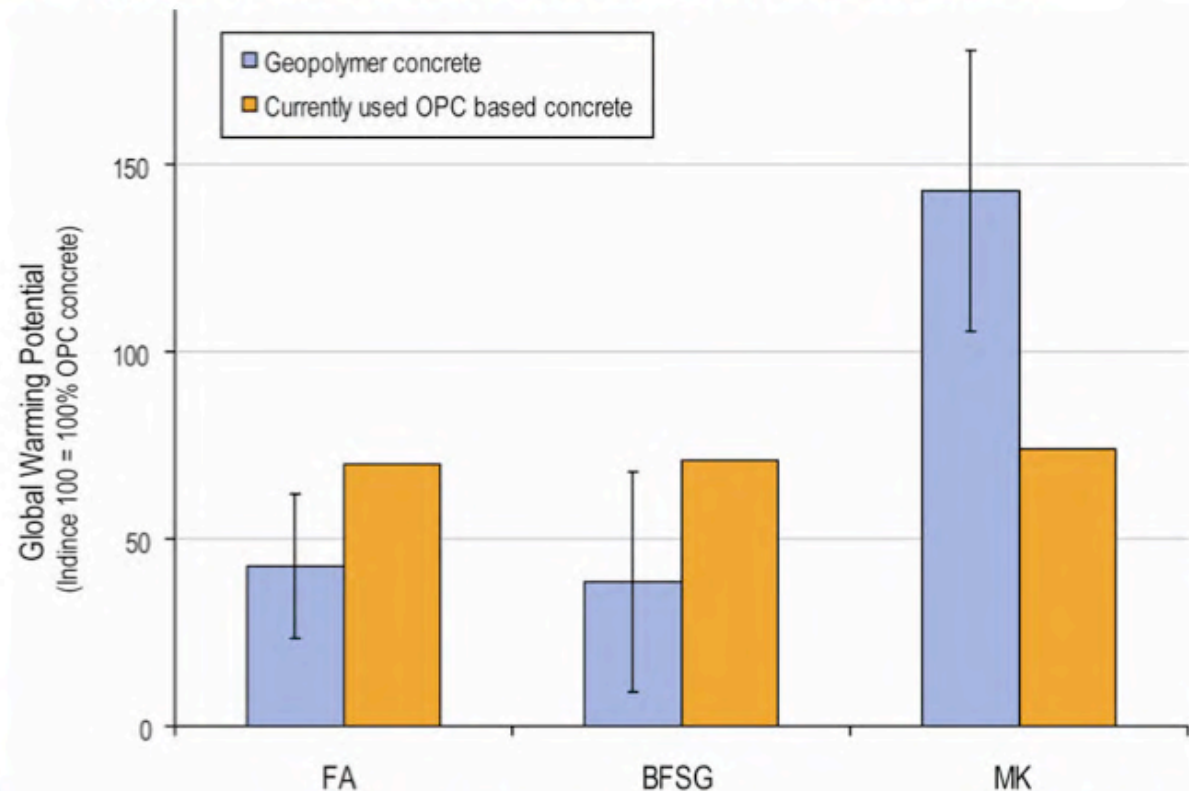
G. Habert (LCPC, Paris)

J.B. d'Espinose (ESPCI, Paris)

N. Roussel (LCPC, Paris)

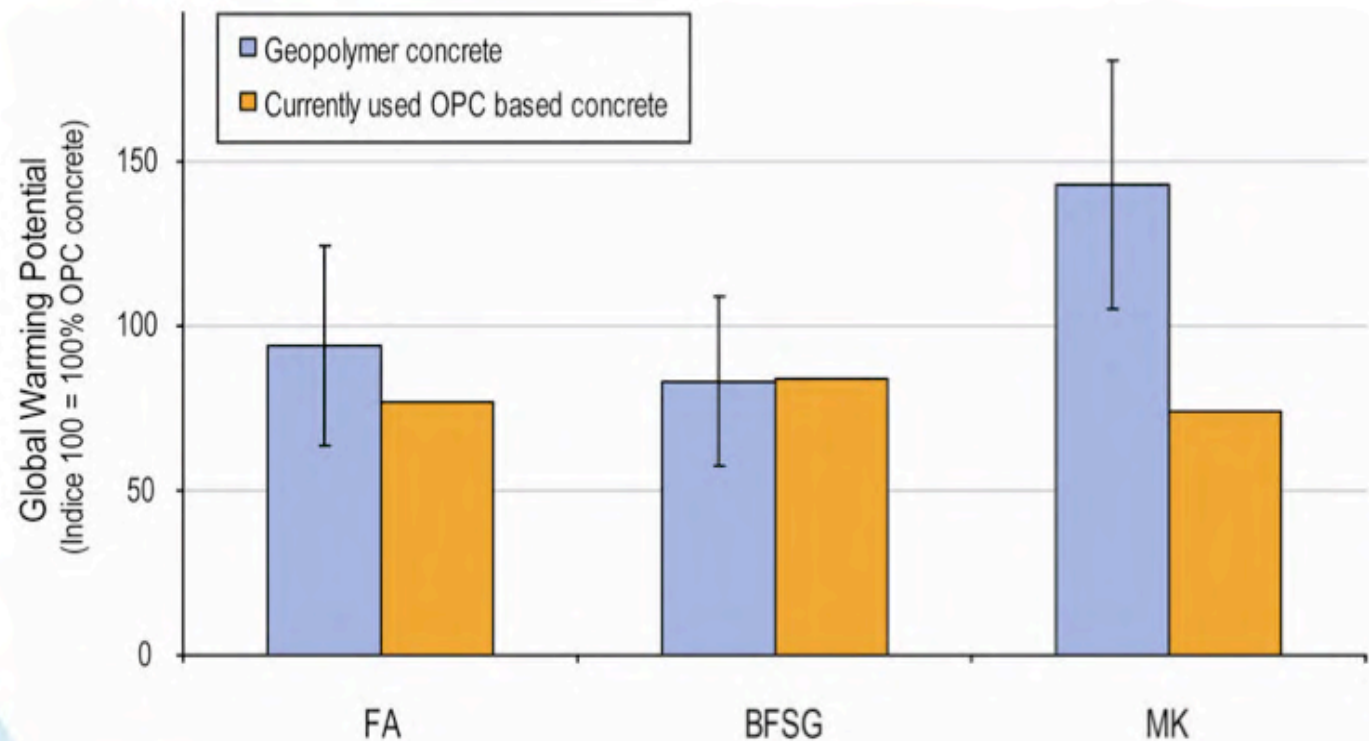
Results: different geopolymer types

- **Concretes made with:** Fly ash, Blast furnace slag or metakaolin
 - **No allocation (waste)**



Mean FA based geopolymer has 25% improvement than currently used concrete

- **Concretes made with: Fly ash, Blast furnace slag or metakaolin**
 - **Economic allocation (by-product)**



No sensitive improvement of using geopolymer compared to currently used cement

July 2011

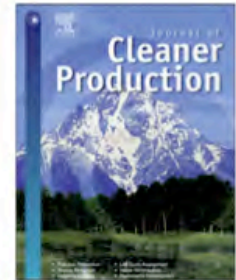


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An environmental evaluation of geopolymer based concrete production: reviewing current research trends

G. Habert^{a,*}, J.B. d'Espinose de Lacaillerie^b, N. Roussel^a

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^b Ecole Supérieure de Physique et Chimie Industrielles, PPMD SIMM, UMR 7615 ESPCI-CNRS-UPMC, 10 rue Vauquelin, 75231 Paris cedex 05, France

July 2011

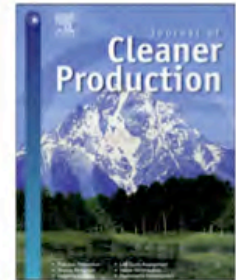


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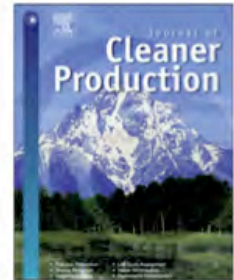
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« However, when the **production** of fly ashes and granulated blast furnace slags is taken into account,.... it appears that geopolymer concrete has a similar impact on global warming than standard concrete. »

« This study highlights that future research and development on geopolymer concrete should focus on two potential solutions:

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- 1) the use of industrial waste that is not recyclable within other industries (?????)

