









# Contraction of the second seco

## Joseph Davidovits

## Geopolymer Institute www.geopolymer.org

# State of the Geopolymer R&D

**2017** 

# S MEET ARE



### Spring 2017

# www.geopolymer.org

EBINAR

#### Geopolymer Webinar Spring 2017 Registered participants,



## Available for free download at <u>www.geopolymer.org</u>

#### **Technical papers**

24 pdf

#### Archaeological papers

9 pdf

#### Category: Technical papers

Papers dealing with geopolymer science and applications



#### # 24 False CO2 Values Published in **Scientific Papers**

7 Dec 2015

Technical paper #24 False Values on CO2 Emission for Geopolymer Cement/Concrete Published in Scientific...



#22 GEOASH: ambient temp. hardening of fly ash-based geopolymer cements

16 Jul 2014



**#23 Technical Paper on Geopolymer Aircraft Pavement** 

27 Oct 2015

Technical paper # 23 GP-AIRPORT in our Library Last year (October 14, 2014), our News was titled 70,000 tonnes...



#### **#21 Geopolymer cement review** 2013

6 Feb 2013

A review on Geopolymer cement, as of January



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GPCamp 2016 13 Jul 2016



## Available for free download at <u>www.geopolymer.org</u>







**Joseph Davidovits** 

Why Alkali Activated Materials are **NOT** Geopolymers ?

Excerpt from the keynote: State of the Geopolymer R&D 2014

© July 2014 - Geopolymer Institute - Geopolymer Camp

- 8 Videos: State of the Geopolymer R&D
  - I I Videos: Special Keynotes

12 Videos: Lectures Spring 2014 and Spring 2016

**3 Videos: Why Alkali Activated Materials** are NOT Geopolymers?

## Why Alkali-Activated Materials (AAM) are not Geopolymers?



#### **Joseph Davidovits**

#### Why Alkali Activated Materials are **NOT** Geopolymers ?

Excerpt from the keynote: State of the Geopolymer R&D 2014

© July 2014 - Geopolymer Institute - Geopolymer Camp

**Part I:** Aug. 2014 Excerpt Geopolymer R&D 2014 GP-Institute > 14,600 YouTube > 5,800

Part 2: Aug. 2015 Excerpt Geopolymer R&D 2015 Part 2: Clarifying statement and historicity. *GP-Institute* > 5,900 *YouTube* > 1,800

Part 3: Aug. 2016 Excerpt Geopolymer R&D 2016 Part 3: What scientists are now writing on this issue. GP-Institute > 2,620 YouTube > 650





# From Theory to Global Industrialization

# Geopolymer binder / resin paint / coating / grout Geopolymer foam Geopolymer cement Geopolymer concrete Geopolymer carbon/composite Geopolymer ceramics

















Plastics are dangerous !! Are organic polymers heat resistant ??



# • No! NATURE states : Only MINERALS provide fire and heat resistance

## • Target: Inorganic polymers

## Geopolymers are

Polymers, processed like organic polymers Yet, **GEO-polymers** Fire and heat resistant

## Chapter 22

#### Fire and Heat resistant

## Geopolymer Foam

Trolit<sup>®</sup> 1987

Too expensive !!









## June 14, 2017 30 years later London Grenfell Tower

80 people died ! Is it too expensive ?







## BASF Germany PCI-GEOFUG®, geopolymer grout and binder

www.pci-augsburg.de



## Milliken Infrastructures USA

Geopolymer mortar systems and grouts for use in rehabilitation

infrastructure.milliken.com



## ASK Chemicals (Ashland) Germany

INOTEC Inorganic Binder System, geopolymer binder for foundries

www.ask-chemicals.com

## BMW SUPPLIER **INNOVATION** AWARD 2014

## Wagners Australia

Earth Friendly Concrete: fly ash / slag geopolymer concrete for infrastructures

www.wagner.com.au





# Pyromeral Systems France

High-tech high-temperature structural geopolymer composite materials for automotive, aircraft industries

www.pyromeral.com



## Éire Composites Ireland

MechTool®: Heated geopolymer composite tooling for manufacture of large composites structures (aerospace, wind mill energy)

www.eirecomposites.com





## Airbus France

Aircraft conduit in geopolymer carbon composite Patent: US 20090197031 A1 FR2007051747





## Schlumberger France

Patent: WO/2008/017414 Pumpable geopolymer formulation for oilfield application

# Schlumberger



## Rockwool Australia

Geopolymer rockwool brickettes used to recycle unused fibers



## Commissariat à l'Énergie Atomique France

Patent WO/2009/050196 Method of preparing a controlled porosity geopolymer for catalysis and filtration



