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Innovative and sustainable materials for high temperature Thermal Energy Storage (TES) systems

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Objective

- To investigate the application of geopolymers (inorganic polymers) based on Construction and Demolition Waste (CDW) in high temperature sensible Thermal Energy Storage (TES) systems.

The investigation is part of the research project "*Development of an innovative low-cost and highly efficient energy storage system (DIAS)*" that is co-funded by the EU and Republic of Cyprus.

Outline

- Why use geopolymers (based on CDW) in sensible energy (heat) storage systems?
- Development of geopolymers stable at high temperatures (> 700 °C)
  - Methodology
  - Results
- Lab-scale evaluation of geopolymers performance in a TES sample
- Conclusions & Next steps

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Sensible thermal energy storage systems

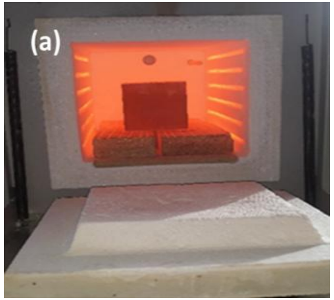
- The sensible heat storage is the simplest and more economical method to store thermal energy
- In the sensible TES systems, energy is stored in a medium by raising its temperature and without affecting its chemistry (phase change or chemical reaction)
  - At temperatures up to 200 °C, low-cost materials are used (water, ceramics, natural rocks)
  - Above 200 °C, molten salts, ceramics and cementitious materials are used
  - Between 300 and 400 °C, solid materials are preferred (concrete is an ideal solution)
  - Above 400 °C, the sensible TES systems are not used
- Structural integrity is the most important challenge for the successful application of TES materials at high temperatures (concentrated solar power systems & industrial processes)

CDW-based Geopolymers as sensible TES materials

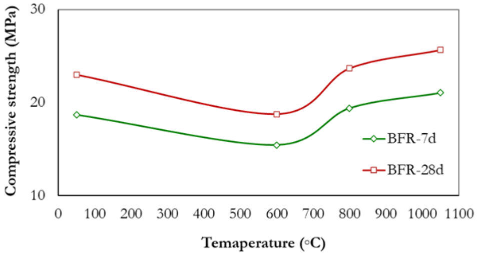
- Geopolymers (inorganic polymers) are synthetic materials resulting from the chemical reaction of inorganic solid materials rich in Al and Si amorphous phases with Na/K based aqueous solutions (poly-condensation process)
  - Low-cost materials with reduced environmental footprint (energy demand and CO_2 emissions)
  - Excellent mechanical strength, fire and acid resistance, thermal stability at high temperatures
- Construction and Demolition Waste represents the largest waste stream in the EU, accounting for over a third of all the EU waste (annual generation ~ 850 million tons)

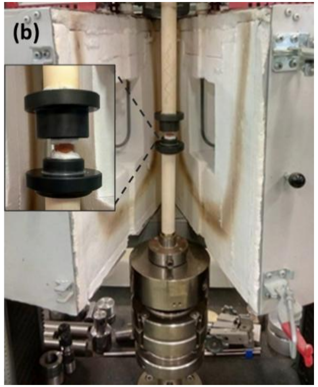
CDW-based geopolymers exposed to high temperatures

Fire resistant geopolymers based on waste bricks (WB)



Exposure to high temperature for 2 hours (muffle furnace)

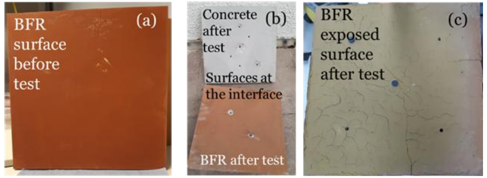




Testing of compression stress under heat flux that simulated fire conditions (Instron 5982 loading machine)

(a) 50 °C (b) 950 °C (c) 1000 °C (d) 1050 °C

Testing of the ISO-834 standard time - temperature curve



Giannopoulou I, Nicolaides D. Inorganic Polymers (Geopolymers) Based on Construction and Demolition Waste for Fire Safety of Buildings and Constructions. Fire Safety Engineering - Measures, Policies, and Applications. IntechOpen; 2025. http://dx.doi.org/10.5772/intechopen.1010424