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- 2) on the production of geopolymer concrete using a mix of blast furnace slag and activated clays.

« This study highlights that future research and development on geopolymer concrete should focus on two potential solutions:

- 1) the use of industrial waste that is not recyclable within other industries (?????)
- 2) on the production of geopolymer concrete using a mix of blast furnace slag and activated clays.

It is only by adopting these directions that geopolymer concrete could allow us to achieve the current objectives for a long term reduction of CO2 emissions. »

« This study highlights that future research and development on geopolymers should focus on two potential solutions:

- 1) the

other inc

-2) on th

blast fur

They are re-inventing the

wheel !!

For whom? LAFARGE.

How ?

It is only by adopting these directions that geopolymers could allow us to achieve the current objectives for a long term reduction of CO2 emissions. »

Search

Public Contracts



IFSTTAR

French institute of science and technology for transport

Both institutes LCPC and INRETS merged on the 1st of january 2011 to create IFSTTAR French institute of science and technology for transport, development and networks.

<http://www.ifsttar.fr>

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Public Contracts



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École des Ponts
ParisTech



COMMUNIQUE DE PRESSE

Paris, le 9 juin 2011

LAFARGE ET L'ÉCOLE DES PONTS PARISTECH RENFORCENT LEUR PARTENARIAT

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Public Contracts



IFSTTAR

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Both institutes LCPC and INRETS merged on the 1st of January 2011 to create IFSTTAR French institute of science and technology for transport, development and networks.

LAFARGE vient de signer un contrat-cadre avec le **Laboratoire Navier**, unité de recherche dans le domaine de la mécanique et de la physique des matériaux, des structures et des géomatériaux, qui rassemble des chercheurs de haut niveau de l'École des Ponts ParisTech, du CNRS et de l'**IFSTTAR**. Dans le cadre de cette collaboration, le Laboratoire Navier contribuera aux recherches sur les propriétés de mise en œuvre, les performances mécaniques et la durabilité des nouveaux bétons développés par Lafarge pour une construction à faible empreinte carbone.

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**This study sponsored by LAFARGE to denigrate
geopolymer cements, **ignores deliberately** the
geopolymer cements industrialized, namely:**

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-E-CRETE Geopolymer Concrete developed by Zeobond Australia (2007)

CO₂ reduction for

CO₂ reduction for Rock-based GP-cement

**CO₂ reduction for
Rock-based GP-cement
(1) by-products (waste)**

CO₂ reduction for Rock-based GP-cement

(1) by-products (waste)

(2) all ingredients

manufactured

**Slag as by-product (waste) and with
K-silicate solution**

Slag as by-product (waste) and with K-silicate solution

Processing	Portland Cement	GP-cement uncalcined	GP-cement calcined
calcination	1,000	0,035	0,140
crushing	0,020	0,018	0,018
K-silicate	0	0,050	0,050
Slag waste	0	0	0
total	1,020	0,103	0,208
reduction	0	90 %	80 %

Slag manufactured and with K-silicate solution

Slag manufactured and with K-silicate solution

Processing	Portland Cement	GP-cement uncalcined	GP-cement calcined
calcination	1,000	0,035	0,140
crushing	0,020	0,018	0,018
K-silicate	0	0,050	0,050
Slag manuf.	0	0,100	0,100
total	1,020	0,203	0,308
reduction	0	80 %	70 %

**Slag as by-product (waste) and with
GP-LAVA**

Slag as by-product (waste) and with GP-LAVA

Processing	Portland Cement	GP-cement uncalcined	GP-cement calcined
calcination	1,000	0,035	0,140
crushing	0,020	0,018	0,018
GP-LAVA	0	0,100	0,100
Slag waste	0	0	0
total	1,020	0,153	0,258
reduction	0	85 %	75 %

Slag manufactured and with GP-LAVA

Slag manufactured and with GP-LAVA

Processing	Portland Cement	GP-cement uncalcined	GP-cement calcined
calcination	1,000	0,035	0,140
crushing	0,020	0,018	0,018
GP-LAVA	0	0,100	0,100
Slag manuf.	0	0,100	0,100
total	1,020	0,253	0,358
reduction	0	75 %	65 %

