

Joseph DAVIDOVITS

GEOPOLYMER

Chemistry & Applications

5th edition



Geopolymer Chemistry and Applications

5th edition

Joseph DAVIDOVITS

©2008, 2011, 2015, 2020 Joseph DAVIDOVITS

ISBN: 9782954453118

5th edition, March 2020.

Published by:

Institut Géopolymère

16 rue Galilée

F-02100 Saint-Quentin

France

Web: www.geopolymer.org

Written and edited by:

Joseph DAVIDOVITS

Web: www.davidovits.info

All Rights Reserved. No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopy, recording or any other information storage and retrieval system, without prior permission in writing from the publisher.

Tous Droits Réservés. Aucune partie de cette publication ne peut être reproduite sous aucune forme ou par aucun moyen, électronique ou mécanique, incluant la photocopie, l'enregistrement ou par système de stockage d'informations ou de sauvegarde, sans la permission écrite préalable de l'éditeur.

About the author



Professor Joseph Davidovits.

Professor Joseph Davidovits is famous for his pioneering work on geopolymers. He is an internationally renowned French materials scientist and archeologist, who was honored by French president Jacques Chirac with one of France's two highest awards, the Chevalier de l'Ordre National du Mérite, in November 1998. Born in 1935, he has a French Degree in chemical engineering and a German Doctorate Degree (PhD) in chemistry, was professor and founder of the Institute for Applied Archaeological Sciences at Barry university, Miami, Florida (1983-1989), Visiting professor at Penn State university, Pennsylvania (1989-1991) and Director of the Geopolymer Institute, Saint-Quentin, France (1979-present). He is a world expert in low-temperature geosynthesis as well as in archaeological science. He is the inventor in 1979 of geopolymers and the chemistry of geopolymerization. He has authored/co-authored hundreds scientific papers, reports, and dozen of books, holds more than 50 patents and has written in 2008 the reference book *Geopolymer Chemistry and Applications*, 5th edition issued in 2020. Since 2009, he is the Chairman of the annual international gathering: Geopolymer Camp.

Contents

I	Polymers and Geopolymers	1
1	Introduction	3
1.1	Historical background	6
1.1.1	The invention of the first mineral resin, October 1975	8
1.2	The scope of the book	12
1.3	Early observations	13
1.4	Phosphate-based geopolymer	15
1.4.1	Phosphate geopolymers	16
1.4.2	High-molecular phosphate-based geopolymers: cristobalitic AlPO_4	17
1.5	Organo-mineral geopolymers	17
1.5.1	Silicone	17
1.5.2	Hybrid organo-mineral geopolymers	18
1.5.3	Humic-acid based: kerogen geopolymer	18
2	The mineral polymer concept: silicones and geopolymers	23
2.1	The polymeric character of silicones	24
2.2	The dispute over ionic or covalent bonding in silicates	25
2.3	Covalent bonding in alumino-silicates / silico-aluminates	30
2.4	Tetra-coordinated Al or tetra-valent Al?	31
2.5	Terminology	32
2.5.1	Poly(siloxo) / poly(siloxonate) / poly(silanol)	32
2.5.2	Poly(sialate)	32
2.5.3	Poly(ferro-sialate)	37
2.6	Polymeric character of geopolymers: geopolymeric micelle	37
3	Macromolecular structure of natural silicates and alumino-silicates	41
3.1	Silicate ionic and covalent structural representations	42
3.2	Ortho-silicate, $1[\text{SiO}_4]$, ortho-siloxonate, Zircon ZrSiO_4	44
3.3	Di-silicate, di-siloxonate, Epidote	44
3.4	Tri-silicate, tri-siloxonate, ring silicate, Benitoite	45
3.5	Tetra-silicate, $4[\text{SiO}_4]$, ring silicate $[\text{Si}_4\text{O}_{12}]$	45
3.6	Hexa-silicate, hexa-siloxonate, ring silicate, Beryl	46
3.7	Linear poly-silicate, poly(siloxonate), chain silicate, Pyroxene, Wollastonite	46

3.8	Branched poly-silicate, poly(siloxonate), ribbon structure, Amphibole $[\text{Si}_4\text{O}_{11}]_n$	48
3.9	Sheet silicate, $[\text{Si}_2\text{O}_5]_n$, 2D-poly(siloxo), composite sheet	50
3.9.1	Kaolinite, poly(siloxo-aluminumhydroxyl)	50
3.9.2	Pyrophyllite $\text{Al}_4(\text{OH})_4[\text{Si}_8\text{O}_{20}]$, poly(siloxo-intra-sialate)	51
3.9.3	Muscovite $\text{K}_2\text{Al}_4[\text{Si}_6\text{Al}_2\text{O}_{20}](\text{OH})_4$, poly(siloxo-intra-sialate)	52
3.10	Other sheet silicates, Melilite, Gehlenite, Akermanite, pentagonal arrangement.	52
3.11	Framework silicate, Quartz, Tridymite, SiO_2	54
3.11.1	Structure of Quartz	54
3.11.2	Structure of Tridymite	55
3.12	Framework silicate, Nepheline $\text{Na}[\text{AlSiO}_4]$ and Kalsilite $\text{K}[\text{AlSiO}_4]$	55
3.13	Framework silicate, Leucite $\text{K}[\text{AlSi}_2\text{O}_6]$	56
3.14	Framework silicate, Feldspar double-crankshaft chain $[(\text{Si},\text{Al})_4\text{O}_8]_n$	57
3.14.1	Anorthite $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$	57
3.14.2	Sanidine $\text{K}[\text{AlSi}_3\text{O}_8]$	58
3.15	Framework silicate, Feldspathoid, Sodalite $\text{Na}[\text{AlSiO}_4]$	58
3.16	Framework silicate, zeolite group	59

II The synthesis of alumino-silicate mineral geopolymers 63

4	Scientific Tools, X-rays, FTIR, NMR	65
4.1	X-ray diffraction	65
4.2	FTIR, infra-red spectroscopy	68
4.3	MAS-NMR spectroscopy	72
4.3.1	^{27}Al MAS-NMR spectroscopy	72
4.3.2	^{29}Si MAS-NMR Spectroscopy	75
5	Poly(siloxonate) and polysilicate, soluble silicate, Si:Al=1:0	81
5.1	History of soluble silicates	81
5.2	Chemical composition of soluble silicates	83
5.3	Manufacture of soluble (Na,K)-poly(siloxonate), soluble silicates	84
5.3.1	Chemical mechanism	84
5.3.2	Furnace route	86
5.3.3	Hydrothermal process	89
5.3.4	Silica fume dissolution	89
5.4	Structure of solid poly(siloxonate), (Na,K)-silicate glasses	89
5.4.1	Molecular structure of poly(siloxonate), alkali silicate glasses	91
5.4.2	Molecular structure of poly(siloxonate), alkali-tridymite glasses	93
5.5	Poly(siloxonate) in solution. Hydrolysis, depolymerization of solid silicates	99
5.6	Structure of poly(siloxonate) solutions, soluble alkali silicates	100
5.6.1	Early studies	100
5.6.2	NMR spectroscopy: identification of soluble species	101

5.6.3	Hydrolysis of poly(siloxonate) alkali-glass into water soluble molecules	103
5.6.4	Hydrolysis of silica fume into water soluble molecules	107
5.7	Density, specific gravity	108
5.8	Viscosity	109
5.9	pH value and stability of alkali silicate solutions	110
5.10	Powdered poly(siloxonates), soluble hydrous alkali silicate powders	110
5.11	Poly(siloxonate) MR=1, Na-metasilicate	112
5.12	Replacement of poly(siloxonate) solution with powdered equivalent product.	113
6	(Na,K)–oligo-sialates: hydrous alumino-silicate gels and zeolites	117
6.1	Zeolite Synthesis	117
6.2	Hypothetical or real oligo-sialates: polymerization mechanism into poly(sialate)	121
6.3	Examples of poly(sialate-multisiloxo) gels	124
6.3.1	Poly(sialate-disiloxo) gel	124
6.3.2	Poly(siloxonate-intra-sialate) gels	126
7	Kaolinite / Hydrosodalite based geopolymer, poly(sialate) with Si:Al=1:1	131
7.1	Geopolymerization mechanism of kaolinite under ionic concept.	132
7.2	Ultra rapid in situ geopolymerization of kaolinite in hydrosodalite	136
7.3	Geopolymerization mechanism of kaolinite under covalent bonding concept	141
7.4	Hydrosodalite Na–poly(sialate) and Zeolite A formation with calcined kaolin	145
8	Metakaolin MK-750 based geopolymer, poly(sialate-siloxo) with Si:Al=2:1	151
8.1	(Na,K)–poly(sialate-siloxo)	151
8.2	Alumino-silicate oxide: dehydroxylated kaolinite, MK-750	158
8.2.1	Characteristic of kaolinite and dehydroxylated kaolinite	160
8.2.2	IV-fold coordination of Al in dehydroxylated kaolinite, earlier studies.	161
8.2.3	MAS-NMR spectroscopy of dehydroxylated kaolinite	162
8.2.4	Dehydroxylation mechanism of kaolinite	166
8.2.5	Reactivity of MK-750, geopolymerization into (Na,K)–poly(sialate-siloxo)	170
8.2.6	Exothermic geopolymerization	172
8.2.7	Geopolymerization into fully condensed poly(sialate-siloxo) requires Al(V) + Al(IV) + Al(VI) species	175
8.2.8	Geopolymerization of poly(sialate-siloxo), function of SiO ₂ :M ₂ O MR ratio	179
8.2.9	Geopolymerization of poly(sialate-siloxo), function of curing temperature	180
8.3	Chemical mechanism: formation of ortho-sialate (OH) ₃ -Si-O-Al-(OH) ₃	181
8.3.1	Chemical mechanism with Al(V) -Al=O alumoxyl.	181