## Alsitek Limited UK

Patent WO/2009/050472 Extruded geopolymer frame profiles for windows or doors

www.alsitek.co.uk



## Matakii Panels Singapore

Patent WO/2009/025620 Precast geopolymer panels

www.matakiipanels.com



## NU-Core A2FR China

Geopolymer Fireproof Composite Panels

www.nu-core.com.cn





## Renca Russia

3D Printer for buildings. Development with Apis-Cor of a 3D printer with a fast setting geopolymer concrete

www.renca.com





## Corning USA

Patent US 7745363 Geopolymer ceramic composites for high temperature

www.corning.com

#### CORNING



## Dow Chemical USA

Patent WO/2010/138351 Geopolymer coating for organic polymer substrates

www.dow.com



## Orexo AB Sweden

Patent WO/2010/128300 Composition for sustained drug delivery comprising geopolymeric binder

www.orexo.com



## INOMAT Germany

Ino-Flamm® Patent WO/2011/029444 Fire resistant geopolymer paint

www.inomat.de



## Sinotec Germany

Sinocoat® Very resistant and acid-proof rigid anti-corrosive geopolymer coating for the protection of surfaces on metallic and mineral basis

www.sinnotec.eu



## GeoPol Czech Rep.

Geopolymer sand binder for cores in foundries

www.geopol-info.com


# Nova Lignum Netherlands

Ceranex<sup>™</sup> Geopolymer composite sidings and façade claddings

www.novalignum.nl





# NanoVoltaics Inc. USA

Nanoporous geopolymer (npGEO<sup>™</sup>) composites for use in water treatment as an adsorbent for the removal of arsenic.

www.nanovoltaics.com



# Allied Foam Tech Corp. USA

GeoFoam: geopolymer foam cement, for lightweight and fireproof applications

www.alliedfoamtech.com



# Vodnis Klo Czech Rep.

Desil Al<sup>™</sup> Geopolymer binder system for foundries

www.vodnisklo.cz



## PolyRap Canada

### Econcrete: geopolymer concrete made out of mine tailings

www.polyrap.net



RECYLED GLASS AS AN ADMIX TO POLYMER AND GEOPOLYMER

## Argio Belgium ArgioBricks: LTGS bricks (low temperature geopolymer setting)

www.argio.com





Architecte : Maarten Martens

+ 25 logements, 2.500 m2 de maçonnerie Argio apparentes.



# Reinforced Concrete Pipes Australia

eCP: geopolymer concrete pipes

www.rcpa.com.au



## Watershed Materials USA

Geopolymer blocks made out of clay, geology, rice husk, lime and slag

watershedmaterials.com



## Bowers Industrial USA

A200 to A600 geopolymer concrete (quartzite fillers) for acid resistant applications

www.bowersindustrial.com



# Aquaminerals Finlands

Solutions for water purification with patented geopolymer nitrogen removal adsorbents

www.aquaminerals.fi



# Amec Foster Wheeler United Kingdom

SIAL® matrix, a specialised geopolymer technique for encapsulating various radioactive waste streams.

www.amecfw.com





# Wincret Brazil

Decorative architectural geopolymer binder panels for inside and outside

www.winblok.com.br



# Néoterre France

Geobiology applications

www.neoterre.com



## **Geopolymer research 1988**



### **1st Geopolymer conference**

### **Geopolymer research 2016**





### Kuala Lumpur, October 12-13, 2



**Conference Information** 

**ICGCGC 2017 : 19th International Conference on Geopolymer Cement and Geopolymer Concrete** 

## WASET fake conferences on Geopolymers ??

waset geopolymer conference 2017								
Tous	Actualités	Images	Vidéos	Shopping	Plus	Parame		
Environ	82 700 résultat	ts (0,65 secol	ndes)					
	waset Tous Environ	waset geopolymer Tous Actualités Environ 82 700 résultat	waset geopolymer conference   Tous Actualités Images   Environ 82 700 résultats (0,65 second)	waset geopolymer conference 2017   Tous Actualités Images Vidéos   Environ 82 700 résultats (0,65 secondes)	waset geopolymer conference 2017   Tous Actualités Images Vidéos Shopping   Environ 82 700 résultats (0,65 secondes)	waset geopolymer conference 2017   Tous Actualités Images Vidéos Shopping Plus   Environ 82 700 résultats (0,65 secondes)		

Search Conferences

icgcgc 2017 - World Academy of Science, Engineering and Technology https://www.waset.org/conference/2017/10/kuala-lumpur/JCGCGC Traduire cette page The ICGCGC 2017: 19th International Conference on Geopolymer Cement and ... ICGCGC 2017 has teamed up with the Special Journal Issue on Geopolymer Cement and ... Please ensure your submission meets WASET's strict guidelines for ...

ICG Prague 2017: 19th International Conference on Geopolymer ... https://www.waset.org/conference/2017/03/prague/ICGT Traduire cette page 23 mars 2017 - The ICGT 2017: 19th International Conference on Geopolymer Technology aims to bring together leading academic scientists, researchers and ...

Call for Papers - World Academy of Science, Engineering and ... https://waset.org/conference/2017/10/kuala.../call-for-papers Traduire cette page The ICGCGC 2017 : 19th International Conference on Geopolymer Cement and Geopolymer Concrete is the premier interdisciplinary platform for the ...

ICGCGC Home - World Academy of Science, Engineering and ... https://waset.org/conference/2017/10/kuala-lumpur/.../home Traduire cette page ICGCGC 2017 : 19th International Conference on Geopolymer Cement and Geopolymer Concrete ... Abstracts : waset.org/abstracts/urban-and-civil- engineering.

ICCCC Istanbul 2017: 19th International Conference on Cement and ... https://www.waset.org/conference/2017/10/istanbul/ICCCC/home Traduire cette page ICCCC 2017 : 19th International Conference on Cement and Concrete Chemistry ... Abstracts : waset.org/abstracts/chemical-and-molecular-engineering ... Geo-polymer, Low Carbon Cement, Low Carbon and Green Development, Standard ...

ICGC Saint Petersburg 2017: 19th International Conference on ... https://www.waset.org/conference/2017/09/saint.../call-for-papers Traduire cette page The ICGC 2017 : 19th International Conference on Geopolymer Concrete is the premier interdisciplinary platform for the presentation of new advances and ...