CO2 reduction

Lafarge Portland cement

CO2 reduction

Lafarge Portland cement

best case: 25%

CO2 reduction

Lafarge Portland cement

best case: 25%

Rock-based Geopolymer cement

CO2 reduction

Lafarge Portland cement

best case: 25%

Rock-based Geopolymer cement

worse case: 65%

CO2 reduction

Lafarge Portland cement

best case: 25%

Rock-based Geopolymer cement

worse case: 65%

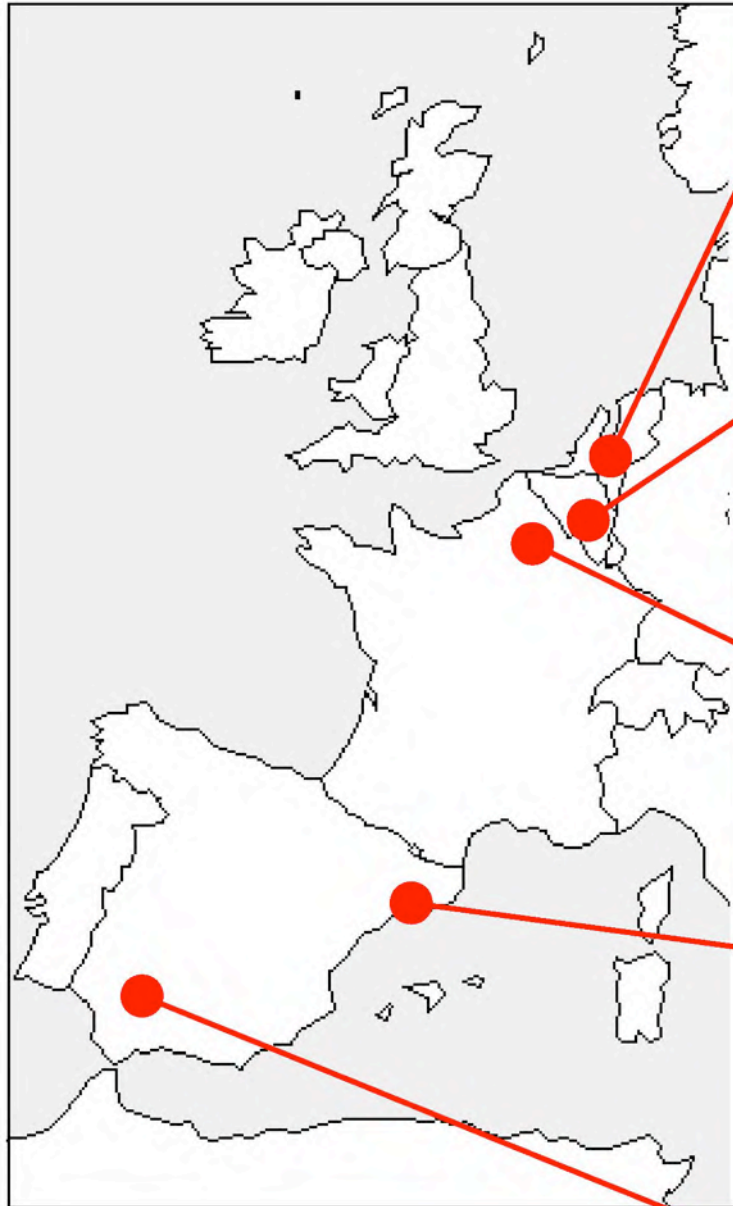
best case: 90 %

(3)

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



GEOASH



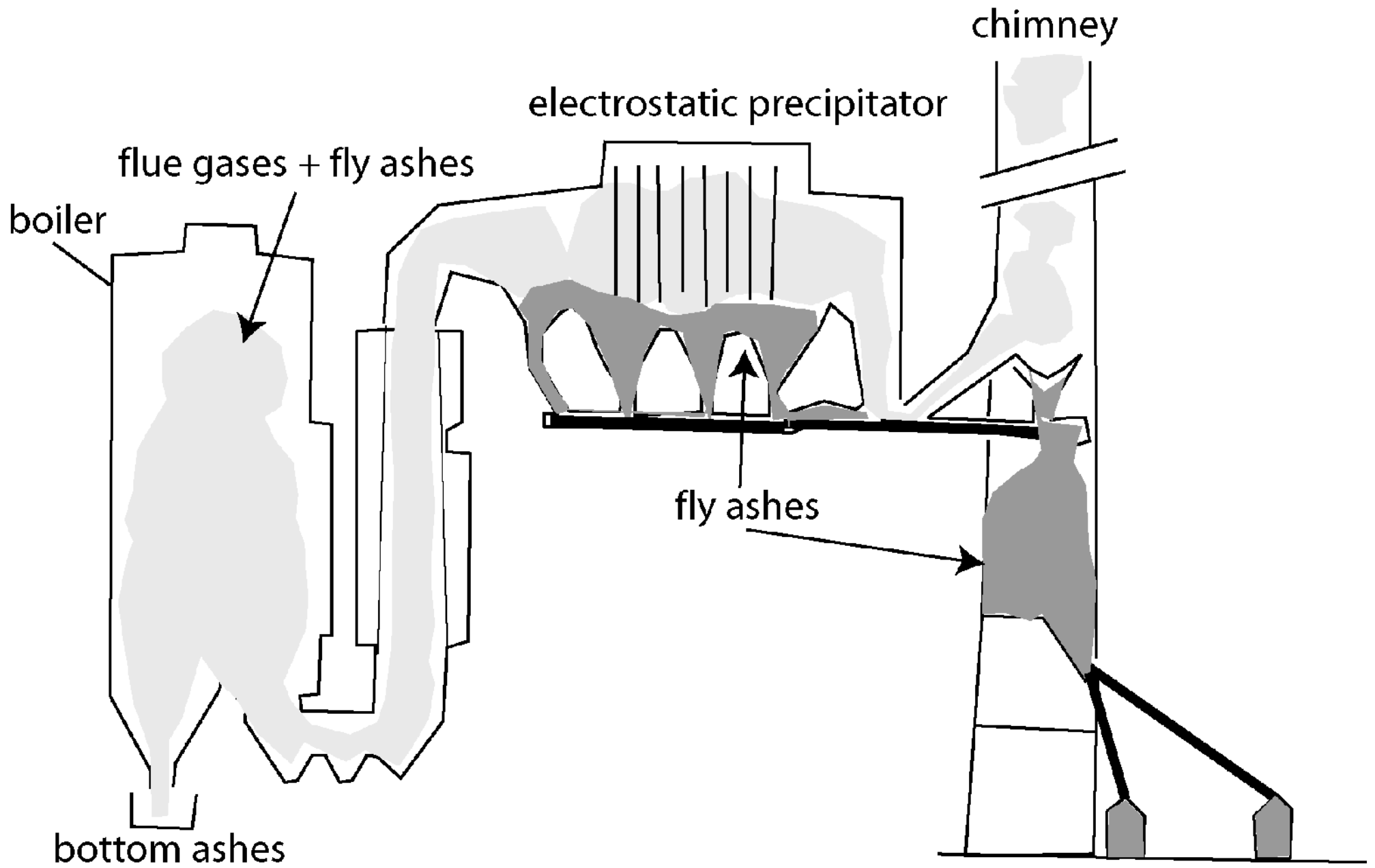
Nederlands
Delft University of Technology
TU Delft, DELFT