8.3.2	Chemical mechanism in Al-O-Al-OH geopolymerization .	182
8.4	Kinetics of chemical attack	183
8.5	Chemical mechanism for Na-based sialate: Si:Al=1, Si:Al=2 and Si:Al=3	185
8.5.1	Phase 1: outer faces/edges reaction; Albite framework with Q ₁ di-siloxonate, Si:Al=3, Na-poly(sialate-disiloxo)	186
8.5.2	Phase 2: inner particulate reaction; Nepheline framework Si:Al=1, Na-poly(sialate)	187
8.5.3	Phillipsite framework with Q ₀ siloxonate, Si:Al=2, Na-poly(sialate-siloxo)	188
8.5.4	To sum up	190
8.6	Chemical mechanism for K-based sialate: Si:Al=1, Si:Al=2 . . .	190
8.6.1	Kalsilite framework, Si:Al=1, K-poly(sialate)	193
8.6.2	Leucite framework with Q ₀ siloxonate, Si:Al=2, K-poly(sialate-siloxo)	195
8.7	Simplified structural model for (Na,K)-based geopolymers	197
8.8	Al-O-Al bond formation in geopolymers	200
8.9	Synthesis of MK-750 type molecules	202
9	Calcium based geopolymer, (Ca, K, Na)-sialate, Si:Al=1, 2, 3	209
9.1	Ca-poly(alumino-sialate), gehlenite hydrate Ca ₂ Al ₂ SiO ₇ , H ₂ O . .	209
9.1.1	Opus Signinum	209
9.1.2	Ca-poly(alumino-sialate), gehlenite synthesis with MK-750	210
9.2	(Ca)-poly(alumino-sialate) + (Na,K)-poly(sialate)	213
9.3	Ca-poly(alumino-sialate), gehlenite based blast furnace slag . . .	215
9.3.1	The manufacture of iron blast furnace slag glass	216
9.3.2	Chemical and mineral composition of gehlenite based slag.217	
9.4	Alkalinization of Ca-poly(alumino-sialate) glassy slag with NaOH and KOH	219
9.4.1	Alkalinization mechanism study with MAS-NMR spectroscopy	219
9.4.2	Alkali-Activated slag	223
9.5	MK-750 / slag based geopolymer	224
9.5.1	Excerpt from Davidovits J. / Sawyer J.L. US Patent 4,509,985, 1985, filed February 22, 1984	224
9.5.2	Which chemical reaction for MK-750 / slag-based geopolymer?	230
9.5.3	Formation of soluble calcium disilicate?	231
9.6	Chemistry mechanism of MK-750 / slag Ca-based geopolymer matrix	239
9.6.1	MAS-NMR Spectroscopy	239
9.6.2	Electron microscopy	242
9.6.3	Chemistry mechanism, solid solution in Ca-based geopolymer matrix	244
9.6.4	Structural molecular model for Ca-based geopolymer matrix	246
10	Rock-based geopolymer, poly(sialate-multisiloxo) 1<Si:Al<5	253

10.1	Alkalinization and dissolution of rock forming minerals	254
10.1.1	Congruent dissolution and ionic bonding concept	255
10.1.2	Incongruent dissolution and covalent bonding concept	255
10.2	(Na,K)–poly(sialate) matrix for rock based geopolymerization	258
10.3	(K,Ca)–poly(sialate-multisiloxo) matrix for rock-based geopolymers.	262
11	Ferro-sialate geopolymers, (-Fe-O-Si-O-Al-O-)	271
11.1	A 1400 years old technique in Pre-Columbian South-America	272
11.2	Ferro-sialate geopolymer binder	274
11.3	Controversial role of iron in geopolymerization	283
11.4	Ferro-kaolinite: substitution of Al^{3+} with Fe^{3+}	284
11.5	Analytical method: Mössbauer spectroscopy	285
12	Silica-based geopolymer, sialate and siloxo link in poly(siloxonate)	
	Si:Al>5	291
12.1	A 5000 year-old technique	291
12.2	Silica Flour	295
12.3	Nano-silica, micro-silica, silica fume SiO_2	295
12.3.1	Fume silica SiO_2	296
12.3.2	Silica Fume / Microsilica	296
12.4	Rice Husk Ash	298
12.5	Applications of SiO_2 nano-particles and rice husk ash	299
12.6	Poly(siloxo) and poly(sialate) cross-links, nanocomposite geopolymer	300
12.6.1	Nano-poly(siloxo) geopolymer	301
12.6.2	^{29}Si MAS-NMR studies on the transition nano-poly(silanol) to nano-poly(siloxo)	303
12.6.3	1H MAS-NMR studies	304
12.6.4	K–nano–poly(sialate) geopolymer composite	307
12.7	Possible health hazards of SiO_2 nanoparticles	308
13	Fly ash-based geopolymer	311
13.1	Production of fly ashes	312
13.1.1	Types of fly ash, composition	313
13.1.2	Morphology	315
13.2	Alkalinization, dissolution and zeolite formation	316
13.3	Fly ash cement in high alkaline milieu (corrosive system)	317
13.3.1	First production of fly ash-based cement	317
13.3.2	Fly ash cement without soluble silicate?	320
13.3.3	Fly ash geopolymerization with addition of soluble silicate.	322
13.4	Geopolymerization in low alkaline milieu (user-friendly)	324
13.4.1	NMR spectroscopy	325
13.5	The GEOASH research project	327
13.5.1	Alkali-activation and geopolymerization	329
13.5.2	Compressive strength	331
13.5.3	Reaction mechanism	334
13.5.4	Leaching properties	336

13.5.5	(Ca,K)-based geopolymer matrix: composition and structure	336
13.6	The future with gasifier slag technology	338
14	Phosphate-based geopolymers	343
14.1	A 4500 year-old Egyptian technology!	343
14.2	Brief survey of phosphate chemistry	345
14.2.1	Ortho-, di-, tri- and poly-phosphoric acid	345
14.2.2	Polyphosphate linear chains	346
14.3	Low-molecular phosphate-based geopolymers	348
14.4	Poly(sialate-siloxo) / phosphate composites	350
14.5	Phospho-siloxonate geopolymer, -Si-O-P-O-Si-	351
14.5.1	Ca-phospho-silicate	352
14.6	AlPO ₄ -based geopolymers	356
14.6.1	Polymeric structures of AlPO ₄ -geopolymers: ²⁷ Al and ³¹ P NMR.	356
14.6.2	Synthesis of AlPO ₄ -geopolymers: the solution and sol-gel routes	358
14.6.3	Synthesis of AlPO ₄ -geopolymers: the modified Al ₂ O ₃ routes	360
14.6.4	MK-750 metakaolin-based AlPO ₄ -geopolymer	361
15	Organic-mineral geopolymer	369
15.1	Poly-organo-siloxanes / silicones	369
15.1.1	Geopolymeric identity	369
15.1.2	Two polymerization mechanisms: acidic and basic	370
15.1.3	Depolymerization and cleavage	372
15.1.4	Properties of technical silicones	372
15.2	Kerogen-geopolymer	375
15.3	Organo-geopolymer compounds	377
15.3.1	Inclusion of hydrophilic polymers, poly(ethylene glycol)	377
15.3.2	Reaction with isocyanate R-N=C=O	379
15.3.3	Reaction with poly(acrylic acid) R-C(=O)-OH	380
15.3.4	Reaction with aqueous phenolic resin and poly(styrene butadiene) latex	380
15.3.5	Reaction with hydrophobic polymers: epoxy, phenolic, silicone	382
III	Properties	385
16	Physical properties of condensed geopolymers	387
16.1	Density and softening temperature	387
16.2	Thermal behavior, shrinkage on dehydroxylation	388
16.2.1	DTA-TGA and Shrinkage on dehydration and dehydroxylation	388
16.2.2	Yield of the conversion of kaolinite into Na-poly(sialate) Na-PS	391

16.3	Thermal Expansion C.T.E.	393
16.3.1	C.T.E. Coefficient of Thermal Expansion	393
16.3.2	Mean linear thermal expansion, the major role of ceramic fillers	394
16.4	Water and moisture absorption	396
16.5	Electrical values: resistivity and dielectric properties	397
16.6	Adhesion	399
16.6.1	Adhesion on natural stone; geopolymer with Si:Al=2	400
16.6.2	Adhesion on steel, aluminum and glass, Geopolymer with Si:Al=2	400
16.6.3	Adhesion on metal, Geopolymer with Si:Al>20	402
16.7	Practical physical properties	403
17	Chemical Properties of condensed geopolymers	407
17.1	Acid resistance	409
17.1.1	Influence of acid on incompletely condensed Na-poly(sialate-siloxo)	410
17.1.2	Acid resistance of geopolymer cement towards sulfuric acid	412
17.1.3	Sulfate resistance of geopolymer cement	415
17.2	Alkali-aggregate reaction	415
17.3	Corrosion of metal bars	417
17.4	Practical chemical properties	417
17.4.1	pH values	417
17.4.2	(K,Ca)-poly(sialate-siloxo) and (K,Ca)-poly(sialate-disiloxo) cements:	418
18	Long-term durability, archaeological analogues, geological analogues	421
18.1	The oldest geopolymer artifact: 25,000 year-old ceramic Venus from Dolní Věstonice	422
18.2	Chemicals extracted from plant ashes	423
18.3	Egyptian Pyramid stone, re-agglomerated limestone concrete, 2700 B.C.	424
18.3.1	Chemistry of the core blocks	427
18.3.2	Chemistry of the casing stones	428
18.3.3	The experimentation: manufacturing 14 tonnes of pyramid stones	429
18.4	Ancient Roman cements and concretes	430
18.4.1	Cements and concretes	431
18.4.2	The first high-performance Roman cement, with Opus Signinum.	432
18.4.3	The second high-performance Roman cement, with Carbunculus.	433
18.4.4	Comparison between Roman and modern geopolymer cements	433
18.5	Ferro-sialate geopolymer sandstone concrete found in pre-Columbian monuments at Pumapunku / Tiwanaku, Bolivia.	439
18.6	Geological analogues	442