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Development of TES geopolymers - Methodology

Step 1

Design of materials synthesis

- Chemical composition of CDW consisting only SiO_2, Al_2O_3 and Na_2O/K_2O
- Ternary systems of metallurgical slags
- Phases withstanding temperatures > 700 °C
- Possible geopolymers compositions

Step 2

Theoretical study of thermal stability

- Chemical composition of geopolymers
- Thermodynamic calculations (FactSage 7.0) - solidus of materials compositions
- Theoretical optimization of geopolymers synthesis

Step 3

Experimental evaluation

- Preparation of the optimized geopolymers
- Heating at 300 - 700 °C for 2 hours
- Structural integrity
- Thermal and mechanical properties
- Characterization

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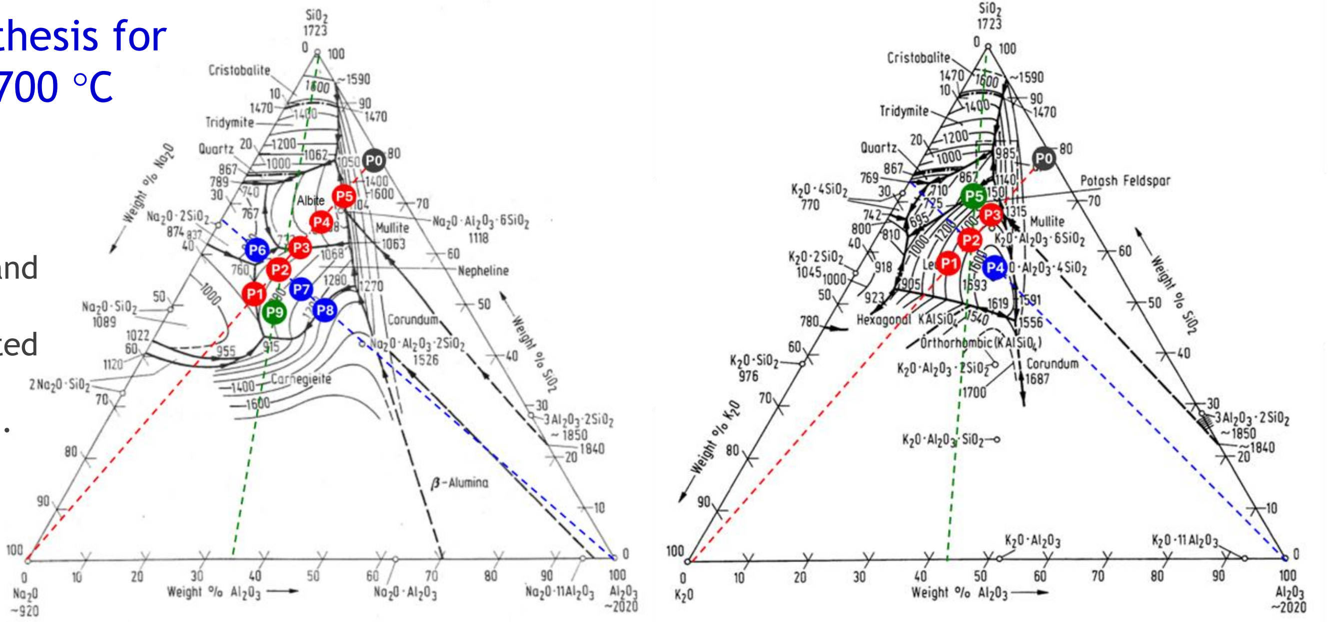
Development of TES geopolymers - Results (1)

Design of materials synthesis for thermal stability up to 700 °C

Figure: Liquidus temperature surface in the Na_2O-SiO_2-Al_2O_3 and K_2O-SiO_2-Al_2O_3 ternary systems and placement of the investigated Na- and K-based geopolymer compositions (fully dehydrated).



