Workshop
Geopolymer Cement and Concrete
07 December 2010
Imperative to find alternative to cement, says French expert

International workshop on ‘Geopolymer cement and concrete’ held

Special Correspondent

CUDALORE: 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 Davide-vits of Geopolymer Institute, France.

Hence, it has become imperative to find an alternative to cement, said Mr. Davide-vits, 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 focused attention on geopolymer technology too because it could be equal to nanotechnology.

Mr. Davide-vits, 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, 4.5 billion tonnes of cement were produced in the world in 2000 and it accounted for 8.5 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 infrastructure 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. Davide-vits added.

R.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 save vast stretches of land and address the pollution problem.

Ramanathan added.

P Parameswaran of National University of Singapore, Singapore, B.Palaniappan, Dean, Faculty of Engineering and Technology, Annamalai University, C Antony Jeyasekar, Head, Department of Civil and Structural Engineering and chairman of organizing committee and S. Thirugnanammanohan, 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*

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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*

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4. Polycondensation into poly(sialates)

5. Reticulation, networking

6. Geopolymer solidification
Blast furnace slag

gehlenite

melilite

akermanite
Slag + KOH

$^{29}$Si NMR

- $Q_0$
- $Q_1$ at -79 ppm
- $Q_2$(1Al) at -82 ppm

+ KOH
Alkalination

gehlenite

(K,Ca)-ortho-sialate hydrate

$\text{Ca}^2+ \text{Si} \text{Al} \text{Ca}^2+ \text{Si} \text{Al}$

$\text{K}^+ \text{O} \text{O} \text{Al} \text{O} \text{OH} \text{OH}
\text{O Si O OH} + \text{Al(OH)}_3$
Alkalination

akermanite

Ca-di-siloxonate hydrate

CSH

Mg(OH)$_2$
Si  Q2 unit
tobermorite with Al substitution

Si Q2 unit
Si $Q_2$ unit

tobermorite with Al substitution

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

\[
\begin{align*}
\text{K}^+ & \\
\text{O} & \\
\text{Si} & \\
\text{Ca} & \\
\text{OH} & \\
\end{align*}
\]

(K,Ca)-ortho-sialate hydrate

\[+ \text{Al(OH)}_3\]

akermanite

\[
\begin{align*}
\text{OH} & \\
\text{O}_1 \text{Si} & \\
\text{O} & \\
\text{Ca} & \\
\text{Si} & \\
\text{Ca} & \\
\text{OH} & \\
\end{align*}
\]

Ca-di-siloxonate hydrate

\[+ \text{Mg(OH)}_2\]
gehlenite

\[
\begin{array}{c}
\text{K}^+ \\
\text{O} \\
\text{Si} \\
\text{Ca} \\
\text{O} \\
\text{OH} \\
\text{OH} \\
\text{Al} \\
\Theta \\
\text{O} \\
\text{OH} \\
\text{Ca} \\
\text{O} \\
\text{O} \\
\end{array}
\]

+ Al(OH)₃

(K,Ca)-ortho-sialate hydrate

akermanite

\[
\begin{array}{c}
\text{HO} \\
\text{Si} \\
\text{Q₁} \\
\text{O} \\
\text{Ca} \\
\text{O} \\
\text{O} \\
\text{Ca} \\
\text{O} \\
\text{O} \\
\text{Si} \\
\text{Q₁} \\
\text{O} \\
\text{Ca} \\
\text{O} \\
\text{O} \\
\text{Ca} \\
\text{O} \\
\text{O} \\
\text{Si} \\
\text{Q₂ (1Al)} \\
\text{O} \\
\text{Ca} \\
\text{O} \\
\text{O} \\
\text{Si} \\
\text{Q₂ (1Al)} \\
\text{O} \\
\text{Ca} \\
\text{O} \\
\text{O} \\
\text{Si} \\
\text{Q₂} \\
\text{O} \\
\text{Ca} \\
\text{O} \\
\text{O} \\
\text{Al(OH)₃} \\
\text{Mg(OH)₂} \\
\text{Ca(OH)₂}
\end{array}
\]

+ Mg(OH)₂

Ca-di-siloxonate hydrate

(K,Ca)-cyclo-ortho(sialate-disiloxo) Ca-di-siloxonate hydrate
gehlenite

(K,Ca)-ortho-sialate hydrate

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

akermanite

c-di-siloxonate hydrate

Ca-di-siloxonate hydrate

\[ \text{(K,Ca)-cyclo-ortho(sialate-disiloxo)} \]
1) MK-750 / slag-based
2) Rock / slag-based
3) Fly ash / slag-based
Geopolymerization
MK-750 + slag
Al\textsubscript{2}O\textsubscript{3}(3Si,OH) 65,55
Al\textsubscript{2}O\textsubscript{2}(2Si,2OH) 74
Al\textsubscript{2}O\textsubscript{4}(4Si) 58,14