E-mail

### Lisbon, April 16-17, 2017

My Account

Excellence in Research and Innovation for Humanity

THE REAL PROPERTY AND A



Presentation Program Conference Program SESSION 1

### **Presented papers**

Chair : Victoria Gooodall

1	Oral	Development of Automatic Farm Manure Spread Barış Ozluoymak, Emin Guzel, Ahmet İnce Cukurova University Turkey
2	Oral	Comparison of Methods for the Detection of I Isolated from Dairy Products Goksen Arik, Mihriban Korukluoglu Uludag University Turkey
3	Oral	Assessment of Germination Loss Due to Dusk Stage and Bug Intensity Ali Hassan, Mian Muhammad Awais, Muhammad F University of Agriculture Faisalabad Pakistan
4	Oral	Exposure of Pacu, Piaractus mesopotamicus G Microscopy Study Wiolene Montanari Nordi, Debora Botequio Moretti, Luiz de Queiroz College of Agriculture, University o
5	Oral	Reversible Adsorption of Water Contaminants of Sandrine Delpeux-Ouldriane, Mickael Gineys, Nath Centre National de la Recherche Scientifique France
6	Oral	Statistical Analysis of Polycyclic Aromatic Hyd Diesel/Biodiesel Blends Sergio Machado Correa Rio de Janeiro State University Brazil
7	Poster	Using Complete Soil Particle Size Distributions Properties Habib Khodaverdiloo, Fatemeh Afrasiabi, Farrokh A Urmia University Iran, Islamic Republic Of
8	Oral	Hidden Markov Movement Modelling with Irregul Victoria Goodall, Paul Fatti, Norman Owen-Smith Nelson Mandela Metropolitan University South Afric
9	Poster	Assessment of Bioaerosol and Microbial Volatile Himanshu Lal, Bipasha Ghosh, Arun Srivastava Jawaharlal Nehru University India
		Internetterne between Ordinar Armerite and P

### ding Machine for Orchards

**Biofilm Formation in Yeast and Lactic Acid Bacteria Species** 

ky Cotton Bug (Oxycarenus laetus) in Relation to Cotton Boll

Rafique Shahid, Farazia Hassan, Shumaila Rasool

### Gill Tissue to a High Stocking Density: An Ion Regulatory and

, Mariana Caroline Pontin, Jessica Pampolini, Raul Machado-Neto of São Paulo Brazil

on Nanoporous Carbon Fibers thalie Cohaut, Francois BéGuin nce

**Irocarbons Emissions and Its Alkyl and Nitro Derivatives from** 

### s for More Precise Predictions of Soil Physical and Hydraulic

Asadzadeh, Martinus Th. Van Genuchten

### ular Data

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le Organic Compounds in Different Sections of Library

Instan Developter A. The continual Observictory and Executive entry.

SESSION	3
Chair : Rid	chard Prawat Presented pape
23 Oral	Cut-Out Animation as an Technic and Develo Armagan Gokcearslan Gazi University Turkey
24 Oral	The Views of Teachers over the Father Involu- Fatma Tezel Sahin, Zeynep Nur Aydin Kilic, Ays Gazi University Turkey
25 Oral	Migration of Meaning in Contemporary Art E K. Özlem Alp Gazi University Turkey
26 Oral	Space Figure Relationship in Contemporary Selda Mant Menay Dumlupinar University Turkey
27 Oral	Types of Handmade Dolls in Turkey Melda Özdemir Gazi University Turkey
28 Poster	Public-Public Partnership and Tourism De Macedonia Dejan Metodijeski, Elizabeta Mitreva, Nako Tas University Goce Delcev Macedonia
29 Oral	A Fine String between Weaving the Text Antithetical Relationships in the Classical and Rima Abu Jaber-Bransi, Rawya Jarjoura Burbar Oranim Academic College Israel
30 Oral	A Sociolinguistic Analysis of Private Letters Mariarosaria Zinzi University of Florence Italy
31 Oral	Hybrid Model of an Increasing Unique Cons and the Pursuit of a Sustainable Competitive Wilhelmus Hary Susilo University of Persada Indonesia Indonesia

### ers

opment inside History Process

vement to Preschool Education Programs segul Akinci Cosgun

Experience

Art

evelopment Strategy: The Case of Municipality of Gazi Baba in

kov, Oliver Filiposki

t and Patching It: Reading beyond the Hidden Symbols and nd Modern Arabic Poetry ra

of Women in Ancient Egypt

sumer Value on Purchases that Influences the Consumer Loyalty e Advantage from the Institutions in Jakarta

### **Tokyo, October 11-12, 2017**





### Saint Petersburg, September 14-15, 2017

### **Conference Information**

Aims and Objectives

Important Dates

### **International Scientific Committee**

..........