Belgium
Institut Scientifique
de Service Public
ISSEP, LIÈGE

France
Cordi-Géopolymère
SAINT-QUENTIN

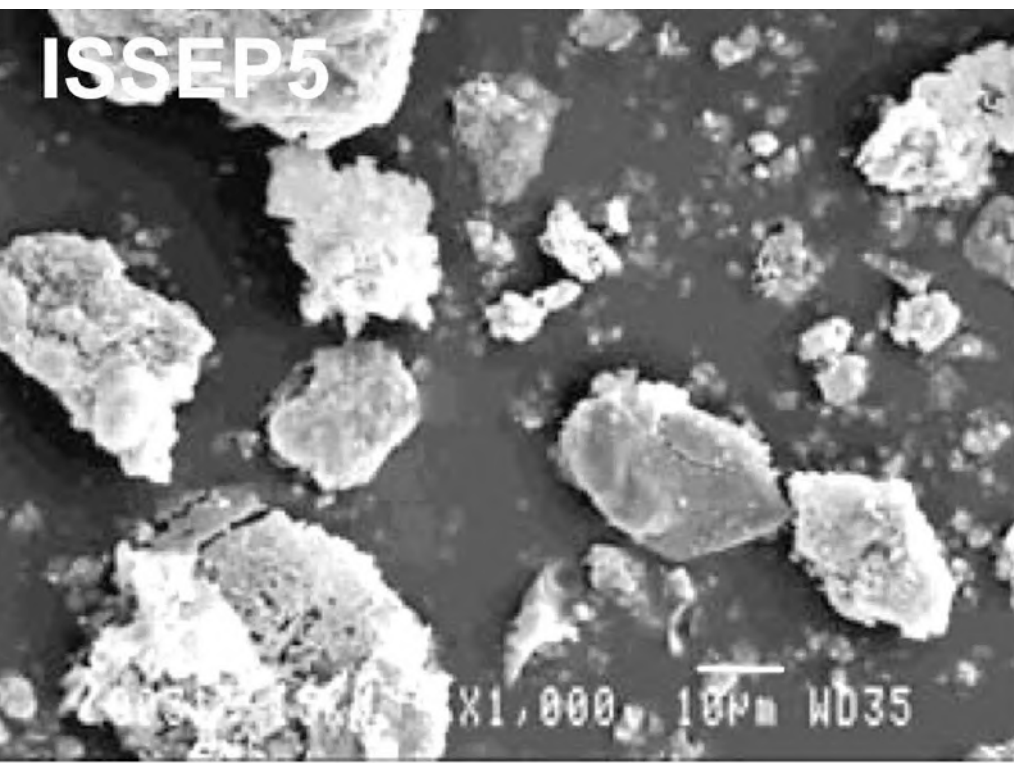
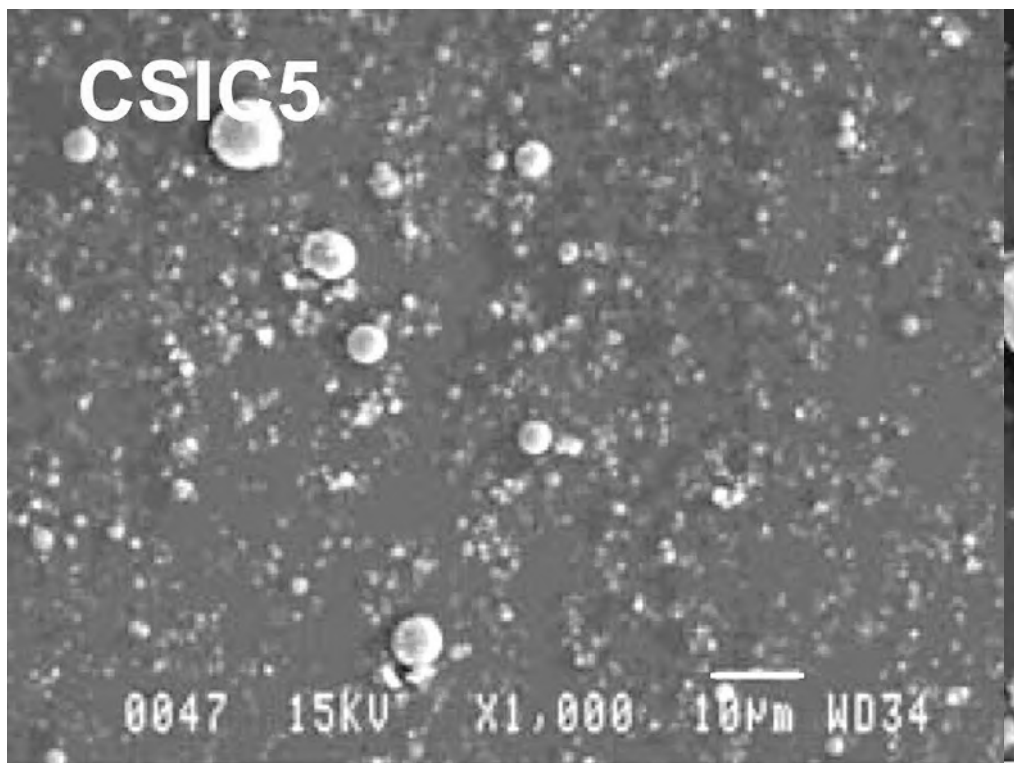
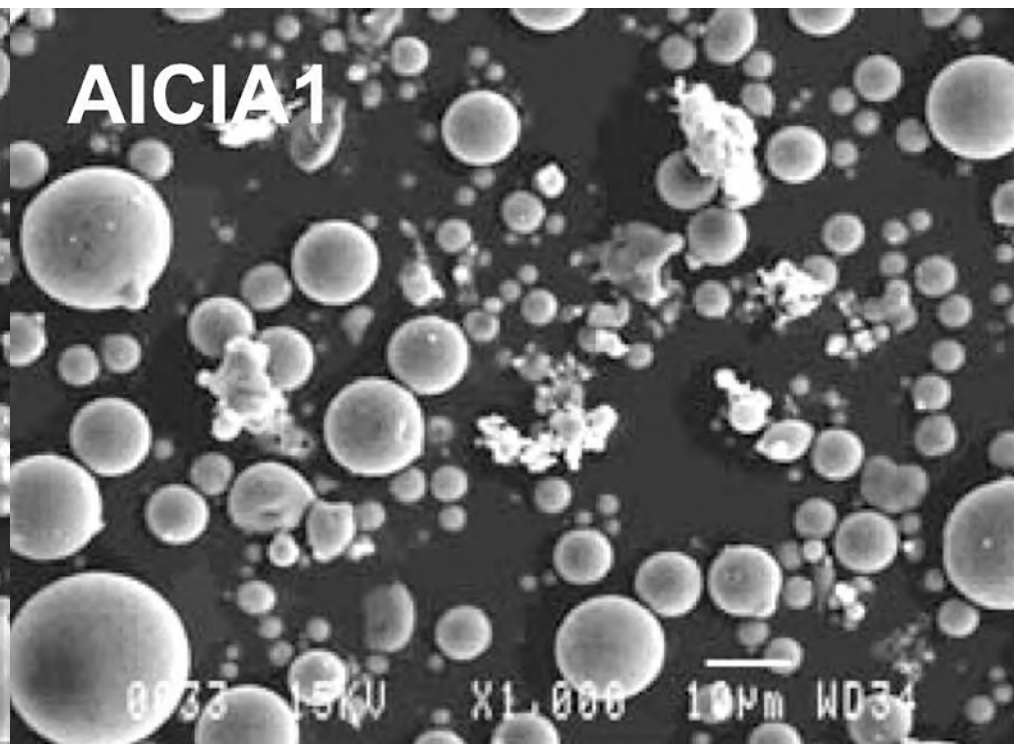
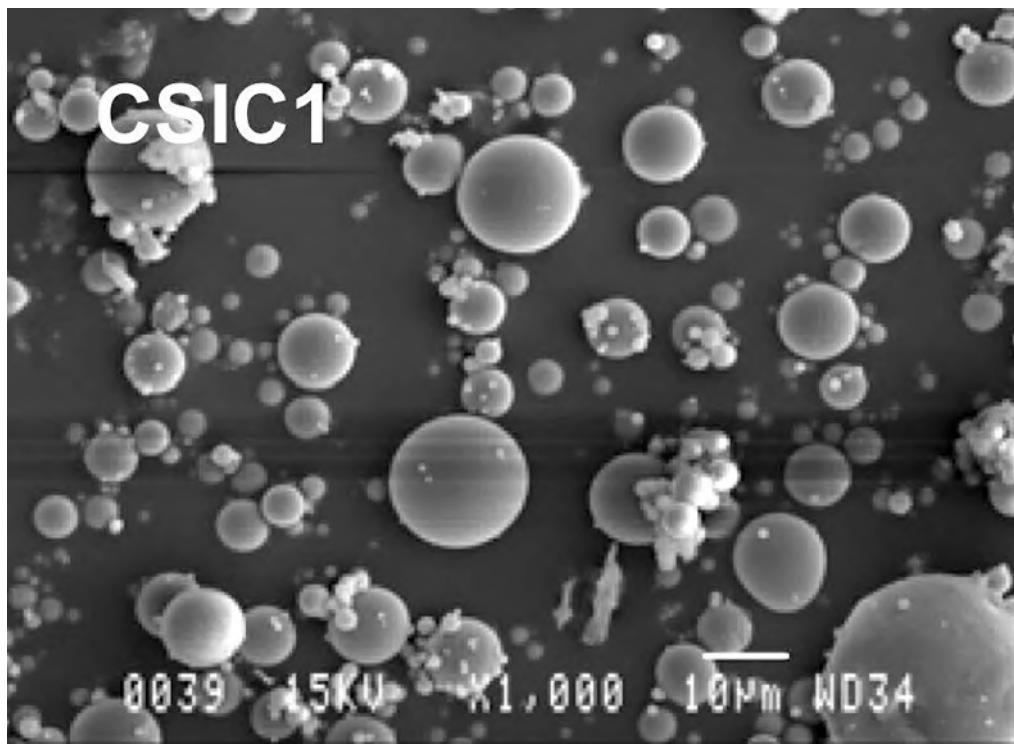
Spain
Consejo Superior de
Investigaciones
Scientificas, BARCELONE