(Ca-K) Geopolymer Cement base

Alkali-activated slag

$^{27}$Al ppm
150 100 50 0 -50 -100
(K,Ca)-cyclo-ortho(sialate-disiloxo) + AlQ_3(3Si) di(sialate-siloxo) → AlQ_4(4Si) poly(sialate-siloxo)

AlQ_3(3Si,OH) 65.55
AlQ_3(2Si,2OH) 74
AlQ_4(4Si) 58.14

(Ca-K) Geopolymer Cement base

Alkali-activated slag

\[ ^{27}\text{Al} \text{ ppm} \]

150 100 50 0 -50 -100
8 day strength / % MK-750

Room temperature

8 day compressive strength MPa

% by weight 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
Ca:Al 0.679 (0.388 to 0.870)   Si:Ca 2.43
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  + 0.41[Ca-poly(di-sialate)], anorthite hydrate;

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g...
$\text{Si:Al} = 1:1$

Ca-Poly(sialate)

Anorthite

Feldspar crankshaft chain
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

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Compressive Strength at 28 days (room temperature hardening):
Si:Al = 3:1
Poly(sialate-disiloxo) geopolymeric cement

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Compressive Strength at 28 days (room temperature hardening):

✦ European raw materials: up to 140 MPa
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
geopolymer matrix

$^{29}\text{Si}$ ppm
Coal-waste tailing
Coal-waste tailing

- 25% plagioclase (feldspar),
- 30% quartz,
- 10% amphibole,
- 27% kaolinite,
- 3-5% coal and
- 6% of other elements.
Coal-waste tailing
- 25% plagioclase (feldspar),
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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 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
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
Results: different geopolymer types

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

![Graph showing comparison between geopolymer concrete and currently used OPC based concrete](image)

No sensitive improvement of using geopolymer compared to currently used cement
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

a Université Paris-Est, IFSTTAR, Département Matériaux, 58 bd Lefebvre, 75732 Paris cedex 15, France
b Ecole Supérieure de Physique et Chimie Industrielles, PPMD SIMM, UMR 7615 ESPCI-CNRS-UPMC, 10 rue Vauquelin, 75231 Paris cedex 05, France
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 Université Paris
 Ecole Supérieure
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.
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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.
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They are re-inventing the wheel!!
For whom? LAFARGE.
How?
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
French institute of science and technology for transport

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COMMUNIQUE DE PRESSE

Paris, le 9 juin 2011

LAFARGE ET L’ÉCOLE DES PONTS PARISTech RENFORCENT LEUR PARTENARIAT
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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- **E-CRETE Geopolymer Concrete** developed by Zeobond Australia (2007)
CO$_2$ reduction for
CO$_2$ reduction for
Rock-based GP-cement
CO₂ reduction for Rock-based GP-cement (1) by-products (waste)
CO$_2$ 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

<table>
<thead>
<tr>
<th>Processing</th>
<th>Portland Cement</th>
<th>GP-cement uncalcined</th>
<th>GP-cement calcined</th>
</tr>
</thead>
<tbody>
<tr>
<td>calcination</td>
<td>1,000</td>
<td>0,035</td>
<td>0,140</td>
</tr>
<tr>
<td>crushing</td>
<td>0,020</td>
<td>0,018</td>
<td>0,018</td>
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<tr>
<td>K-silicate</td>
<td>0</td>
<td>0,050</td>
<td>0,050</td>
</tr>
<tr>
<td>Slag waste</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>total</td>
<td>1,020</td>
<td>0,103</td>
<td>0,208</td>
</tr>
<tr>
<td>reduction</td>
<td>0</td>
<td>90 %</td>
<td>80 %</td>
</tr>
</tbody>
</table>
Slag manufactured and with K-silicate solution
<table>
<thead>
<tr>
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<th>Portland Cement</th>
<th>GP-cement uncalcined</th>
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<td>0,035</td>
<td>0,140</td>
</tr>
<tr>
<td>crushing</td>
<td>0,020</td>
<td>0,018</td>
<td>0,018</td>
</tr>
<tr>
<td>K-silicate</td>
<td>0</td>
<td>0,050</td>
<td>0,050</td>
</tr>
<tr>
<td>Slag manuf.</td>
<td>0</td>
<td>0,100</td>
<td>0,100</td>
</tr>
<tr>
<td>total</td>
<td>1,020</td>
<td>0,203</td>
<td>0,308</td>
</tr>
<tr>
<td>reduction</td>
<td>0</td>
<td>80 %</td>
<td>70 %</td>
</tr>
</tbody>
</table>
Slag as by-product (waste) and with GP-LAVA
### Slag as by-product (waste) and with GP-LAVA