Ahadollah Azami Xi Wang Thanh Nguyen P. Sherif El - Safty Dmitriy Kuvshinov

Eastern Mediterranean University, Famagusta City, North Cyprus, Turkey, TR National Institute for Materials Science, JP Okayama University, JP National Institute for Materials Science, JP University of Sheffield, UK



### **Paper Submission**

### Paper Submission

Paper Submission GUIDE

### **Conference Registration**

Author Registration

Listener Registration

Payment

Yinghong Qin Anna Stepien Mahsa Armaghan Cheng-Yu Wang Mohammad Sajjad Nej Mohammed Mahmood Heba Mansour Rohit Kumar Tiziano Zarra Tahar Laoui Mohammed Mashrei Asad Hanif Olesia Mikhailova Mohamed Gabr Nor Salwati Othman Uche Okafor

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	Michigan Technological Universiity, US
	University of Technology, PL
	Azad University, Scienceand Research Branch, IR
	National Chiao Tung University, TW
jad	Islamic Azad University, Borujerd, Iran, IR
1	Diyala University, IQ
	National Research Centre, EG
	National Institute of Technology, IN
	University of Salerno, IT
	King Fahd University of Petroleum and Minerals, SA
	University of Thi-qar- Iraq, IQ
	The Hong Kong University of Science and Technology, Hong Kong,
	Brno University of Technology, Czech Republic
	Kanazawa Institute of Technology, Japan
	Universiti Tenaga Nasional, Malaysia
	University of Nigeria, Nigeria

**Beware of fake geopolymer conferences** USD), often under the names of real conferences. I am confident that all researchers and members of the WASET's conferences are void of any scientific value. mistakenly participates to such fake conferences!

- Organisations such as WASET run fake "conferences" in
- order to make profit with the registration fees (450-500)
- geopolymer science community will immediately realise that
- Please spread the word among your contacts so that nobody



## State of the Geopolymer R&D 2017

## I) Geopolymer science

## 2) Geopolymer technologies

## 4) Geopolymer and archaeology

3) Geopolymer Cements / Concretes

## State of the Geopolymer R&D 2017

## 1) Geopolymer science

2) Geopolymer technologies

3) Geopolymer Cements / Concretes

4) Geopolymer and archaeology

## They cannot be called GEO-POLYMERS

2 very different systems!

Why Alkali-Activated Materials (AAM) are not Geopolymers?

- Because
- Alkali-activated Materials <u>are not POLYMERS</u>.

- It is a big <u>scientific mistake</u> to use both as synonyms.
- Alkali-activation is a wrong terminology for geopolymers.





# Why Alkali-Activated Materials (AAM) are not Geopolymers?

## Part 4

## Legal and Patent issue !



patents is available (many companies asked me).

- **Question** From Danemark :
- I did my Master thesis on geopolymer cement for oil well cementing (with
- focus on High Temperatures). Waiting an offer for Geopolymer Concrete
- PhD from UTS (Sydney). Interested to know how much room for new

- Example Geopolymer-Cement:
- trial (patent lawsuit) at European Patent Office.

Red Lion Cement Technology Ltd vs PQ and BASF (world chemistry companies);



Davidovits patent filed in France, July 2006

### (12) United States Patent Davidovits et al.

### **GEOPOLYMERIC CEMENT BASED ON FLY** (54)(56) ASH AND HARMLESS TO USE

### (57)ABSTRACT

Geopolymeric cement based on aluminosilicate fly ashes of class F, which, contrary to the prior art, are harmless to use and harden at ambient temperature, favoring their use in common applications in the construction and civil engineering fields. This harmlessness is achieved thanks to a mixture containing: 10 to 15 parts by weight of a non corrosive alkali metal silicate solution in which the M<sub>2</sub>O:SiO<sub>2</sub> molar ratio is less than 0.78, preferably less than 0.69 and the SiO<sub>2</sub>:M<sub>2</sub>O ratio greater than 1.28, preferably greater than 1.45, M denoting Na or K; added to this are 10 to 20 parts by weight of water and 5 to 15 parts by weight of blast furnace slag having a specific surface area less than  $400 \text{ m}^2/\text{kg}$  preferably less than 380 m<sup>2</sup>/kg and 50 to 100 parts by weight of class F aluminosilicate fly ash.

### (10) Patent No.: (45) **Date of Patent:**

### US 8,202,362 B2 Jun. 19, 2012

**References** Cited



U.S. PATENT DOCUMENTS









(12)



- (45) Date de publication et mention de la délivrance du brevet: 28.04.2010 Bulletin 2010/17
- (21) Numéro de dépôt: 07823342.6
- (22) Date de dépôt: 26.07.2007
- D'EMPLOI.

GEOPOLYMERIC CEMENT BASED ON FLY ASH AND HARMLESS TO USE





### EP 2 061 732 B1 (11)

### FASCICULE DE BREVET EUROPEEN

(51) Int Cl.: C04B 28/00 (2006.01)

C04B 18/08 (2006.01)

- (86) Numéro de dépôt international: PCT/FR2007/001285
- (87) Numéro de publication internationale: WO 2008/012438 (31.01.2008 Gazette 2008/05)

### (54) CIMENT GÉOPOLYMÉRIQUE À BASE DE CENDRES VOLANTES ET À GRANDE INNOCUITÉ

- UNSCHÄDLICHER GEOPOLYMERZEMENT AUF DER BASIS VON FLUGASCHE

## **April 2010**: European Patent granted

- 9 months grace period
- **February 2011:** Opposition by BASF and PQ Corp.
  - based on alkali-activation = geopolymer
    - i.e. public domain, not patentable
- **24 November 2014** : EPO Judgment EPatent = OK



Beschwerdekammern **Boards of Appeal** Chambres de recours

- **December 2014**: BASF appeal of decision
- repeating claim alkali-activated materials = geopolymer
  - = public domain, not patentable
  - January 23, 2017 : Appeal trial

European Patent Office 80298 MUNICH GERMANY Tel. +49 (0)89 2399-0 Fax +49 (0)89 2399-4465