Giannopoulou, I.; Georgiou, L.; Oikonomopoulou, K.; Spanou, M.; Michaelides, A.; Nicolaides, D. Study on the Design and Development of Advanced Inorganic Polymers for Thermal Energy Storage (TES) Systems. *Energies* **2025**, *18*, 3107. https://doi.org/10.3390/en18123107

Development of TES geopolymers - Results (2)

Theoretical study of materials thermal stability up to 700 °C

- **FactSage 7.0** software
- Module "**Equilib**"
- Databases **FToxide** and **FactPS**
- Thermodynamic calculations in the temperature range of **500 -1500 °C**

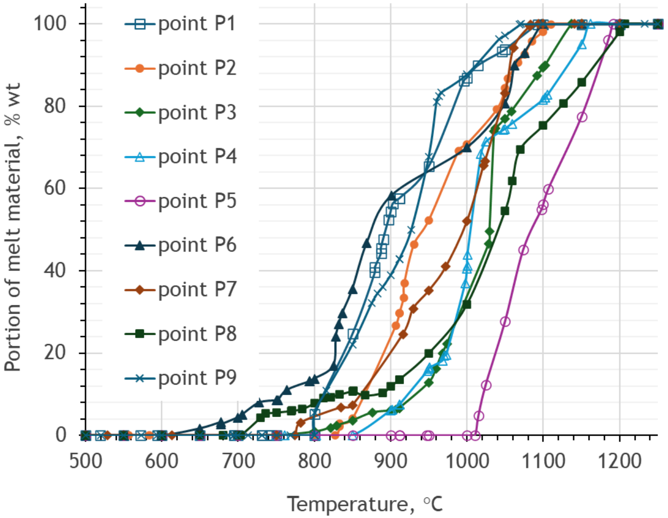


Figure: Portion of melt (wt%) between solidus and liquidus temperatures of geopolymer compositions P1–P9 (fully dehydrated) versus temperature.

Points	*Solidus*
P1	800
P2	827
P3	778
P4	850
P5	1010
P6	630
P7	774
P8	704
P9	800

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Development of TES geopolymers - Results (3)

Experimental evaluation

	Points	Code name	Composition
Na-based geopolymers	Na-P1	WB-N6	WB, NaOH solution
	Na-P3	WB-N7	WB, NaOH solution
	Na-P2	WB-N8	WB, NaOH solution
	Na-P4	WB80-MK20-N7	WB, NaOH solution, Metakaolin
	Na-P5	WB90-MK10-N7	WB, NaOH solution, Metakaolin
	Na-P9	WB-SS1-SH1-N7	WB, NaOH and Na_2SiO_3 solutions
K-based geopolymers	K-P1	WB-K4	WB, KOH solution
	K-P2	WB-K5	WB, KOH solution
	K-P3	WB-K6	WB, KOH solution
	K-P4	WB80-MK20-K5	WB, KOH solution, Metakaolin
	K-P5	WB-PS1-PH1-K5	WB, KOH and K_2SiO_3 solutions

Solid phase: Mixing of solid raw materials (waste bricks and metakaolin)

Liquid phase: Mixing of alkaline - silicate solutions (NaOH/KOH and Na_2SiO_3/K_2SiO_3)

Well mixing to form a homogeneous paste

Molding, Curing (70 °C / 2 days) and Hardening (RT / 7 days)

Geopolymer

Figure: Flowsheet of geopolymer synthesis

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Development of TES geopolymers - Results (3)