<table>
<thead>
<tr>
<th>Processing</th>
<th>Portland Cement</th>
<th>GP-cement uncalcined</th>
<th>GP-cement calcined</th>
</tr>
</thead>
<tbody>
<tr>
<td>calcination</td>
<td>1,000</td>
<td>0,035</td>
<td>0,140</td>
</tr>
<tr>
<td>crushing</td>
<td>0,020</td>
<td>0,018</td>
<td>0,018</td>
</tr>
<tr>
<td>GP-LAVA</td>
<td>0</td>
<td>0,100</td>
<td>0,100</td>
</tr>
<tr>
<td>Slag waste</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>total</td>
<td>1,020</td>
<td>0,153</td>
<td>0,258</td>
</tr>
<tr>
<td>reduction</td>
<td>0</td>
<td>85 %</td>
<td>75 %</td>
</tr>
</tbody>
</table>
Slag manufactured and with
GP-LAVA
# Slag manufactured and with GP-LAVA

<table>
<thead>
<tr>
<th>Processing</th>
<th>Portland Cement</th>
<th>GP-cement uncalcined</th>
<th>GP-cement calcined</th>
</tr>
</thead>
<tbody>
<tr>
<td>calcination</td>
<td>1,000</td>
<td>0,035</td>
<td>0,140</td>
</tr>
<tr>
<td>crushing</td>
<td>0,020</td>
<td>0,018</td>
<td>0,018</td>
</tr>
<tr>
<td>GP-LAVA</td>
<td>0</td>
<td>0,100</td>
<td>0,100</td>
</tr>
<tr>
<td>Slag manuf.</td>
<td>0</td>
<td>0,100</td>
<td>0,100</td>
</tr>
<tr>
<td>total</td>
<td>1,020</td>
<td>0,253</td>
<td>0,358</td>
</tr>
<tr>
<td>reduction</td>
<td>0</td>
<td>75 %</td>
<td>65 %</td>
</tr>
</tbody>
</table>
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%
Fly ash / slag - based geopolymer cement
# Combustion technologies and operating temperatures

<table>
<thead>
<tr>
<th>Technology</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>fluidized-bed</td>
<td>850°C</td>
</tr>
<tr>
<td>pulverized coal combustion 1</td>
<td>1250°C</td>
</tr>
<tr>
<td>pulverized coal combustion 2</td>
<td>1500°C</td>
</tr>
<tr>
<td>Coal gasification IGCC</td>
<td>1800°C</td>
</tr>
</tbody>
</table>
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
Conventional method: alkali-activation dissolution and zeolite formation

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

- 0.3-0.4 L/kg, NaOH 12M,
- 24h room temperature ageing,
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.
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:
Geopolymeric method:

room temperature hardening
Geopolymeric method:
room temperature hardening
polycondensation
Geopolymeric method:

room temperature hardening
polycondensation

- fly ash........................................50 to 85
Geopolymeric method:

room temperature hardening polycondensation

- fly ash.................................50 to 85
- K-silicate solution SiO2:K2O >1.4........10
Geopolymeric method:

room temperature hardening polycondensation

- fly ash........................................50 to 85
- K-silicate solution SiO2:K2O >1.4........10
- blast furnace slag..........................15
Geopolymeric method:

room temperature hardening polycondensation

- fly ash..............................50 to 85
- K-silicate solution SiO2:K2O >1.4.......10
- blast furnace slag.........................15
- water........................................5
Geopolymeric method:

room temperature hardening
polycondensation

- fly ash.................................50 to 85
- K-silicate solution SiO2:K2O >1.4........10
- blast furnace slag..........................15
- water...........................................5

User-friendly.
28 day compressive strength

alkali-activated fly ash MPa

geopolymer fly ash MPa

1:1
Hardening at ROOM TEMP.
28 day compressive strength

MPa

100
75
50
25
0

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

GEOASH

Flash-set
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),

\[(\text{Ca,K})-(\text{Si-O-Al-O-Si-O-})\]

with Si:Al = 2
From Low-Tech to High-Tech Development of USER-FRIENDLY systems
pH
User-hostile Systems
User-friendly Systems
<table>
<thead>
<tr>
<th>Corrosive and irritant chemicals</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hostile</strong></td>
</tr>
<tr>
<td>CaO (quick lime)</td>
</tr>
<tr>
<td>NaOH</td>
</tr>
<tr>
<td>KOH</td>
</tr>
<tr>
<td>Sodium metasilicate</td>
</tr>
<tr>
<td>$\text{SiO}_2:\text{Na}_2\text{O}=1$</td>
</tr>
<tr>
<td>Any soluble silicate</td>
</tr>
<tr>
<td>$\text{MR } \text{SiO}_2:\text{M}_2\text{O}&lt;1.45$</td>
</tr>
</tbody>
</table>
GEOPOLYMER
Chemistry & Applications
Joseph DAVIDOVITS