СОЮЗ СОВЕТСНИХ СОЦИАЛИСТИЧЕСНИХ РЕСПУБЛИН

ГОСУДАРСТВЕННЫЙ КОМИТЕТ СССР ПО ДЕЛАМ ИЗОБРЕТЕНИЙ И ОТНРЫТИЙ

# К АВТОРСКОМУ СВИДЕТЕЛЬСТВУ

### Filed 1981, Published 1983

Krivenko (21) 3354207/29-33 (22) 04.11.81 (46) 30.03.83. Бюл **ж** 12 И.А. Панжов, С.И. Чурсин, (72) П.В. Кривенко и Е.С. Казалерова (71) Киевский ордена Трудового Красного Знамени инженерно-строительный институт (53) 666.943(088.8) (56) 1. Авторское свидетельство СССР № 772989, кл. С 04 В 7/14, 1979. 2. Авторское свидетельство СССР № 419489, кл. С 04 В 7/14, 1972.



(54) (57) ВЯЖУЩЕЕ, ВКЛЮЧающее доменныя гранулированныя шлак, растворимое стекло и золу-унос, о т л и ч а ю щ е е с я тем, что, с целью увеличения сроков схватывання, повышения прочности и снижения объемной массы, оно содержит указанные компоненты в следующем соотношении, вес. 8: Доменный гранулированный шлак 50-67 Растворимое

стекл¢ Зола∸унос. 8-15 25-35

(54)(57) BINDER, comprising granulated blast-furnace slag, water glass and fly ash, characterized in that with the object of increasing setting times, enhancing strength and reducing bulk weight, it comprises said 25 components in the following ratio, wt. \*: MR=1.0Granulated blast-furnace slag 50-67 corrosive, 8-15 Water glass **User Hostile** 25-35 Fly ash - -

- January 23, 2017 :
- all BASF claims were defeated, European patent valid
  - i.e. alkali activation AAM lost against geopolymer

Boards of Appeal of European Patent Office

appeal rejected.

## Basic chemistry is in Public Domain. Alkali activated materials AAM not patentable,

Geopolymer materials, patentable when based on new science.
# Metakaolin MK-750 Chemical Reactivity

## Exothermicity

Chapter 8



GEOPOLYA

ER

6

Joseph DAVIDOVITS

## GEOPOLYMER Chemistry & Applications 4th edition

GÉOPOLYMÈRE

www.geopolym







## MK-750 NMR





### **AI(5)**



**AI(4)** 



**AI(6)** 



MK-750 Al NMR

## Making of metakaolin MK-750





Intra-dehydroxylation

Inter-dehydroxylation

### **Al is** trivalent





**Courtesy Imerys** 



Kiln	AI-OH	AI=O	AI-O-AI	Al(5) +
type	AI(6) %	AI(5) %	AI(4) %	reactivi
<i>Rotary</i> M1000	35	50	15	65





Kiln type	AI-OH AI(6) %	AI=O AI(5) %	AI-O-AI AI(4) %	Al(5) + reactivi
<i>Rotary</i> M1000	35	50	15	65
<i>Flash</i> M1200S	25	55	20	75





Kiln type	AI-OH AI(6) %	AI=O AI(5) %	AI-O-AI AI(4) %	Al(5) + reactivi
<i>Rotary</i> M1000	35	50	15	65
<i>Flash</i> M1200S	25	55	20	75
<i>Vertical</i> MetaStar 501	24	49	27	76





### Christine Pélegris Axel Compere





Poly(sialate-siloxo) type K-PSS resin



# Pragmatic approach in designing a high-performance geopolymer ceramic in a 3D printed mould

# From theory to practice



# Reactivity test, observing exothermicity see: J. Davidovits, Geopolymer Chemistry and Applications, Chapter 8.









Christine Pélegris Nadine Ngoungoure Florient Rousseau



Ralph Davidovits

From theory to practice

# 2017 lab. studies Designing high-performance MK-750-based geopolymers. Poly(sialate-siloxo) type K-PSS binder



## State of the Geopolymer R&D 2017

I) Geopolymer science

# 2) Geopolymer technologies

3) Geopolymer Cements / Concretes

4) Geopolymer and archaeology

# Geopolymer Route to High-Temperature Ceramics See Chapter 23

#### Keynote Prof. W. Kriven

- Cesium geopolymers crystallize into pollucite CsAlSi<sub>2</sub>O<sub>6</sub> on heating to  $\sim$ 1050°C.

glass-ceramics.



MK-750 based Geopolymers can be converted to a high strength ceramic material on heating: Sodium geopolymers crystallize into nepheline NaAlSi2O6 on heating to 900°C-1100°C Potassium geopolymers crystallize into leucite KAISi2O6 on heating to 900°C-1200°C, These ceramic materials have unusual properties such as refractoriness (1693°C-1940°C), relatively low density and high fracture toughness. Their properties enable these geopolymer ceramics to be used as reinforcements in thermal barrier coatings or to increase toughness in

Cengiz Bagci,<sup>‡,§,†</sup> Gregory P. Kutyla,<sup>‡</sup> Kevin C. Seymour,<sup>‡</sup> and Waltraud M. Kriven<sup>‡</sup> <sup>‡</sup>Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801 <sup>§</sup>Department of Metallurgical and Materials Engineering, Faculty of Engineering, Hitit University, Corum 19030, Turkey

SEM micrographs of KGP-18C/ 2 h after being fired to 1500°C, in flowing argon, with needle-like morphology.