IV Applications	445
19 Quality control	449
19.1 Raw-materials	449
19.1.1 Solid elemental composition	449
19.1.2 pH determination of the raw-materials	451
19.1.3 Granulometry	453
19.2 Determination of the geopolymeric reactivity	454
19.3 Fluidity and Viscosity of metakaolins MK-750 in K-Silicate solution.	456
19.4 Reactivity and Exothermicity of metakaolins MK-750: standardized method.	457
19.4.1 Exothermic reactivity in isothermal conditions	458
19.4.2 Exothermic reactivity: Cumulative exothermal heat flow in non-isothermal conditions.	459
19.5 Working time (pot-life), resin and paste	462
19.5.1 Working time (pot-life)	463
19.5.2 Role of additional water	464
19.5.3 Control on the hardening paste: penetrometer	465
19.5.4 Plasticizers and retarders	466
19.6 Compressive strength and tensile strength	467
19.6.1 Compressive strength	467
19.6.2 Tensile strength	470
19.7 Additional fast testing on hardened geopolymers	470
19.7.1 Boiling water / steam	470
19.7.2 Freeze-Thaw / Wet-Dry	471
19.7.3 Thermal behavior, expansion at 250°C, thermal dilatometry	472
20 Development of user-friendly systems	475
20.1 Definitions	475
20.2 The need for user-friendly systems	476
20.3 The position of civil engineers	478
20.4 The pH values of geopolymers	480
20.5 K ⁺ versus Na ⁺	481
21 How to quantify and develop geopolymer formulas	485
21.1 Detailed knowledge of the raw material composition and structure	486
21.1.1 (K,Na)-silicate solutions	487
21.1.2 Metakaolin MK-750	489
21.2 How to calculate a formula	490
21.2.1 Mathematical equation for calculating the molar ratio Na, K:Al=1	491
21.2.2 Three geopolymer formulas	492
21.3 The strict implementation of a process method for optimal results	495
21.3.1 Respecting the mixing order	496
21.3.2 Always make the binder first	497
21.3.3 Finding the right filler	498
21.3.4 Curing and hardening	499

21.3.5	Final chemical testing	500
22	Castable geopolymer, industrial and decorative applications	501
22.1	The 5000 year-old Egyptian stone vases	501
22.2	K-poly(sialate-siloxo) for castable artifacts.	505
22.3	Tooling materials and techniques	510
22.3.1	Advanced geopolymer tooling	510
22.3.2	Instruction for use	511
22.4	Modern geopolymer stone artifacts	513
22.5	Decorative stone tiles for floor and wall	515
22.6	Restoration of ceramic works of art	516
23	Geopolymer – fiber composites	519
23.1	Fundamental remarks on heat and fire resistance	520
23.1.1	Heat resistance applications in racing cars	521
23.1.2	Review of carbon/geopolymer and other ceramic-ceramic composites	522
23.2	The development of high performance geopolymer matrices	524
23.2.1	K-poly(sialate) K-PS/K-PSS matrix	525
23.2.2	Improvement of the matrices: K-PSDS, F,M-PSDS and K-nano-PSS	527
23.2.3	Improvement with high-temperature post-treatment of the matrices K-PS / K-PSS	529
23.3	Principles in geopolymer-composite manufacture	530
23.3.1	Hand lay-up	531
23.3.2	Vacuum bagging	531
23.3.3	Filament winding	532
23.3.4	Resin Transfer Molding, RTM (injection molding)	532
23.3.5	Infusion (infiltration) process	532
23.3.6	Autoclave curing	533
23.4	Geopolymer-composite tools fabrication	534
23.5	Fire resistance with K-nano-poly(sialate) laminates	535
23.5.1	Fabrication of K-nano-poly(sialate) carbon composite for fire-resistance testing	537
23.5.2	Flammability of organic and geopolymer composites	538
23.5.3	Flashover temperature	539
23.5.4	Residual strength after fire exposure	540
23.6	Fatigue loading of K-nano-poly(sialate) / carbon composite	541
23.7	K-nano-poly(sialate) / carbon / E-glass composite	542
23.8	Geopolymer composite sandwiches for heat barrier	543
23.9	Geopolymer composite for strengthening concrete structures	544
23.10	Geopolymer composite for fire resistant structural elements	547
24	Foamed geopolymer	553
24.1	Geopolymer foam fabrication	554
24.1.1	Foaming with Na perborate	554
24.1.2	Foaming with H ₂ O ₂	555
24.1.3	Insulating value of geopolymer foam	556
24.2	High-temperature insulation	557

24.3	Passive cooling of buildings in hot / arid climate	558
24.4	Passive Cooling in big cities	560
25	Geopolymers in ceramic processing	563
25.1	Low Temperature Geopolymeric Setting of ceramic, LTGS	563
25.1.1	Geopolymeric setting at room temperature below 65°C .	564
25.1.2	Geopolymeric setting at temperatures ranging between 80°C and 450°C	566
25.1.3	Resistance to water	566
25.2	Archaeological ceramics	566
25.2.1	Evidence of LTGS in ancient ceramics	567
25.2.2	The making of Etruscan Ceramic (Bucchero Nero) in 600–700 B.C.	569
25.2.3	The making of Ceramic with black or brown-black finish in a wood campfire, at temperature lower than 500°C . .	571
25.2.4	User-friendly LTGS	572
25.3	Low-energy modern ceramic processing and sustainable develop- ment	574
25.4	The making of foamed clay bricks	578
25.5	Ceramics with no clay?	579
25.6	The geopolymer route to high-temperature ceramics	580
25.6.1	High-tech Leucite and Kalsilite from geopolymer pre- cursors	580
25.6.2	High-tech Pollucite, β -Spodumene, Liebenbergite from geopolymer precursors	582
25.6.3	Gallium-, Germanium-based geopolymers	583
25.6.4	Rock wool fiber manufacture	585
26	The manufacture of geopolymer cements	589
26.1	Room temperature hardening geopolymer cements	589
26.1.1	Portland cement chemistry vs Geopolymer cement chem- istry	590
26.1.2	Geopolymer cement is not alkali-activated cement	591
26.2	Geopolymer cement categories	593
26.2.1	Slag-based geopolymer cement	593
26.2.2	Rock-based geopolymer cement	594
26.2.3	Ferro-sialate-based geopolymer cement	594
26.2.4	Slag/fly ash-based geopolymer cement	594
26.3	Greenhouse CO ₂ mitigation fosters the development of geopoly- mer cements	595
26.3.1	Cement CO ₂ emissions in developing countries	596
26.3.2	Comparison between CaO, Na ₂ O and K ₂ O cementitious systems	598
26.3.3	Examples of energy needs and low-CO ₂ mitigation with geopolymer cements	600
26.3.4	Geopolymer cement for CO ₂ storage and sequestration .	603
26.4	Additional Raw-Materials from industrial wastes	604
26.4.1	Muscovite based mine tailings	604
26.4.2	Kaolinitic shale wastes	605

26.4.3	Coal-waste mine tailings	605
26.4.4	Coal honeycomb briquette ash	606
26.4.5	Public water reservoir sludge	607
26.4.6	Ferronickel slag	608
26.5	The need for dry mix geopolymer cement	609
26.5.1	The use of solid silica + solid alkalis	609
26.5.2	Manufacture of powdered K-silicate with MR $\text{SiO}_2:\text{K}_2\text{O}$ < 2	610
26.5.3	Not realistic for mass production of geopolymer cements	611
26.6	Replacement of (Na,K) soluble silicates with synthetic lavas . . .	611
26.6.1	The manufacture of synthetic lavas	612
26.6.2	Molecular structure of synthetic lava	615
26.6.3	The molecular structure of lava-based geopolymer cement	617
26.6.4	Geopolymer cement mass production with synthetic lava?	618
27	Geopolymer concrete	623
27.1	Heat-cured fly ash-based geopolymer concrete	625
27.1.1	Mixing, casting, and compaction of heat-cured fly ash- based geopolymer concrete	627
27.1.2	Heat-curing of fly ash-based geopolymer concrete	628
27.1.3	Design of heat-cured fly ash-based geopolymer concrete mixtures	630
27.2	Ambient-cured slag/fly ash-based geopolymer concrete	631
27.2.1	Design of ambient-cured slag/fly ash-based geopolymer concrete mixtures	632
27.2.2	Heat of reaction, temperature rise during hardening . . .	634
27.2.3	Drying Shrinkage	634
27.3	Short-term properties of fly ash-based geopolymer concrete . . .	636
27.3.1	Behavior in compression	636
27.3.2	Compressive strength of aggregates weaker than geopo- lymer matrix	637
27.3.3	Indirect tensile strength	638
27.3.4	Unit-weight	639
27.4	Long-term properties of fly ash-based geopolymer concrete	639
27.4.1	Compressive strength	639
27.4.2	Creep and drying shrinkage	641
27.5	Reinforced geopolymer concrete beams and columns, heat cured .	643
27.6	Better than Portland cement concrete?	646
28	Geopolymers in toxic waste management	651
28.1	Containment with barriers	654
28.2	Waste encapsulation requires MK-750-based geopolymers	655
28.2.1	Structural model for safe encapsulation	655
28.2.2	Safe chemical bonding with MK-750-based geopolymers	656
28.3	Heavy metals in mine tailings	657
28.3.1	Solidification procedure	658
28.3.2	Leachate testing	658
28.4	The use of geopolymers for paint sludge disposal	660
28.4.1	Experimental	661