Experimental evaluation

Figure: Compressive strength of the Na-based geopolymers

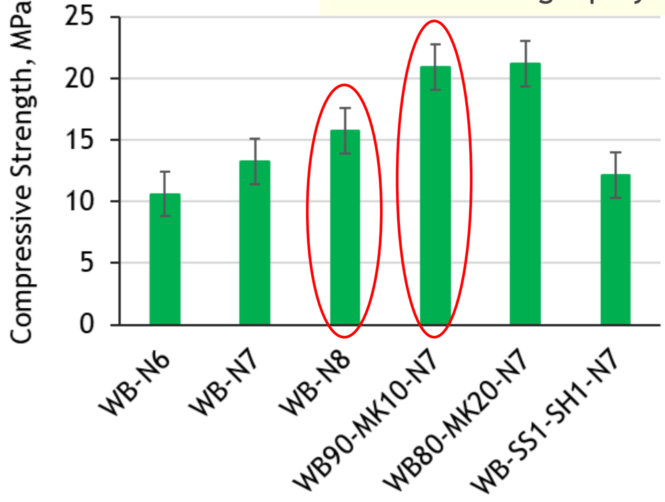
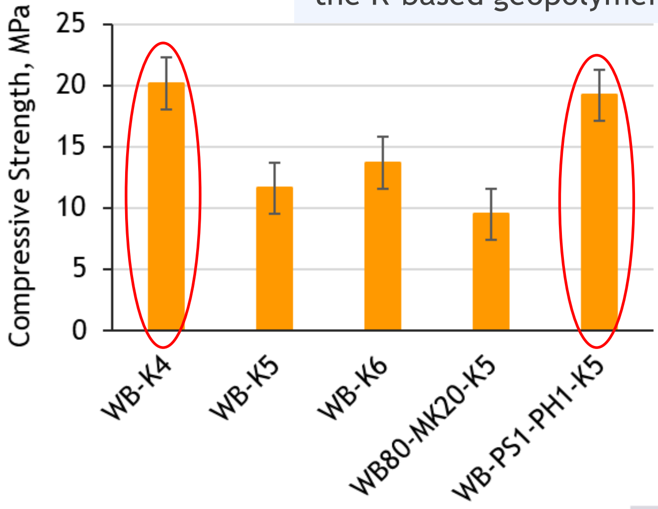


Figure: Compressive strength of the K-based geopolymers



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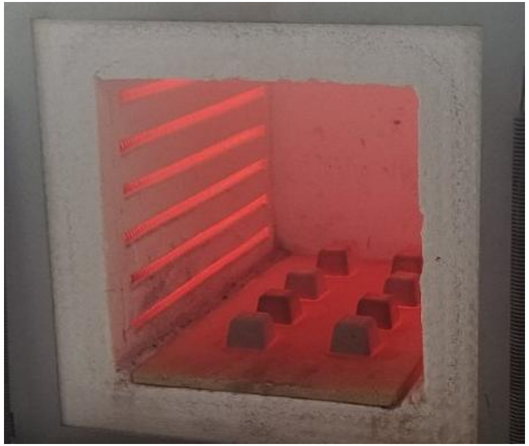
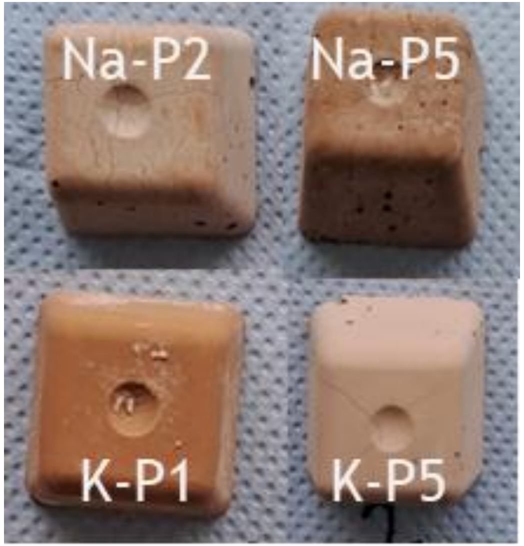
Development of TES geopolymers - Results (3)

Experimental evaluation

Exposure to elevated T



After exposure to 800 °C



After compression testing

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Development of TES geopolymers - Results (3)

Experimental evaluation

- Structural integrity up to 800 °C
- Thermal stability up to 800 °C
- Compressive strength > 20 MPa up to 500 °C
- Compressive strength decreased at temperature ≥ 700 °C