No extremely high temperature (e.g., 2500°C) needed as for the traditional process.



J. Am. Ceram. Soc., 1–10 (2016) DOI: 10.1111/jace.14254 © 2016 The American Ceramic Society

#### Synthesis and Characterization of Silicon Carbide Powders Converted from Metakaolin-Based Geopolymer





# Tuesday, July 11, 2017 Focused session: Geopolymer composites



## **3rd Virtual Journal on Geopolymer Science**

May 31 2016



The third issue of what will become the Virtual Journal on Geopolymer Science is online at

**Reinforced Geopolymer Composites** 

The Virtual Journal on Geopolymer Science is a collection of already published research



A critical review



NEWS JOURNAL ARTICLES WEBINARS COMMENT FEATURES PODCASTS PRODUCTS EVENTS JOBS JOURNALS ➢ POLYMERS HOME » POLYMERS AND SOFT MATERIALS » FEATURES » REINFORCED GEOPOLYMER COMPOSITES: A CRITICAL REVIEW

#### Reinforced Geopolymer Composites: A critical review

31 May 2016 | Joseph Davidovits

This critical review is the follow up of two feature articles titled **Geopolymers based on natural and** synthetic metakaolin, (on line on 17 January 2016) and Environmental implications of Geopolymers, (online on 20 June 2015). It has been written in compliance with a decision of Elsevier and Geopolymer Institute to join forces, distill and distribute the best research publications contained in their combined archives, through a series of Elsevier-Geopolymer Institute Virtual Special Issues on Geopolymer Science. On line 29 June 2015.

The invention of mineral geopolymers of the types poly(sialate) -Si-O-Al-O- (Si:Al=1), poly(sialate-siloxo) -Si-O-Al-O-Si-O- (Si:Al=2), poly(sialate-disiloxo) -Si-O-Al-O-Si-O-Si-O- (Si:Al=3), poly(sialate-multisiloxo) (Si:Al>>3) goes back to 1972, when, in the aftermath of various catastrophic fires in France causing hundreds of casualties in public buildings which involved common organic plastic, research on non-flammable and noncombustible plastic materials became our priority.

We founded a private research company in 1972, Cordi SA (called later Cordi-Géopolymère), to develop new inorganic fire-resistant polymer materials which we called «geopolymers» (mineral polymers resulting from geochemistry or geosynthesis). We knew that we would not reach fire resistance and zero toxicity with organic chemistry. When, ten years later, we started the development of a geopolymer matrix composite concept, the objective was to fabricate molding tools and patterns, to replace metal tooling for small production runs in the plastic processing industry and the foundry industry. The targeted working



carbon-fiber-composite



#### 31 May 2016

Figure 1a: K-poly(sialate-multisiloxo)-

#### **Features**

**Polymers and soft** materials Nanomaterials Surface science

#### metalpowder

A BEAR

You might also like...

#### 

#### Additive manufacturing of multidirectional preforms for composites: opportunities and challenges

Volume 18, Issue 9, Pages 503-512 | Zhenzhen Quan, Amanda Wu, Michael Keefe, Xiaohong Qin, Jianyong Yu, Jonghwan Suhr, Joon-Hyung Byun, Byung-Sun Kim, Tsu-Wei Chou

#### Comment now

JOURNAL

## **Geopolymer-fiber-composites:** heat and fire resistance









Time to Flashover, minutes

## "Geopolymer-based Composites"

Elsevier, Oxford, UK, in press (2017).



- Waltraud M. Kriven
- Materials Science and Engineering, University of Illinois at Urbana-Champaign, USA
- Vol. 5, Ceramics and Carbon Matrix Composites, edited by Marina Ruggles-Wrenn. Part of an 8 volume set of books entitled Comprehensive Composite Materials II, Peter Beaumont and Carl Zweben, Co-editors-in-chief. Published by

	Wt % Additions	Flexural strength (MPa)
93	8	52
	13	7.6 (7 % strain)
80	7	12.4
	30	20.5
	50	11.4
	5.5	31.55
	8.3	18.86
mboo dispersed	5	7.5
	10	7.50
	10	7.61



## State of the Geopolymer R&D 2017

### I) Geopolymer science

2) Geopolymer technologies

4) Geopolymer and archaeology

3) Geopolymer Cements / Concretes



## The Rise and Rise of Geopolymer **Concrete Researches Binds Us Together**

ASA / Blog / Research / The Rise and Rise of Geopolymer Concrete Researches Binds Us Together

The exponential rise in geopolymer research is capturing industry interest. Published research papers covering geopolymer concrete, such as different mixes, methods and example of how much focus is being placed upon much geopolymer research.

amount of research, technical and commercial papers being produced and published industry and the promotion with reduced CO2 benefits

### Australian Slag Association

Posted 10-04-2017 Category Research

- applications are challenging the conventional use of concrete. The association's involvement
- in the Cooperative Research Centre for Low Carbon Living research project is just one

  - As geopolymer concrete knowledge increases, so does its interest. The increasing
- supports this view. Geopolymer concrete is becoming more widely accepted within the





## My recommendations to the Slag industrie:

- we have the same problems with slag GGBS
  - as with metakaolin MK-750:
  - Each slag tested reacts diferently

### Australian Slag Association



### high increase **University Consortium Prepares for Spike in Decommissioning**

The Consortium for Decommissioning and Abandonment (CODA), a University of Texas at Austin is a response to the growing number of onshore and offshore wells, platforms and infrastructure that are approaching the end of economic viability and soon must be plugged and removed. Toward those ends, university researchers have developed several systems, including geopolymer cements .....