28.4.2	Results	662
28.5	Treatment of arsenic-bearing wastes	663
28.5.1	Nature of the Problem	663
28.5.2	Geopolymeric Solidification	664
28.6	Uranium mining waste treatment	666
28.6.1	Specificity of uranium immobilization	667
28.6.2	The uranium waste sludge	668
28.6.3	Two-Step solidification technology	668
28.6.4	Results	669
28.6.5	Pilot-scale experimentation	672
28.7	Geopolymers in other toxic-radioactive waste management ap- plications	674

Part I

Polymers and Geopolymers

Chapter 1

Introduction

The discovery of a new class of inorganic materials, geopolymer resins, binders, cements and concretes, resulted in wide scientific interest and kaleidoscopic development of applications. From the first industrial research efforts in 1972 at the Cordi-Géopolymère private research laboratory, Saint-Quentin, France, until the end of 2019, thousands of papers and patents were published dealing with geopolymer science and technology. On August 31. 2005, the Geopolymer Institute (a non-profit scientific organization founded in 1979) was proud to announce in its News on line (www.geopolymer.org): "*Since 1997, 80000 papers have been downloaded by 15000 scientists around the world at the geopolymer.org website*". The extent of international scientific and commercial interest in geopolymers was evidenced by several large conferences. In France, the First European Conference on Soft Mineralurgy, organized by the Geopolymer Institute and sponsored by the European Economic Commission, was held at the University of Technology of Compiègne in June 1988 (*Geopolymer '88*). Eleven years later in June-July 1999, the Geopolymer Institute organized the Second International Conference *Geopolymere '99*, held in Saint-Quentin; the published proceedings included 32 papers presented to the 100 scientists from over 12 countries. The Third International Conference, *Geopolymer 2002* was held in Melbourne, Australia, in October 2002.

Since 2003, several national and international scientific institutions have organized "geopolymer sessions", "geopolymer seminars" and "geopolymer conferences". The Geopolymer 2005 World Congress was a tribute to the 26th anniversary of the creation of the Geopoly-

mer Institute by J. Davidovits. The main topic of the world congress was *Geopolymer-chemistry and sustainable Development*. It gathered two major events in two different locations: the Fourth International Conference in Saint-Quentin, France, June-July, 2005, organized by the Geopolymer Institute; the International Workshop on Geopolymer Cements and Concrete in Perth, Australia, September 2005, chaired by V.J. Rangan, organized by Curtin University of Technology, Perth, the University of Alabama, USA, and sponsored by the National Science Foundation, USA. More than 200 scientists attended the congress and 85 international public and private research institutions presented a total of 75 papers. They cover a wide scope of topics ranging from geopolymer chemistry, industrial wastes and raw materials, geopolymer cements, geopolymer concretes (including fly ash-based geopolymers), applications in construction materials, applications in high-tech materials, matrix for fire/heat resistant composites, and applications in archaeology. The published proceedings (*Geopolymer 2005*) includes 60 selected papers and is titled: *Geopolymer, Green Chemistry and Sustainable Development Solutions*. In 2007, I started writing the 1st edition of this book; the 2nd edition was published in 2008, the 3rd in 2011 and the 4th in 2015. In 2009, we agreed to propose every year two international events: a Geopolymer Symposium in January, at Daytona Beach, Florida, USA, within the frame of the International Conference on Advanced Ceramics and Composites, organized by the American Ceramic Society and Prof. W. Kriven from Illinois University, and a Geopolymer Camp in July, at Saint-Quentin, France, organized by the Geopolymer Institute. The 11th Geopolymer Camp 2019 was a tribute to the 40th anniversary of the creation of the Institut Géopolymère (Geopolymer Institute).

Geopolymers are ceramic-like inorganic polymers produced at low temperature, generally below 100°C. They consist of chains or networks of mineral molecules linked with covalent bonds. Because they are polymers, they must get a polymer terminology, very different from the traditional way in use by ceramicists or cement scientists. For example, the formula of one major clay mineral, kaolinite, is:

for a ceramicist $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$,
for a chemist, $\text{Si}_2\text{O}_5\text{Al}_2(\text{OH})_4$.

From a geopolymer standpoint we write $[\equiv\text{Si-O-Al}(\text{OH})_2]_n$ with the covalent aluminum hydroxyl $-\text{Al}(\text{OH})_2$ side groups branched to the poly(siloxo) hexagonal macromolecule $[\equiv\text{Si-O}]_n$.

This polymeric approach has profound consequences with regard to a better understanding of the geopolymerization mechanisms. In particular, metakaolin results from the dehydroxylation of the -OH groups in kaolinite, according to the reaction:



The reactive molecule consists of two different alumino-silicate oxides $\text{Si}_2\text{O}_5\text{Al}_2\text{O}_2$, namely:



This suggests strong chemical reactivity, as opposed to the traditional way of writing $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$. Metakaolin is not alumina Al_2O_3 ! See the detailed chemical reaction mechanisms in the following sections. Other starting raw-materials are:

- rock-forming minerals, alumino-silicates,
- amorphous silica,
- and industrial by-products (alumino-silicates) like coal fly ashes, blast furnace slag.

They chemically react within two different synthesis routes:

- alkaline medium with (Na, K) hydroxides and soluble alkali-silicates yielding poly(silicates), poly(siloxo), poly(silico-aluminates), poly(sialate) types and,
- acidic medium (here with phosphoric acid) yielding poly(alumino-phospho) types.

Geopolymers comprise following molecular units (or chemical groups) presently studied and implemented in several industrial developments:

- Si-O-Si-O- siloxo, poly(siloxo),
- Si-O-Al-O- sialate, poly(sialate),
- Si-O-Al-O-Si-O- sialate-siloxo, poly(sialate-siloxo),
- Si-O-Al-O-Si-O-Si-O- sialate-disiloxo, poly(sialate-disiloxo),
- (R)-Si-O-Si-O-(R) organo-siloxo, poly-silicone,
- Al-O-P-O- alumino-phospho, poly(alumino-phospho),
- Fe-O-Si-O-Al-O-Si-O- ferro-sialate, poly(ferro-sialate).

Hardening, or setting, or geopolymerization, occurs at low temperature, below 100°C, or at room temperature. The nature of the hardened geopolymer is either X-ray amorphous at ambient and medium temperatures, or X-ray crystalline at temperatures above 500°C for Na-based, and above 1000°C for K-based species respectively.

How should we consider geopolymers? Are they a new material, a new binder or a new cement for concrete? Geopolymers are

all of these. They are new materials for coatings and adhesives, new binders for fiber composites, waste encapsulation and new cement for concrete. The properties and uses of geopolymers are being explored in many scientific and industrial disciplines: modern inorganic chemistry, physical chemistry, colloid chemistry, mineralogy, geology, and in all types of engineering process technologies. The wide variety of potential applications includes: fire resistant materials, decorative stone artifacts, thermal insulation, low-tech building materials, low energy ceramic tiles, refractory items, thermal shock refractories, bio-technologies (materials for medicinal applications), foundry industry, cements and concretes, composites for infrastructures repair and strengthening, high-tech composites for aircraft interior and automobile, high-tech resin systems, radioactive and toxic waste containment, arts and decoration, cultural heritage, archaeology and history of sciences.

1.1 Historical background

My chemistry background had focused on organic polymer chemistry and in the aftermath of various catastrophic fires in France between 1970–72, which involved common organic plastic, research on nonflammable and noncombustible plastic materials became my objective. In 1972, I founded the private research company Cordi SA, later called Cordi-Géopolymère. In my pursuit to develop new inorganic polymer materials, I was struck by the fact that the same simple hydrothermal conditions governed the synthesis of some organic plastics in alkali medium, as well as mineral feldspathoids and zeolites.

Thus, phenol and formaldehyde polycondense into the famous Bakelite invented by Bakeland at the beginning of the 20th Century, one of the oldest man-made plastic (Figure 1.1).

On the other hand, the alumino-silicate kaolinite reacts with NaOH at 100–150°C and polycondenses into hydrated sodalite (a tectoalumino-silicate, a feldspathoid), or hydroxysodalite (Figure 1.2).

From the study of the scientific and patent literature covering the synthesis of zeolites and molecular sieves — essentially in the form of powders — it became clear that this geochemistry had so far not been investigated for producing mineral binders and mineral polymers. I proceeded therefore to develop amorphous to semi-crystalline

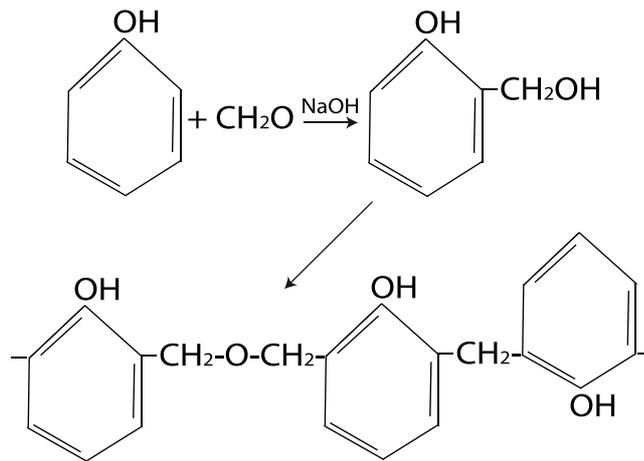


Figure 1.1: Phenoplast polycondensation between phenol and formaldehyde, in alkali medium.