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

COAL FLY-ASH GEOPOLYMERIZATION

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

Conventional method: alkali-activation

Conventional method: alkali-activation dissolution and zeolite formation

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- 0.3-0.4 L/kg, NaOH 12M,

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- 24h room temperature ageing,

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- 0.3-0.4 L/kg, NaOH 12M,
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Conventional method: alkali-activation dissolution and zeolite formation

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

User-hostile

Geopolymeric method:

Geopolymeric method: room temperature hardening

Geopolymeric method:

**room temperature hardening
polycondensation**

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**room temperature hardening
polycondensation**

- fly ash.....50 to 85

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- K-silicate solution $\text{SiO}_2:\text{K}_2\text{O} > 1.4$10

Geopolymeric method:

room temperature hardening polycondensation

- fly ash.....50 to 85
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- blast furnace slag.....15

Geopolymeric method:

room temperature hardening polycondensation

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- blast furnace slag.....15
- water.....5

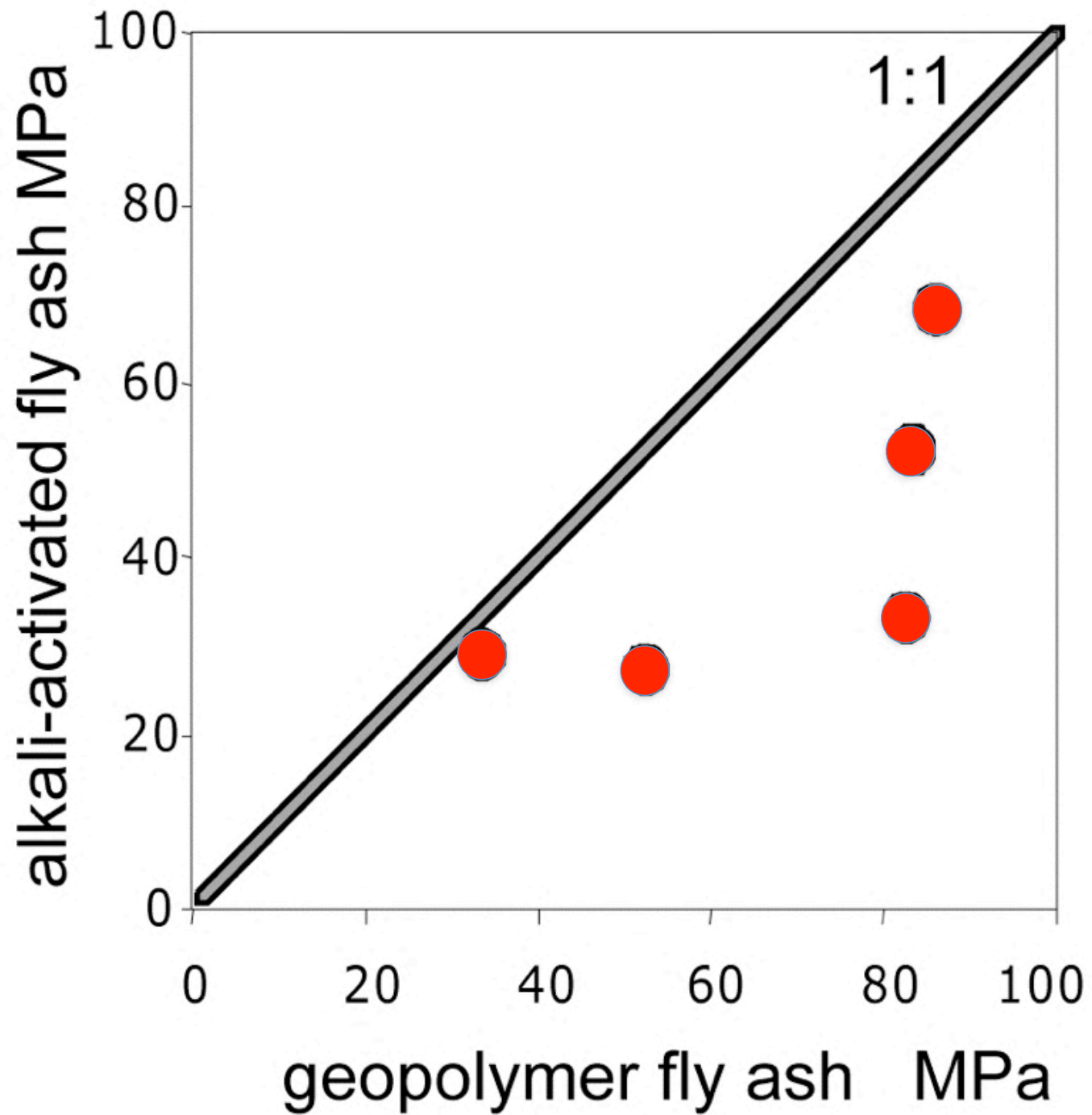
Geopolymeric method:

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User-friendly.