#### HOME TOPICS TECHNOLOGY





Tests of the newly designed cement also indicate significant self-healing properties. ...The system's designers are scheduled to present a paper (paper SPE 184675) on the geopolymer cement at the March SPE/IADC Drilling Conference in The Hague.

### SPE/IADC-184675-MS IADC Society of Petroleum Engineers True Self-Healing Geopolymer Cements for Improved Zonal Isolation and Well Abandonment

Xiangyu Liu, Matthew J. Ramos, Sriramya D. Nair, Hanna Lee, D. Nicolas Espinoza, and Eric van Oort, The University of Texas at Austin





#### (19) United States (12) Patent Application Publication (10) Pub. No.: US 2017/0144933 A1 May 25, 2017 Allouche et al. (43) **Pub. Date:**

- **GEOPOLYMER WITH NANOPARTICLE** (54)**RETARDANT AND METHOD**
- Applicant: Louisiana Tech Research (71)Corporation, Ruston, LA (US)

(57)

#### **Publication Classification**

(51)	Int. Cl.	
	C04B 28/00	(2006.01)
	C04B 40/06	(2006.01)
	C04B 14/06	(2006.01)
	COAD 11/07	2000 01

### ABSTRACT

A method of controlling the setting time of a geopolymer by coating aluminosilicate particles with nanoparticles to slow the geopolymerization reaction. The coating effectiveness of

[0039] Geopolymer paste samples 1A were prepared by premixing for approximately 30 seconds 20 grams of fly ash (e.g., Dolet Hills fly ash) with halloysite nanotubes in an amount that was 3% of the fly ash weight. The dry mixture



	Geopolymer Paste Control	Geopolymer Paste 1A (3% halloysite)	Geopolymer Paste 1B (6% halloysite)	Geopolymer Paste 2A (3% halloysite)	Geopolymer Paste 2B (6% halloysite)
Initial Setting Time	18 min. 24 sec	70 min 35 sec	175 min	47 min 55 sec	117 min
Final Setting Time	25 min 43 sec	85 min 45 sec	205 min	49 min 49 sec	147 min

Only valid for class C fly ashes

[0039] Geopolymer paste samples 1A were prepared by premixing for approximately 30 seconds 20 grams of fly ash (e.g., Dolet Hills fly ash) with halloysite nanotubes in an amount that was 3% of the fly ash weight. The dry mixture

### TABLE 3

# Last words on AAM alkali-activated materials

Geopolymer cement

VS

## Portland Cement



## Portland Cement



#### K-oligo(sialate-siloxo)



**Polycondensation** 

## Geopolymer is a **Polymer Chemistry** (poly-sialate)

K-poly(sialate-siloxo)

Si

O-Si-O-Al-O-Si-O-

K+

U,

b)



## **Portland cement** CaO.SiO<sub>2</sub>.H<sub>2</sub>O Calcium Silicate Hydrate C-S-H

- Alkali-activated-materials scientists
  - substitution of Ca with Na, K
    - Geopolymer
- Na2O.Al2O3.2SiO2.H2O Sodium-Alumino-Silicate-Hydrate
  - N-A-S-H
- K2O.Al2O3.2SiO2.H2O Potassium-Alumino-Silicate-Hydrate
  - K-A-S-H

# According to AAM specialists from RILEM "GEOPOLYMER" is a type of

- alkali-alumina-HYDRATE, a precipitate,
  - N-A-S-H, K-A-S-H
    - Nothing else !!!
      - WRONG





 $AIQ_4(4Si)$ 

SiQ<sub>4</sub>(2Al)

### (12) United States Patent Skorina et al.

(54) ALKALI METAL ION SOURCE WITH MODERATE RATE OF ION RELEASE AND METHODS OF FORMING

There is a growing need for alternative sources of alkali metals, such as, but not limited to, potassium ... (traditional potassium fertilizing agent) .... making local manufacturing of potassium fertilizer increasingly attractive....

Therefore, a need exists to produce a source of potassium ion that releases the

nutrient (K cation) at a moderate rate, lower than the infinite dissolution rate of a traditional salts, but faster than the rate generally exhibited by naturally-

of a traditional salts, but faster than the occurring minerals.

# (10) Patent No.: US 9,340,465 B2 (45) Date of Patent: May 17, 2016

(56) References Cited

U.S. PATENT DOCUMENTS


### **U.S. Patent**

<u>Claim</u>: ... The method wherein the weight percent of K(Na)-A-S-H gel of the alkali metal ion source is between about 10% and about 100%.