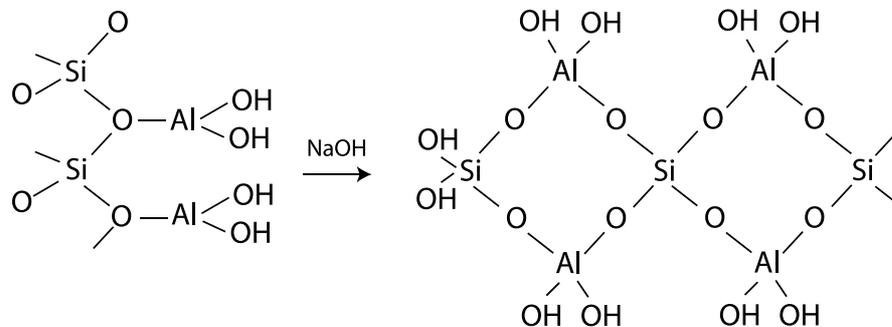


Figure 1.2: Polycondensation of kaolinite $\text{Si}_2\text{O}_5, \text{Al}_2(\text{OH})_4$ in alkali medium.

three-dimensional silico-aluminate materials, which I call in French "géopolymères", geopolymers (mineral polymers resulting from geochemistry or geosynthesis).

The first applications were building products developed in 1973–1976, such as fire-resistant chip-board panels, comprised of a wooden core faced with two geopolymer nanocomposite coatings, in which the entire panel was manufactured in a one-step process (Davidovits, 1973). We coined it "*Siliface Process*". An unusual feature was observed to characterize the manufacturing process: for the first time, the hardening of organic material (wood chips and organic resin based on urea-formaldehyde aminoplast) occurred simultaneously with the setting of the mineral silico-aluminate (Na-poly(sialate) / quartz nanocomposite), when applying the same thermosetting parameters as for organic resin: 150–180°C temperature (Davidovits, 1976).

1.1.1 The invention of the first mineral resin, October 1975

Since 1972, we were involved in applying a methodology based on the transformation of kaolinitic clays. The material was wet clay and could only be processed through compression or extrusion. We did not have at our disposal a fluid binder, so far. The real breakthrough took place when, in 1975, we discovered at the CORDI laboratory a geopolymeric liquid binder based on metakaolin and soluble alkali silicate. I recognized the potential of this discovery and presented an *Enveloppe Soleau* for registration at the French Patent Office (Figure 1.3). Here is the English translation of the hand written text:

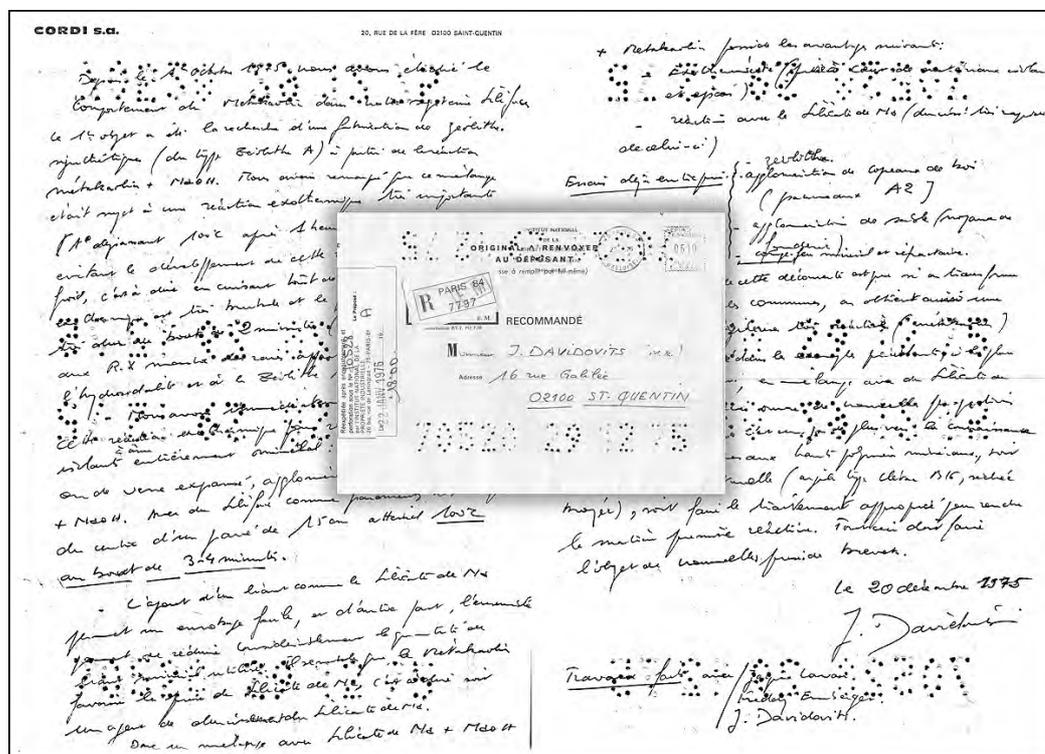


Figure 1.3: *Enveloppe Soleau* filed on 29/12/1975

Text of the Enveloppe Soleau filed on 29/12/1975, number 70528, at Institut National de la Propriété Industrielle, INPI, Paris. English translation from French:

"Since October 1, 1975 we study the behaviour of metakaolin in our Siliface system. The first goal was to find a process for the manufacture of synthetic zeolites (type Zeolite A) by reacting metakaolin + NaOH. We noticed that this mixture was prone to a very important exothermic reaction [t° exceeding 100°C after 1 hour of storage in a bag]. If we do not let this exothermic reaction to start at room

temperature, namely if we cure immediately the mixture, then the exothermic reaction becomes very powerful and the product obtained is very hard after 2 minutes at 120°C; X-ray diffraction shows peaks attributed to hydrosodalite and to Zeolite A. We immediately planned to use this exothermic reaction in the manufacturing of insulating blocks consisting entirely of a mineral core made of expanded shale or expanded glass spheres, agglomerated with metakaolin + NaOH. In a panel covered with a Siliface facing, the temperature in the center of a 15 cm thick core reaches 100°C after only 3–4 minutes. The addition of a binder such as Na-Silicate leads to a liquid coating, and allows reducing the quantity of mineral binder used in the process. It seems that metakaolin behaves as a hardener for Na-Silicate.

Consequently, a mixture involving Na-Silicate + NaOH + Metakaolin has the following advantages:

- Exothermicity (hardening to the heart of thick material);
- Reaction with Na-Silicate (very fast hardening of the liquid binder).

Tests already undertaken on: - zeolites; - agglomeration of wood chips (A2 panels); - sand agglomeration (foundry cores); - mineral and refractory fire barrier.

Another consequence of this discovery is that one can treat common clays at 500–600°C, to obtain a very reactive argillaceous raw material (metakaolin type) being able to be used in the preceding examples in place of pure metakaolin, together with Na-Silicate, or alone. This opens very interesting new prospects. It is a step towards more knowledge on the specific reactions involving mineral polymers, either by using natural raw materials for example standard clay like Clérac B16, dried, ground, or by performing the suitable treatment to transform them into reactive raw material. New patent filings will sanction all these discoveries. On December 20, 1975, J. Davidovits" *End of translation.*

It was the first mineral resin ever manufactured. The title of the patent, *Mineral polymer*, was self evident (Davidovits, 1979). The commercial product, coined Geopolymite™, was a good fire resistant alternative to organic resin. Then, Neuschäffer (1983) at the licensed German Company Dynamit Nobel (later Hüls Troisdorf AG) discovered the high reactivity of silica and alumina fumes, by-products of the manufacture of high-tech ceramics.

In early 1983, the Chairman of Lone Star Industries Inc., at this time the leading cement manufacturer on the American continent,

was traveling in Europe and learned about our new geopolymeric binders. Lone Star Industries and Shell Oil Company had just announced the formation of a corporation to develop, produce, and market a new class of materials that were expected to have a wide-ranging impact on construction, architectural, and engineering applications. These materials were made from mineral aggregates combined with organic polymers and monomers. In other words, it was an "organic polymer concrete". Shell Oil supplied the chemical expertise in organic polymers, while Lone Star supplied the mineral aggregates. By enlisting our new inorganic geopolymers, Lone Star took the opportunity to challenge Shell Oil's chemical expertise. In August 1983, with James Sawyer as Head of Lone Star's research laboratory in Houston, Texas, I started to develop early high-strength geopolymeric binders and cements based on both geopolymeric and hydraulic cement chemistries. Within one month, Lone Star Industries Inc. formed the development company, Pyrament, which was exclusively dedicated to the implementation of this new class of cement. A few months later, Lone Star separated from the Shell Oil deal. It was discovered that the addition of ground blast furnace slag, which is a latent hydraulic cementitious product, to the poly(sialate) type of geopolymer, accelerates the setting time and significantly improves compressive and flexural strength. The first Davidovits and Sawyer (1985) patent was filed in Feb. 22, 1984, and titled "Early High-Strength Mineral Polymer" (US Patent). The corresponding European Patent, filed in 1985, is titled "Early High-Strength Concrete Composition" and these patents disclose our preliminary finding from the research carried out in August-September of 1983. Geopolymer cements are acid-resistant cementitious materials with zeolitic properties that can be applied to the long-term containment of hazardous and toxic wastes.