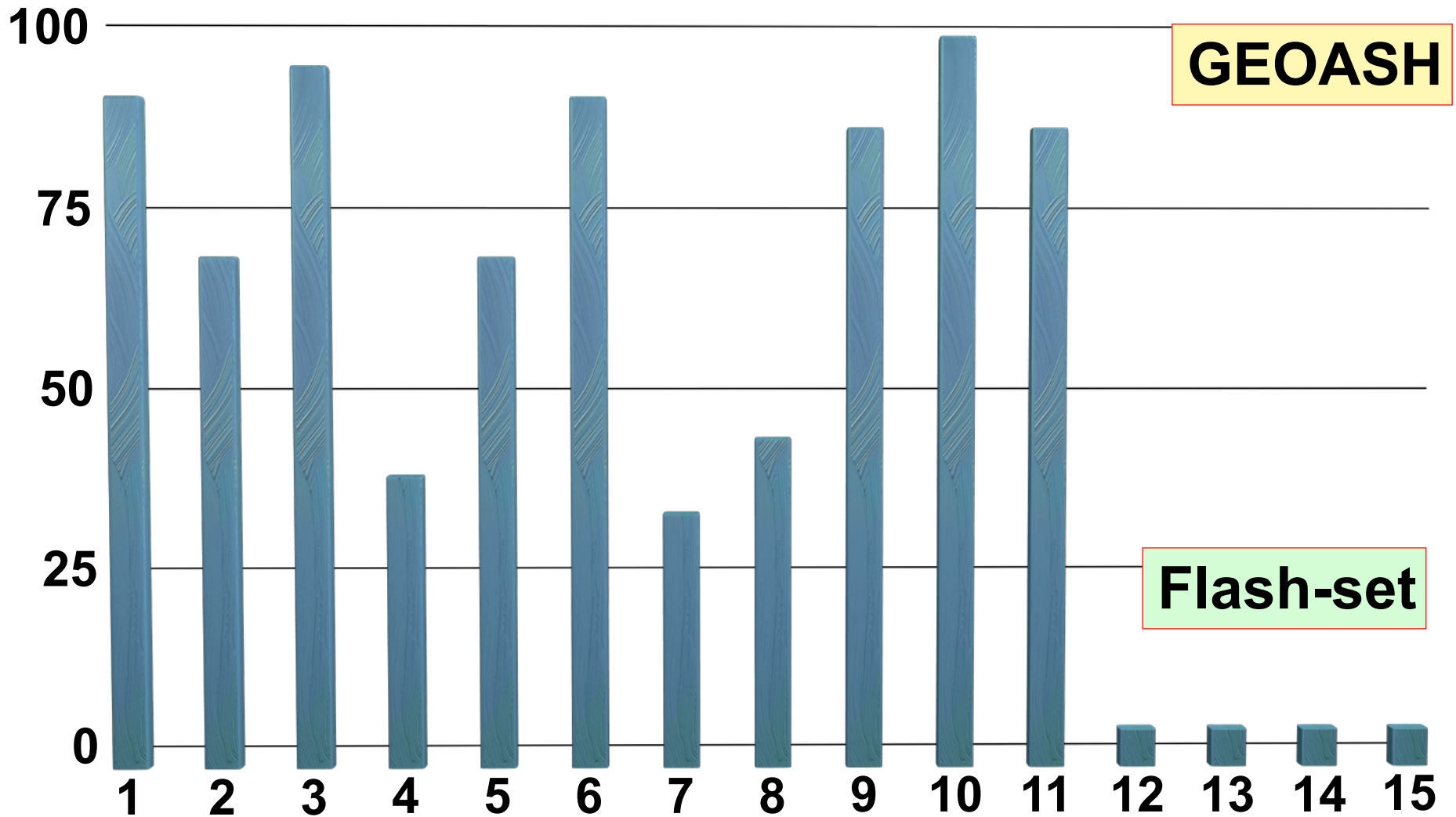
**28 day
compressive
strength**



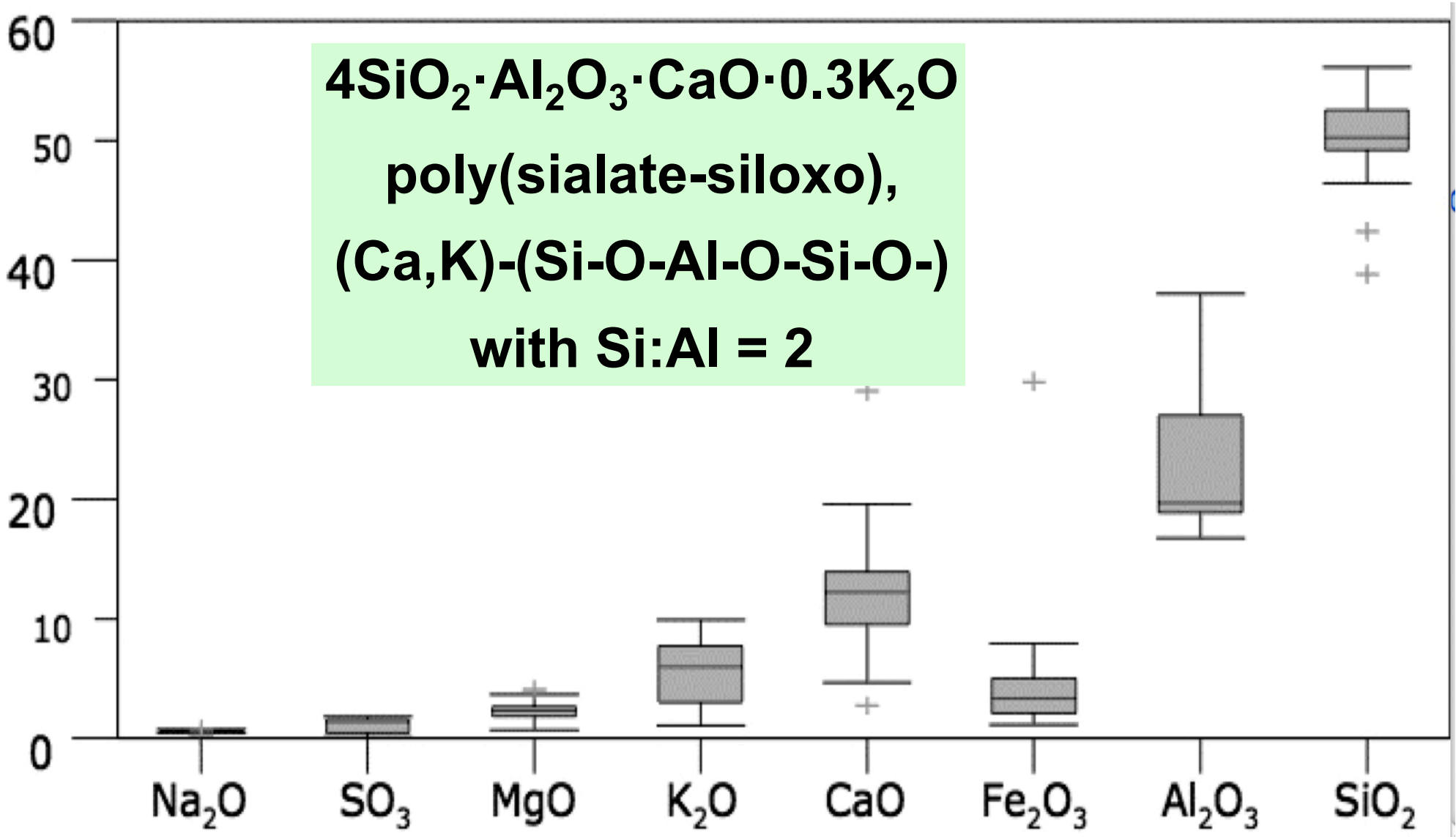
Hardening at ROOM TEMP.