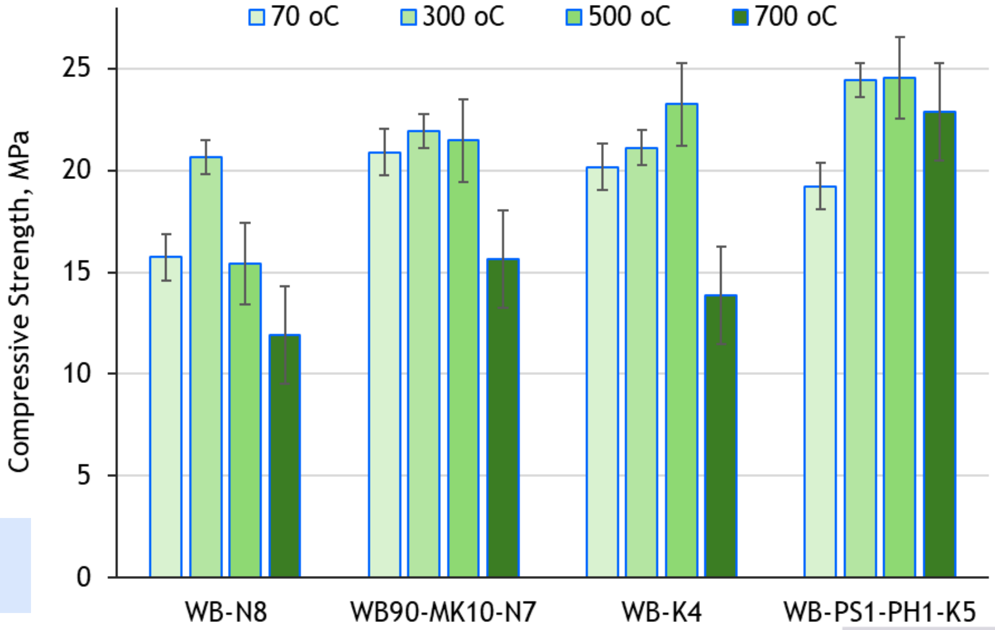

Figure: Compressive strength of the optimized geopolymers

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Development of TES geopolymers - Results (3)

Experimental evaluation

- Small decrease from 100 to 300 °C
- Almost constant between 300 and 500 °C

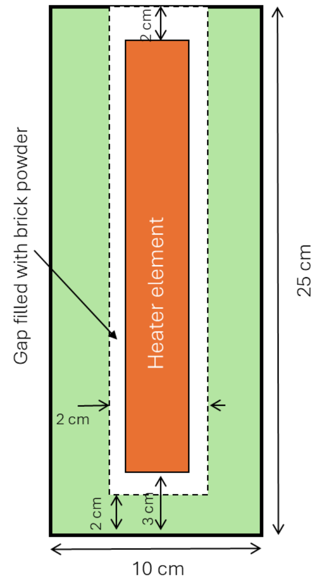
Table: Thermal properties of optimized geopolymers at 100, 300, and 500 °C.

Code Name	Cp (J kg^{-1} $^{0}C^{-1}$)	a x 10^{-7} (m^2 s^{-1})	λ (W m^{-1} $^{0}C^{-1}$)
		100 °C	
WB-N8	924.66	5.2	0.96
WB90-MK10-N7	956.94	4.7	0.89
WB-K4	1090.93	5.0	1.13
WB-PS1-PH1-K5	904.44	5.3	1.03
		300 °C	
WB-N8	641.81	5.1	0.66
WB90-MK10-N7	933.79	4.4	0.81
WB-K4	968.40	4.8	0.95
WB-PS1-PH1-K5	690.16	5.3	0.77
		500 °C	
WB-N8	606.91	5.2	0.60
WB90-MK10-N7	1049.18	4.7	0.95
WB-K4	903.72	4.8	0.90
WB-PS1-PH1-K5	729.17	5.6	0.88