At Lone Star, in 1984, Richard Heitzmann and James Sawyer likewise blended Portland cement with geopolymer. Their purpose was to take advantage of the good properties of geopolymeric cement along with the low manufacturing cost of Portland cement. The resulting Pyrament[®] Blended Cement (PBC) was very close to alkali-activated pozzolanic cement. It comprised 80 % ordinary Portland cement and 20 % of geopolymeric raw materials (Heitzmann *et al.*, 1989). Pyrament PBC was recognized in the construction industry for its ability to gain very high early strength quite rapidly (US Army

Corps of Engineers, 1985). It was the ideal material for repairing runways made of concrete, industrial pavements, and highway roads. In the case of a runway, a 4–6 hours hardening is enough to allow the landing of an Airbus or a Boeing. The geopolymeric cement reaches a compression strength of 20 MPa after 4 hours, whereas plain concrete gets to this strength after several days. As of fall 1993, Pyrament concrete was listed for over 50 industrial facilities and 57 military installations in the USA, and 7 in other countries, and for nonmilitary airports. In 1994 the US Army Corps of Engineers released a well-documented study on the properties of Pyrament Blended Cements based concretes, which are performing better than had ever been expected for high-quality concretes.

In the field of so-called high-tech applications, since 1982, the French aeronautic company Dassault Aviation (Vautey, 1990) has used geopolymer molds and tooling in the development of French Airforce fighters (Davidovits *et al.* 1991). More than a hundred tooling and other items have been delivered for aeronautic applications and SPF Aluminum processing. In 1994 the American Federal Aviation Administration (FAA) with R. Lyon, initiated a cooperative research program to develop environmentally friendly, fire resistant matrix materials for aircraft composites and cabin interior applications. The Geopolymer composites were selected by FAA as the best candidate for this program (Lyon, 1997).

Environmentally-driven geopolymer applications are based on the implementation of (K,Ca)–poly(sialate-siloxo) / (K,Ca)–poly(sialate-disiloxo) cements. In industrialized countries (Western countries) emphasis is put on toxic waste (heavy metals) and radioactive waste safe containment. On the other hand, in emerging countries, the applications relate to sustainable development, essentially geopolymeric cements with very low CO₂ emission. Both fields of application are strongly dependent on politically driven decisions. Heavy metal waste encapsulation with geopolymer started in 1987, in Canada, with the financial support of CANMET Ottawa, Ontario Research Foundation, Toronto, and Comrie Consulting (Davidovits and Comrie, 1988). The safe containment of uranium mine tailings and radioactive sludge started in 1994 within the European research project GEOCISTEM, funded by the European Union. The GEOCISTEM project was aimed at manufacturing cost-effectively new geopolymeric cements (Geocistem, 1997). It was experimented on two important uranium-mining locations of Wismut, former East Germany,

with the collaboration of BPS Engineering, Germany. Our results clearly show that solidification with geopolymeric cement (K,Ca)-poly(sialate-siloxo) is a prime candidate to cost-efficiently fill the gap between conventional concrete technology and vitrification methods (Hermann *et al.*, 1999).

Major efforts were dedicated to greenhouse CO₂ mitigation with the development of low CO₂ geopolymer cements. My research on this very important geopolymer application started in 1990 at Penn-State University, Materials Research Laboratory, USA. The production of 1 tonne of kaolin based-geopolymeric cement generates 0.180 tonnes of CO₂, from combustion carbon-fuel, compared with 1 tonne of CO₂ for Portland cement, i.e. six times less. Fly ash based-geopolymeric cement has attracted intensive research world-wide because it emits even less CO₂, up to nine times less than Portland cement. This simply means that, in newly industrializing countries, six to nine times more cement for infrastructure and building applications might be manufactured, for the same emission of greenhouse gas CO₂ (Davidovits, 1993). One particular project, GEOASH, dealt with the study of European fly ashes and the implementation of user-friendly processes (GEOASH, 2004–2007). However, new global-warming concerns are no longer supporting the implementation of fly ash-based cement technologies. The Geopolymer Institute recommends instead the development of Ferro-sialate geopolymer cements. See our recent article on the subject titled "*A continent is on fire: stop promoting fly ash based geopolymer cements*", as well as in Chapter 13 and Chapter 26, section 26.3.3.2 (Davidovits, 2020).

1.2 The scope of the book

Although review articles and conference proceedings cover various aspects of the science and application of geopolymers, a researcher or engineer is still at a loss to readily obtain specific information about geopolymers and their use. It is this void that we hope to fill with this book.

There are two main purposes in preparing this book: it is an introduction to the subject of geopolymers for the newcomer to the field, for students, and a reference for additional information. Background details on structure, properties, characterization, synthesis, chemistry applications are included.

Each chapter is followed by a bibliography of the relevant published literature including patents. There are many examples in geopolymer science where an issued patent is either a primary reference or the only source of essential technical information. Excerpts from the more important patents are included in some chapters.

The industrial applications of geopolymers with engineering procedures and design of processes is also covered in this book.

1.3 Early observations

In the 1930s, alkalis, such as sodium and potassium hydroxide, were originally used to test iron blast furnace ground slag to determine if the slag would set when added to Portland cement. In the course of studying the testing systems for slag, Belgian scientist Purdon (1940) discovered that the alkali addition produced a new, rapid-hardening binder (see Table 1.1). Alkali-activated slag cements (called Trief cements) were used in large-scale construction as early as the 1950s. The usual activation called for adding 1.5 % NaCl and 1.5 % NaOH to 97 % ground slag mix (U.S. Army Engineer Waterways Experiment Station, 1953). In 1957, Victor Glukhovsky, a scientist working in the Ukraine at the KICE (Kiev Institute of Civil Engineering in the USSR) developed alkali-activated slag binders and in the 1960s and 1970s made major contribution in identifying both calcium silicate hydrates, and calcium and sodium alumino-silicate hydrates as solidification products. He also noted that rocks and clay minerals react during alkali treatment to form sodium alumino-silicate hydrates, confirming earlier work carried out on clay reactivity (see below). Glukhovsky called the concretes produced with this technology "soil silicate concretes" (1959) and the binders "soil cements" (1967). More recently, cement scientists coined these products AAM, alkali-activated-materials and also claimed that geopolymer cements were AAM, generating confusion. Alkali-activated-materials are not geopolymers because they are not polymers, only hydrates of the types NASH and KASH (see for more details in Chapter 26, section 26.1.2 and the video series *Why AAM are not geopolymers*).

Earlier, Flint *et al.* (1946), at the National Bureau of Standards were developing various processes for the extraction of alumina starting from clays and high-silica bauxites. One intermediary step of the extraction process involved the precipitation of a sodalite-like com-

Table 1.1: Milestones in alumino-silicate chemistry.

	Zeolite molecular sieve	Alkali-activation (slag)	Hydrosodalite (kaolin)	Geopolymer
1930			1934 : Olsen (Netherland)	
1940	1945 : Barrer (UK)	1940 : Purdon (Belgium)	1945 : US Bureau of Standard (USA) 1949 : Borchert, Keidel (Germany)	
1950	1953 : Barrer, White (UK) 1956 : Milton (USA)	1953: Trief Cement (USA) 1957: Glukovsky (Ukraine) <i>soil-silicate concrete</i>		
1960			1963 : Howell (USA) 1964 : Berg <i>et al.</i> (USSR) 1969 : Besson <i>et al.</i> (France)	
1970			1972 : Davidovits (France) <i>Siliface Process</i>	1976 : Davidovits (<i>IUPAC terminology</i>) 1979 : Davidovits (France) <i>Geopolymer</i>

pound. Borchert and Keidel (1949) prepared hydrosodalite (Na-PS) by reacting kaolinite in a concentrated NaOH solution, at 100°C. Howell (1963) obtained a Zeolite A type, using calcined kaolin (meta-kaolin) instead of kaolinite, preventing the formation of hydrosodalite.

In 1972, the ceramicist team Jean Paul Latapie and Michel Davidovics confirmed that water-resistant ceramic tiles could be fabricated at temperatures lower than 450°C, i.e. without firing. One component of clay, kaolinite, reacted with caustic soda at 150°C. In fact, the industrial application of this kaolinite reaction with alkali began in the ceramic industry with Niels Olsen (1934) and was later on reinvented in 1964 by Berg *et al.* (1970), a Russian team, but without any successful industrial implementation.

In 1969, Besson, Caillère and Hénin at the French Museum of Natural History, Paris, carried out the synthesis of hydrosodalite from various phyllosilicates (kaolinite, montmorillonite, halloysite) at 100°C in concentrated NaOH solution, (Besson *et al.*, 1969).

In 1972, at CORDI laboratory in Saint-Quentin, we developed a technology based on this geosynthesis, which has been disclosed in various patents issued on the applications of the so-called "Siliface-Process" (Davidovits and Legrand, 1974). To a natural kaolinite/quartz blend (50/50 weight ratio) was added and mixed solid NaOH in the proportion of 2 moles or less of NaOH for 1 mole Al_2O_3 of the contained kaolinite, and water (1–1.5 g water for 1 g NaOH). The resulting granules were cold-pressed at 15 MPa into a green body, which was then hot-pressed (thermosetting process) in a mold equipped with a porous layer for water evaporation.

The thermosetting parameters were:

- Temperature: 130°C to 180°C;
- Applied hydraulic pressure: higher than the saturated vapor pressure of water, for the selected temperature, i.e. 10 to 30 bars;
- Time: one minute per millimeter thickness at 150°C or 10 minutes for a 10 millimeters thick plate. 65 to 75 % of the total time is devoted to degassing water.

The setting time is relatively short. In the absence of any pervious device, i.e. when degassing is not working, the polycondensation into hydrosodalite occurs very rapidly in a time as short as 15–20 seconds per millimeter thickness, at 180°C and 40 kg/cm² hydraulic pressure. Yet, due to the high internal pressure of water and the danger of explosion, the press must be equipped with safety devices (see for more details in Chapter 7). Otherwise, it is recommended to wait until the item has cooled down to room temperature before opening the press.