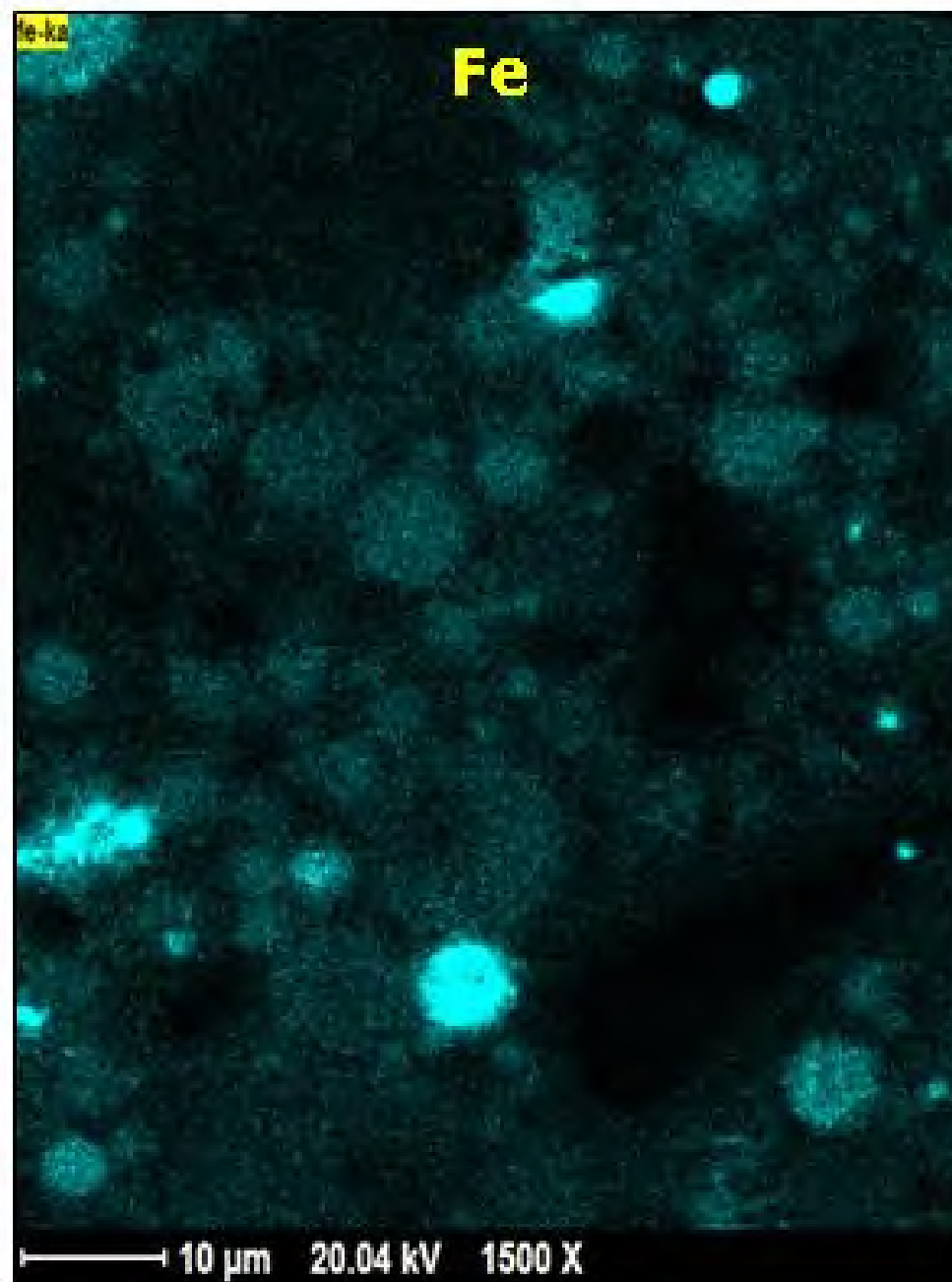
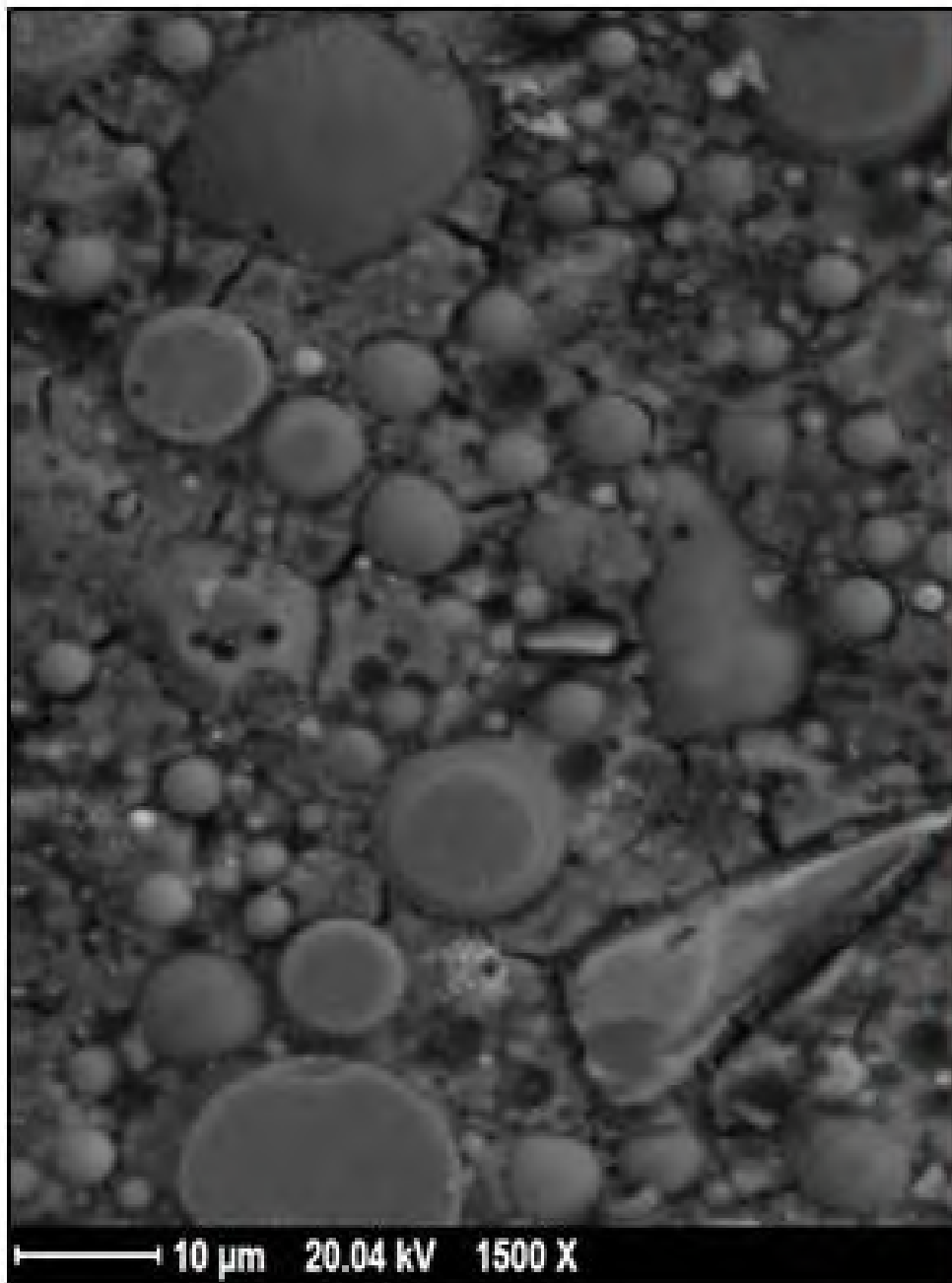
28 day compressive strength