Lab-scale evaluation of materials performance

Operation of a geopolymer-based TES sample in batch cycles

TES unit design and arrangement



- Operation in batch cycles of charging and discharging by heating the TES sample for 6 h at constant temperature: **400, 500, 600** and **700 °C**
- Each complete cycle lasted approximately 24 h
- Real-time measurements were carried out to monitor the operational performance of the Geo-TES sample: the temperature was recorded by thermocouples located at two points near to the Geo-TES sample surface (at 1 cm depth from surface)
- In total, 15 batch cycles were performed

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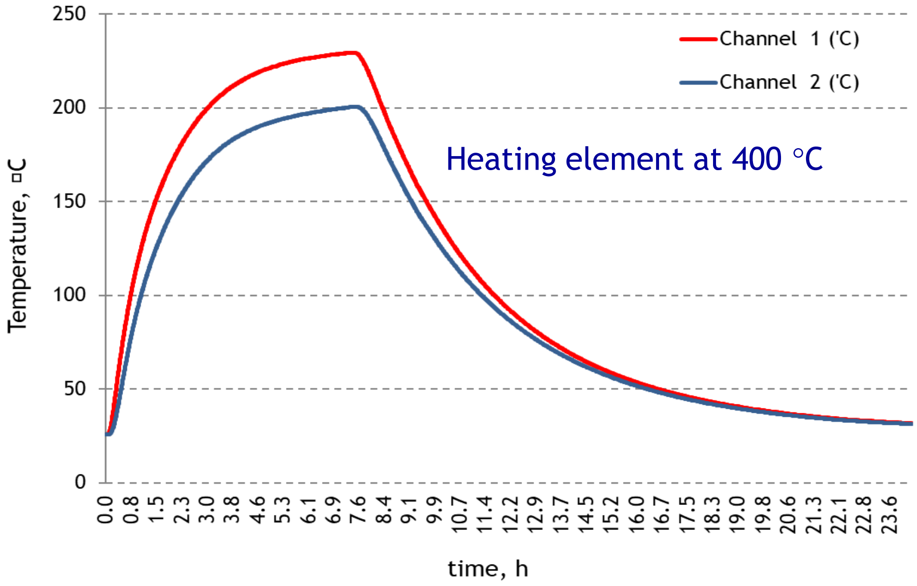
Lab-scale evaluation of materials performance

Operation in batch cycles



No	T_{heater} (oC)	$T_{surface}$ (oC)	t (h)	Q (MJ/m^3)
1-Layer of insulation				
1	400	202	7.0	333.5
2	400	229	7.4	384.4
3	600	336	7.0	586.0
4	600	331	7.0	576.5
5	700	381	7.4	670.8
6	700	379	7.2	667.0
2-Layers of insulation				
7	400	259	6.2	440.9
8	500	320	7.0	555.9
9	600	379	7.3	667.0
10	700	435	7.3	772.5

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Lab-scale evaluation of materials performance

Operation in batch cycles

- Operation in batch cycles is repeatable
- Improving of the thermal insulation increased the performance of TES module
- The volumetric thermal storage capacity of the geopolymer-based TES (1.5 MJ/m^3 °C) is lower but comparable to concrete (~ 1.8 – 2.0 MJ/m^3 °C)

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9	600	379	7.3	667.0
10	700	435	7.3	772.5

After tests with 1-L of insulation

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Conclusions

- The CDW-based geopolymers were proved promising candidates for high temperatures sensible energy storage applications
  - The optimized materials presented structural integrity and thermal stability up to 800 °C
  - The compressive strength was higher than 20 MPa and almost stable up to 500 °C. Then it was (slightly) decreased but remained higher than 12 MPa, which is adequate for TES applications
  - All thermal properties were comparable to those of the solid materials currently used in sensible heat storage applications
- The lab-scale testing in batch charging / discharging cycles of a TES sample prepared by the optimized CDW-based geopolymer revealed promising performance

➢ Next steps: Improvement of the TES sample performance and operation in continuous cycles

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RESEARCH & INNOVATION FOUNDATION

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Thank you!

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