1.4 Phosphate-based geopolymer

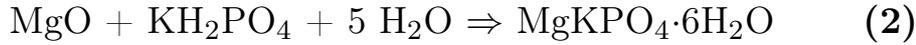
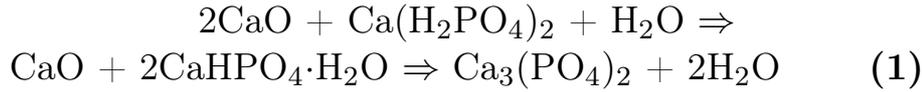
Phosphate ceramics are synthesized at room temperature and they set rapidly like conventional polymers. They contain naturally occurring mineral phases, notably apatite. They represent another variety of mineral geopolymer, where Si is totally or partially replaced by P. They are formed by an acid-base reaction between a metal oxide and an acid phosphate. Virtually any divalent or trivalent oxide that is sparingly soluble may be used to form these phosphate geopolymers.

They have found a wide range of applications such as dental cements, construction materials, oil well cements, and hazardous and

radioactive waste stabilization. The main difference between the silicate based geopolymers and phosphate geopolymers, however, is their syntheses. Poly(sialate) geopolymers and their derivatives are synthesized in alkaline environment, but phosphate geopolymers are fabricated by acid-base reactions.

1.4.1 Phosphate geopolymers

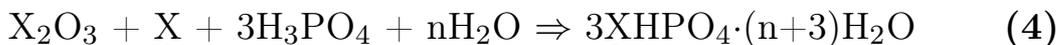
A very wide range of phosphate geopolymers may be synthesized by acid-base reaction between an inorganic oxide (preferably that of divalent and trivalent metals) and an acid phosphate. The reaction product is generally a poly(hydrophosphate) or an anhydrous poly(phosphate) that consolidates into a ceramic. The following are the most common examples (Wagh and Yeong, 2003; Wagh, 2004)



These reactions occur at room temperature. By controlling the rate of reaction, ceramics can be formed. With trivalent oxides, similar ceramics can be formed at a slightly elevated temperature. A good example is berlinite (AlPO_4), which is formed by the reaction between alumina and phosphoric acid:



It was also demonstrated that phosphate geopolymers of trivalent oxides such as Fe_2O_3 and Mn_2O_3 might be produced by reduction of the oxide and then acid-base reaction of the reduced oxide with phosphoric acid. The reaction may be described by the following equation:



where X is Fe or Mn.

1.4.2 High-molecular phosphate-based geopolymers: cristobalitic AlPO_4

Berlinite (AlPO_4) is the only known mineral to be isostructural with quartz. Isostructural means that they have the same structure although the two minerals have rather different chemistries. Quartz, SiO_2 , would seem to be very different from berlinite, AlPO_4 . But if the formula of quartz is written as SiSiO_4 instead of $2(\text{SiO}_2)$ then the similarity is obvious. The reason that berlinite is able to have the same structure as quartz is because the aluminum and phosphorus ions are of similar size to silicon ions with following bond lengths Si-O 1.63 Å, P-O 1.63 Å, Al-O 1.73 Å. Thus the same structure can be achieved since the aluminums and phosphorus can completely replace the silicons without alteration of the quartz structure. The cristobalite form of aluminum phosphate may be obtained by heating the normal berlinite form of aluminum phosphate at an elevated temperature which is preferably in excess of 1000°C.

The synthesis of cristobalitic (high-molecular) AlPO_4 geopolymers follows two different routes. The first process includes sol-gel chemistry whereas the second system involves the reaction between phosphoric acid and metakaolinite MK-750 (see in Chapter 14).

1.5 Organo-mineral geopolymers

1.5.1 Silicone

The similarity of the siloxane (Si-O-Si) structure in organo-silicones to the chains, rings, and networks of silicon and oxygen found in silica and the silicate minerals, for example in quartz, has been pointed out many times. Almennigen *et al.* (1963) reported the correspondence in a study of disiloxane $\text{H}_6\text{Si}_2\text{O}$. As observed by Noll (1968) it is possible to pass from the polymeric silicate to the polymeric covalent molecules of an organosiloxane by replacing the bridging oxide ions of the silicate anions with methyl groups. The structures that result from this replacement closely resemble the silicate and aluminosilicate molecules: monomers, dimers, trimers, etc., rings, chains, sheets and frameworks of corner-sharing silicate $[\text{SiO}_4]$ groups.

Chapter 2 and Chapter 15 focus on silicone poly(organo-siloxane). When the organic radical is methylene the structures of the oligomeric

poly-methyl-siloxanes are identical with those of poly(siloxonate) (Si-O-Si-O) and poly(sialate) (Si-O-Al-O-Si) geopolymers.

1.5.2 Hybrid organo-mineral geopolymers

This new class of compounds was first obtained by incorporating the geopolymer into the organic polymer structure, adapting the chemical composition of the components. For example a bi-functional epoxy resin, Diglycidyl Ether of Bisphenol A (DGEBA), was mixed with 20 wt% of MK-750 based geopolymer slurry, with a curing agent in an aqueous medium. The resulting hybrid material has excellent mechanical properties and improved fire resistance.

The new developments are focusing on improving the mechanical and physical properties of the geopolymer itself. However, both organic and geopolymer phases are physically incompatible. Obtaining a homogeneous mixture without phase separation requires a new approach (see in Chapter 15).

1.5.3 Humic-acid based: kerogen geopolymer

T.K. Yen and his team, working on the transformation of geomolecules through geochemical processes during diagenesis, (Kim *et al.*, 2004, 2006) have drawn attention to the concept of geopolymer in association with kerogen and petroleum. Kerogen-geopolymer is the most stable material and the final alternating product in the Earth. Some geopolymeric materials can last for a long time due to their unique geopolymeric structure, so-called three-dimensional crosslink. Geopolymers can be classified into two major groups: pure inorganic geopolymers and organic containing geopolymers, synthetic analogue of naturally occurring macromolecules (Kim *et al.*, 2004, 2006). The small content of organics is a key parameter governing the strength and durability of material in a large volume of inorganics. Organic compounds can be incorporated into refractory macromolecules such as lignin and melanodin or humic materials (Henrichs 1992). Humic materials represent an inorganic-organic structure.

Diagenesis of organic matter leads from biopolymers synthesized by organisms through "humins" to Kerogen, a geopolymer, by partial destruction and rearrangement of the main organic building blocks (Figure 1.4). Kerogen is considered to be the major starting material for most oil and gas generation as sediments are subjected to

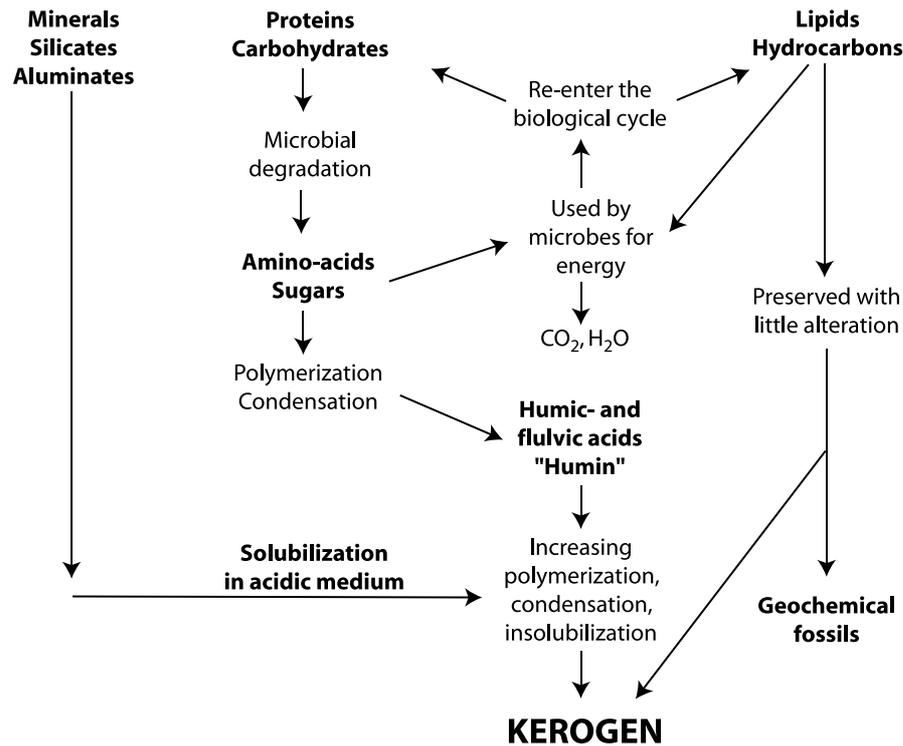


Figure 1.4: Evolution of organic matter to kerogen-geopolymer

geothermal heating in the subsurface. It is the most abundant form of organic carbon on Earth, about 1000 times more abundant than coal, which forms primarily from terrigenous remains of higher plants. Kerogen is a geopolymer that contains a high content of organics. Kerogen geopolymers generally occur in numerous forms: some have more organics and less inorganics, while others have the opposite. It is, however, evident that both inorganics and organics are required in a mix at a certain ratio, which will result in a geopolymeric structure. This geopolymeric structure exhibits a similar organization to human bone and teeth, typical inorganic-organic composites that show extreme durability and mechanical strength. The mechanism of geomacromolecule formation involves the crosslink reaction between the inorganic and organic materials.