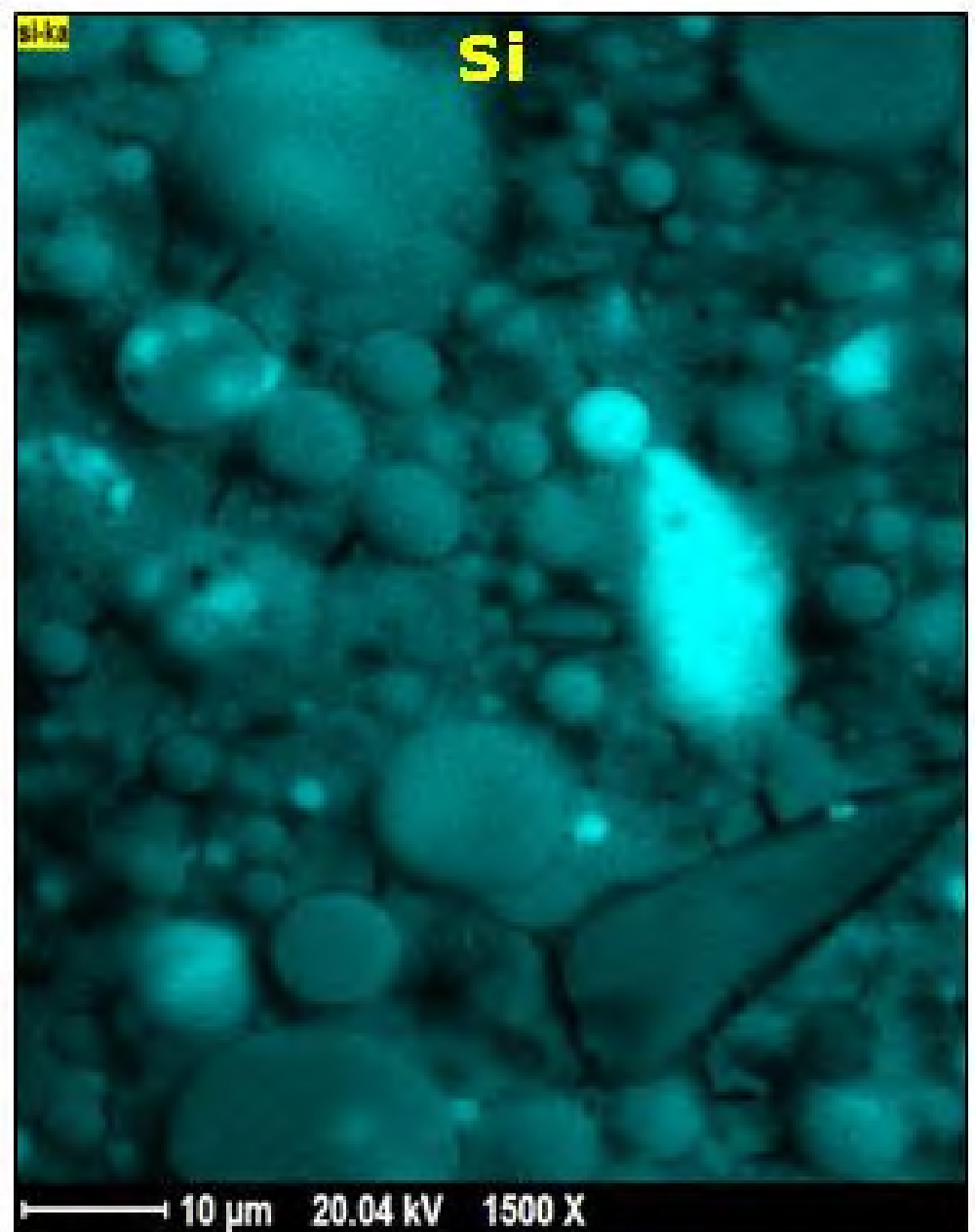
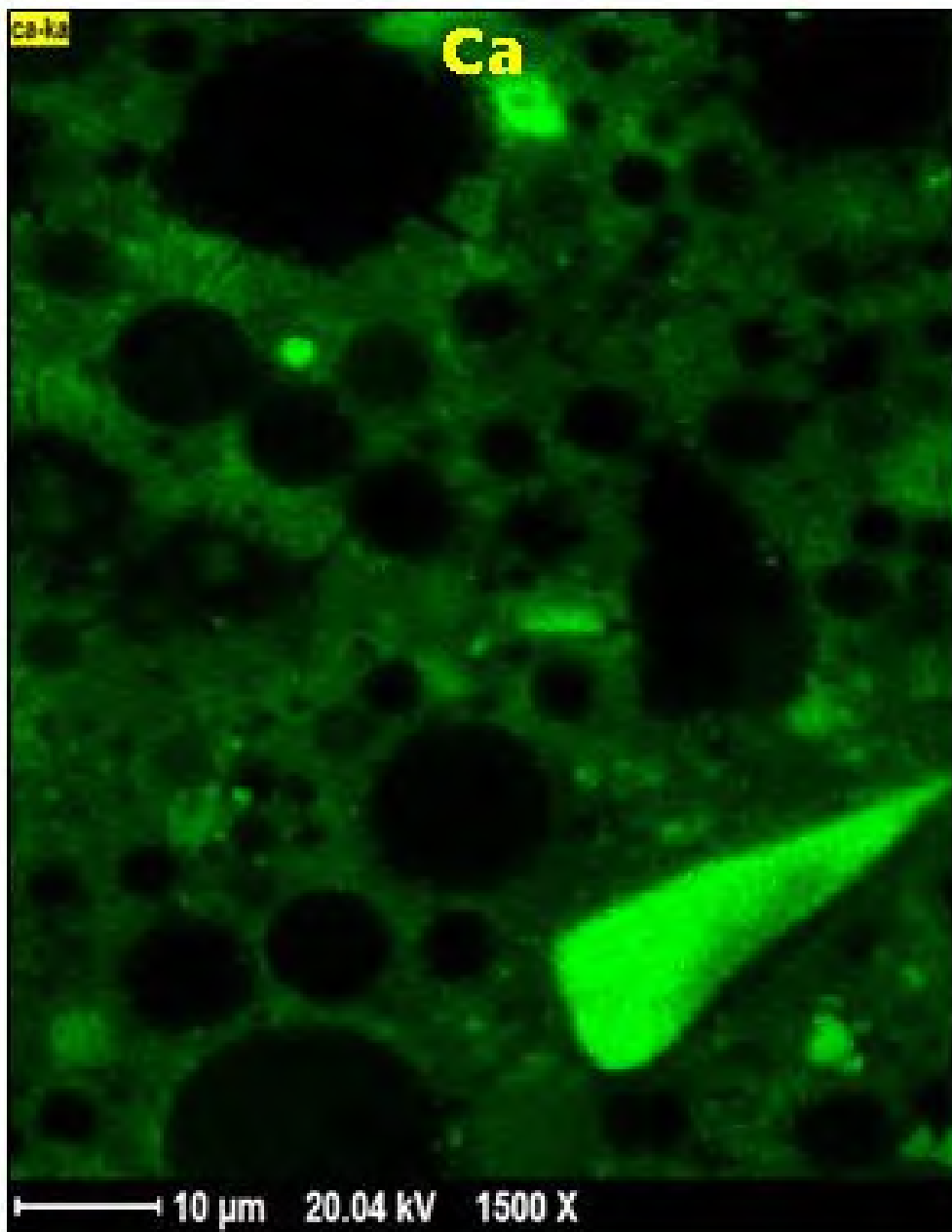
MPa



Ca-based geopolymer fly ash matrix composition







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



pH





pH



CORROSIVE



IRRITANT



User- hostile Systems



User- friendly

Systems

Corrosive and irritant chemicals



Hostile

Friendly



CaO (quick lime)

Ca(OH)₂

NaOH

Portland cement

KOH

Iron slag

Sodium metasilicate

**Slurry soluble silicate/
kaolin**

SiO₂:Na₂O = 1

kaolin

MR 1.25 < SiO₂:M₂O < 1.45

Any soluble silicate

Any soluble silicate

MR SiO₂:M₂O < 1.45

MR SiO₂:M₂O > 1.45

Joseph DAVIDOVITS

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