<u>Applicant:</u> Massachusetts Institute of Technology M.I.T., Cambridge, Boston. Sheet 6 of 9

US 9,340,465 B2



## N-A-S-H Sodium Aluminosilicate Hydrate Alkali-Activated Materials





## Poly(sialate-siloxo) geopolymer ceramic



## Poly(sialate-siloxo) geopolymer concrete



### Global Change Institute, Univ. Queensland, Brisbane, Australia

### Toowoomba-Brisbane-West Wellcamp Airport, by WAGNERS, Australia October 2015



### 100,000 tonnes Slag/fly ash-based geopolymer concrete EFC (Earth Friendly **Concrete**)





### State of the Geopolymer R&D 2017

I) Geopolymer science

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## 4) Geopolymer and archaeology



## Tuesday, July 11, 2017

## Third session: Geopolymer and archaeology

Ancient Roman concrete (100 BC): rapid setting

### 11th International Congress of Egyptologists, Florence, Italy, 23-30 August, 2015



## Non-destructive analysis on 11 Egyptian blue faience tiles from the 2nd and 3rd Dynasties. (accepted for publication in the Proceedings)

Frédéric Davidovits





www.geopolymer.org

Joseph Davidovits Ralph Davidovits

ШП MASSACHUSETTS INSTITUTE OF TECHNOLOGY



DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

#### October 4, 2016

### Non-destructive analysis on 11 Egyptian blue faience tiles from the 2nd and 3rd Dynasties (2650 BC).





Zoser Step Pyramid Saqqarah 3rd Dynasty 2700 BC

35,000 faience tiles in subterranean galleries





efflorescence self-glazing process: migration of alkali salts and CuO then firing at 800-850°C turquoise-blue glaze



### Why Djoser's blue Egyptian faience tiles are not blue?

### Manufacturing Djoser's faience tiles at temperatures as low as 250°C?

Joseph Davidovits Institut Géopolymère, 02100 Saint-Quentin, France

**Ralph Davidovits** Cordi-Géopolymère SA Laboratoire de Recherche sur les Nouveaux Matériaux 02100 Saint-Quentin

#### To replicate the self-glazing process with soluble silicate SiO2,K2O,Na2O + synthetic turquoise (mafkat): aluminium phosphate hydrate + copper phosphate hydrate



at 250°C.

Lucien Viola, Galerie l'Ibis, Marrakech

Thermoluminescence analysis for datation: ceramics that are fired at  $t^{\circ} > 500^{\circ}C$ 

**RESULT:** It is not possible to issue a result for this piece as the sample is too low-fired and lacks radioactive inclusions. We are therefore unable to complete our analysis and draw any conclusions regarding its age.





#### OXFORD AUTHENTICATION Ltd

**Boston House** Grove Technology Park Oxfordshire OX12 9FF

#### Sample No: N109p38

#### THERMOLUMINESCENCE ANALYSIS REPORT

The object was presumed to be: A turquoise faience tablet

The following samples were taken in powder form on: 24 October 2009 Helen Mason of Oxford Authentication Ltd

Sample A: Into break on side

**Result:** 

It is not possible to issue a result for this piece as the sample is too low-fired and lacks radioactive inclusions. We are therefore unable to complete our analysis and draw any conclusions regarding its age.

oneham for Oxford Authentication Ltd

cation takes no responsibility for financial loss incurred

ere obtained. If the object has suffered restoration the

different from the date of manufacture if the object has

ve not been exposed to ionising radiation. vill be that of the original firing and not the date of re-











	13. 1000	
ement	Wt%	At%
Si	59,93	68,63
Cu	20,21	10,23
Mg	5,64	7,46
Ca	4,31	3,46
A1	2,19	2,61
Na	1,84	2,57
C1	4,43	4,02
S	0,45	0,45
Fe	1,00	0,58
otal	100,00	100,00

 $Cu_2Cl(OH)_3$ (Mg,Ca)CuSi\_4O\_{10} Atacamite **Egyptian Blue** 







### Glaze











## white body

Name Det WD - 100-um

Ser -	Element #	Wt% ¤	At
1 Been	Ca ¤	1,90 ¤	1,4
	Cu ¤	7,69 ¤	3,:
- Frid	Si ¤	82,27 ¤	86,
AST A	Cl ¤	2,53 ¤	2,
	Κ¤	1,08 ¤	0,8
Carl -	Mg¤	1,86 ¤	2,2
	Na ¤	1,66 ¤	2,
	Al ¤	1,01 ¤	1,
	Total ¤	100,00 ¤	100





, Magn Det WD μ 250x BSE 91 For















Element <b>#</b>	Wt% I	At% "
Si ¤	34,60 =	43,81 =
Mg ¤	7,13 ¤	10,43 =
Cu ¤	34,43 =	19,27 =
Cl ¤	15,20 ¤	15,24 ¤
Ca ¤	3,21 "	2,84 "
Na ¤	5,43 ¤	8,40 =
Total ¤	100,00 ¤	100,00 ¤





### low-temperature foam < 250°C





	Element ¤	Wt% ¤	At
	Si ¤	69,02 ¤	77,
	Mg ¤	5,94 ¤	7,6
	Cu ¤	18,45 =	9,1
	Cl ¤	<b>4,09 ¤</b>	3,6
	Ca ¤	2,03 ¤	1,6
	Na ¤	0,28 ¤	0,3
	K¤	0,19 ¤	0,1
	Total ¤	100,00 ¤	100
	3		
ont 200 am			



## CONCLUSIONS

- Production of 30.000 tiles feasible in open garden fire at low temperature <250°C.
- The "glaze" is a coating comprising 3 successive layers:
  - 1) efflorescence (low-temperature self glazing);
  - 2) <u>either a white calcium sulfate or/and calcium phosphate or</u>
    - green Na-paratacamite Cu<sub>2</sub>Cl(OH)<sub>3</sub>;
  - 3) blue low-temperature "geopolymer enamel" (the only shiny external layer) with blue paratacamite  $Cu_2Cl(OH)_3$ .



### 2017 **GEOPOLYMERCAMP**



## Joseph Davidovits Geopolymer Institute www.geopolymer.org

# State of the Geopolymer R&D

2017