References

- Almennigen A., Bastiansen O., Ewing V., Hedberg K. and Traetteberg M., (1963), *Acta Chem. Scand.* 17, 2455–2460.
- Berg L.C., Demidenko B.A., Reminikova V.I. and Nisamov N.S., (1970), *Stroitel'nye Materialy* (USSR), 10, 22.
- Besson H., Caillère S. and Henin S., (1969), Conditions de préparation de l'hydro-sodalite à basse température, *C. Rend. Acad. Sci.*, D269, 1367.

- Borchert W. and Keidel J., (1949), *Heidelb. Beitr. z. Min. u. Petr.*, 1. 2.
- Davidovits J., (1972), Procédé de fabrication de panneaux agglomérés et panneaux résultant de l'application de ce procédé, *French Patent Application FR 72.38746* (FR 2,204,999) and *FR 73.35979* (FR 2,246,382); *US Patent 3,950,470*, Process for the fabrication of sintered panels and panels resulting from the application of this process.
- Davidovits J. and Legrand J.-J., (1974) *French Patent FR 2,324,427* filed Jan. 11. 1974; see also *US Patent 4,028,454* (1977), filed Dec. 31. 1974 ; *United Kingdom Patent UK 1.481.479* (1977), filed Jan. 9, 1975; *German Patent DE 25 00 151* (1979), filed Jan. 3, 1975.
- Davidovits J., (1976), Solid phase synthesis of a mineral blockpolymer by low temperature polycondensation of alumino-silicate polymers, *IUPAC International Symposium on Macromolecules* Stockholm; Sept. 1976; Topic III, New Polymers of high stability.
- Davidovits J., (1979), Polymère Minéral, *French Patent Application FR 79.22041* (FR 2,464,227) and *FR 80.18970* (FR 2,489,290); *US Patent 4,349,386*, Mineral polymer.
- Davidovits J., (1993), Carbon-Dioxide Greenhouse-Warming: What Future for Portland Cement, *Proceedings, Emerging Technologies Symposium on Cement and Concretes in the Global Environment*, 21p, Portland Cement Association, Chicago, Illinois, March 1993.
- Davidovits J., (2020), A continent is on fire: stop promoting fly ash based geopolymer cements, *Research Gate, DOI:10.13140/RG.2.2.34889.29283*.
- Davidovits J. and Sawyer J.L., (1985), Early high-strength mineral polymer, *US Patent 4,509,985*, 1985, filed February 22, 1984.
- Davidovits J. and Comrie D., (1988), Archaeological long-term durability of hazardous waste disposal: preliminary results with geopolymer technologies, *Division of Environmental Chemistry, American Chemical Society*, Toronto, 1988, Extended Abstracts, 237–240. See also: Long Term Durability of Hazardous Toxic and Nuclear Waste Disposals, *Geopolymer '88 Proceedings*, 125–134.
- Davidovits J. and Davidovics M., (1991), Geopolymer: Ultra-High Temperature Tooling Material for the Manufacture of Advanced Composites", *SAMPE Symposium*, Vol.36, 2, pp. 1939–1949, Society for the Advancement of Material and Process Engineering, Covina, California, USA.
- Flint E.P., Clarke W.F., Newman E.S., Shartsis L., Bishop D.L. and Wells L.S., (1946), *J. Res. Nat. Bur. Stand.*, 36, 63.
- GEOASH (2004–2007), The GEOASH project was carried out with a financial grant from the Research Fund for Coal and Steel of the European Community. The GEOASH project is known under the contract number RFC-CR-04005. It involved: Antenucci D., ISSeP, Liège, Belgium; Nugteren H. and Butselaar-Orthlieb V., Delft University of Technology, Delft, The Netherlands; Davidovits J., Cordi-Géopolymère Sarl, Saint-Quentin, France; Fernández-Pereira C. and Luna Y., University of Seville, School of Industrial Engineering, Sevilla, Spain; Izquierdo and M., Querol X., CSIC, Institute of Earth Sciences "Jaume Almera", Barcelona, Spain.
- Geocistem (1997), BRITE-EURAM European research project BE-7355-93, GEOCISTEM, Synthesis Report and Final Technical Report, July 1997. GEOCISTEM is the acronym for "cost effective GEOpolymeric Cements fo Innocuous Stabilisation of Toxic EleMents". The primary objective of the Geocistem re-

- search project was the fabrication of alkali-melilitic glass $(\text{Ca,Na,K})_2[(\text{Mg,Fe}^{2+}, \text{Al,Si})_3\text{O}_7]$. Vitrification at temperatures ranging from 1200°C to 1350°C and mineral binder formulations were performed by J. Davidovits in the laboratory of Cordi-Géopolymère SA, Saint-Quentin, France. The selection of European geological materials was carried out by – P. Rocher, BRGM Bureau de Recherches Géologiques et minières, Orléans, France, – D. Gimeno, Geology Dept. University of Barcelona, Spain, – C. Marini and S. Tocco, University of Cagliari, Italy. MAS-NMR spectroscopy was performed by Z. Gabelica at that time in Namur University, Belgium.
- Glukhovsky V.D., (1965), Soil silicates, Their Properties, Technology and Manufacturing and Fields of Application, *Doct Tech Sc. Degree thesis*, Civil Engineering Institute. Kiev, Ukraine (former USSR).
- Heitzmann R.E, Gravitt, B.B. and Sawyer, J.L., Cement Composition Curable at Low Temperature, *US Patent 4,842,649*, 1989.
- Henrichs S.M., (1992), Early diagenesis of organic matter in marine sediments: progress and perplexity. *Mar. Chem.* 39, 119–149.
- Hermann E., Kunze C., Gatzweiler R., Kiessig G. and Davidovits J., (1999), Solidification of various radioactive residues by Geopolymere with special emphasis on long-term stability, *Geopolymer '99 Proceedings*, 211–228.
- Howell P.A., (1963), *US Patent 3,114,603*.
- Kim D., Lai H.-T., Chilingar G.V., Yen T.F., (2006), Geopolymer formation and its unique properties, *Environ. Geol*, 51[1], 103–111.
- Kim D., Petrisor I.G., Yen T.F., (2004), Geo-polymerization of biopolymers: a preliminary inquiry. *Carbohydr Polym.* 56, 213–217.
- Lyon R.E., Foden A.J., Balaguru P.N., Davidovits J. and Davidovics M., (1997), Properties of Geopolymer Matrix-Carbon Fiber Composites, *Fire and Materials*, 21. 67–73.
- Neuschäffer K.H., Engels H.W., Gebert H.J., Laube R.W. and Zoche G., (1985), *US Patent 4,522,652*; see also K.H. Neuschäffer, P. Spielau, G. Zoche and H.W. Engels *US Patent 4,533,393* (1985); K.H. Neuschäffer, P. Spielau, H.W. Engels and G. Zoche *US Patent 4,608,795* (1986).
- Noll W., (1968), Chemistry and Technology of Silicone, *Academic Press, N.Y.* in particular, Chapter 6.3 (pp. 287 -317) on the "Siloxane Bonds in Molecules of Siloxanes and Anions of Silicates.", (First published in the German language under the title "Chemie und Technologie der Silicone", 1960, Verlag Chemie, Germany).
- Olsen N., (1934), *German Patent 600,327*.
- Purdon A.O., (1940), L'action des alcalis sur le laitier de haut-founeau (The action of alkalis on blast furnace slag), *Journal de la Société des Industries Chimiques*, Bruxelles, Belgium, (Journal of the Society of Chemical Industry), 59, 191–202.
- US Army Corps of Engineers, (1986), Malone P.G., Randal C.A. and Kirkpatrick T., Potential for Use of Alkali-Activated Silico-Aluminate Binders in Military Applications, *Report WES/MP/GL-85-15*, Corps of Engineers, Vicksburg, Mississippi.
- US Army Corps of Engineers, (1994), Performance of Concretes Proportioned with Pyrament Blended Cement, by Tony B. Husbands, Philip. G. Malone, Lilian D. Wakeley, US Army Corps of Engineers, *Final Report CPAR-SL-94-2*, April 1994.

Vautey P., (1990), Thermoplastic and Thermosetting Composites for Structural Applications, Comparison of Mechanical Properties, *French Aerospace '90 Aeronautical Conference*, Washington, D.C., June 12–14, 1990 pp. 1–22.

Wagh A.S., and Jeong S.Y., (2003), Chemically Bonded Phosphate Ceramics: I. A Dissolution Model of Formation, *J. Ceram. Soc.*, 86 [11] 1838–1844.

Wagh A.S., (2004), Chemically Bonded Phosphate Ceramics – A Novel Class of Geopolymers, *Proceedings of the 106th Ann. Mtg. of the American Ceramic Society*, Indianapolis.

Publications of the Geopolymer Institute

(www.geopolymer.org)

Geopolymer '88, Proceedings of the First European Conference on Soft Mineralulgy, June 1988, Compiègne, France, edited by Joseph Davidovits and Joseph Orlinski.

Geopolymere '99, Proceedings of the Second International Conference Géopolymère '99, Saint-Quentin, France, June 30-July 2, 1999, edited by Joseph Davidovits, Ralph Davidovits and Claude James.

Geopolymer 2005, Proceedings of the World Congress Geopolymer 2005, Geopolymer, Green Chemistry and Sustainable Development Solutions, 4th International Geopolymer Conference, Saint-Quentin, France, July 2005, Geopolymer Workshop, Perth, Australia, Sept. 2005, edited by Joseph Davidovits.

Geopolymer Chemistry and Applications, by Joseph Davidovits, 1st edition march 2008, 2nd edition June 2008, 3rd edition July 2011, 4th edition November 2015, 5th edition March 2020.

Why Alkali-Activated-Materials (AAM) are not Geopolymers, video series (Parts 1-4) at <https://www.geopolymer.org/faq/alkali-activated-materials-geopolymers/> and *Technical Paper 25* in the Geopolymer Institute Library.