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Consiglio Nazionale delle Ricerche

Geopolymer-based adsorbents: a tunable platform for pollutants removal

Elettra Papa
CNR-ISSMC - National Research Council of Italy - Institute of Science, Technology and Sustainability for Ceramics

GEA
GEopolymer based Adsorbents

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BRIEF DESCRIPTION OF THE PROJECT AND EXPECTED RESULTS

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GEA - GEopolymer based Adsorbents for effective adsorption and selective separation of CO_2 and eutrophication pollutants

Principal investigator: Valentina Medri (coordinator)
Duration: 24 month (16/10/2023)
Total Funding: 203.604,00 €
Action: PRIN: PROGETTI DI RICERCA DI RILEVANTE INTERESSE NAZIONALE – Bando 2022
Consortium: Consiglio Nazionale delle Ricerche (CNR-ISSMC); DICAM – Università di Bologna

GEA
GEopolymer based Adsorbents

- RESULTS of GEA ⟶ customize eco-friendly materials for specific adsorption purposes.
- Identify geopolymer matrices ⟶ able to increase in composites the performances of other adsorbent such as zeolites, hydrotalcites, .. ⟶ comparison with benchmark adsorbents.
- Set protocols for the development of geopolymer adsorbents ⟶ suitable for large scale production ⟶ optimized processes, high reproducibility.
- Geopolymers platform ⟶ link adsorption/desorption ability and selectivity to compositional and morphological VARIABLES (stoichiometry, phase composition and textural properties) ⟶ project able to give a complete overview.

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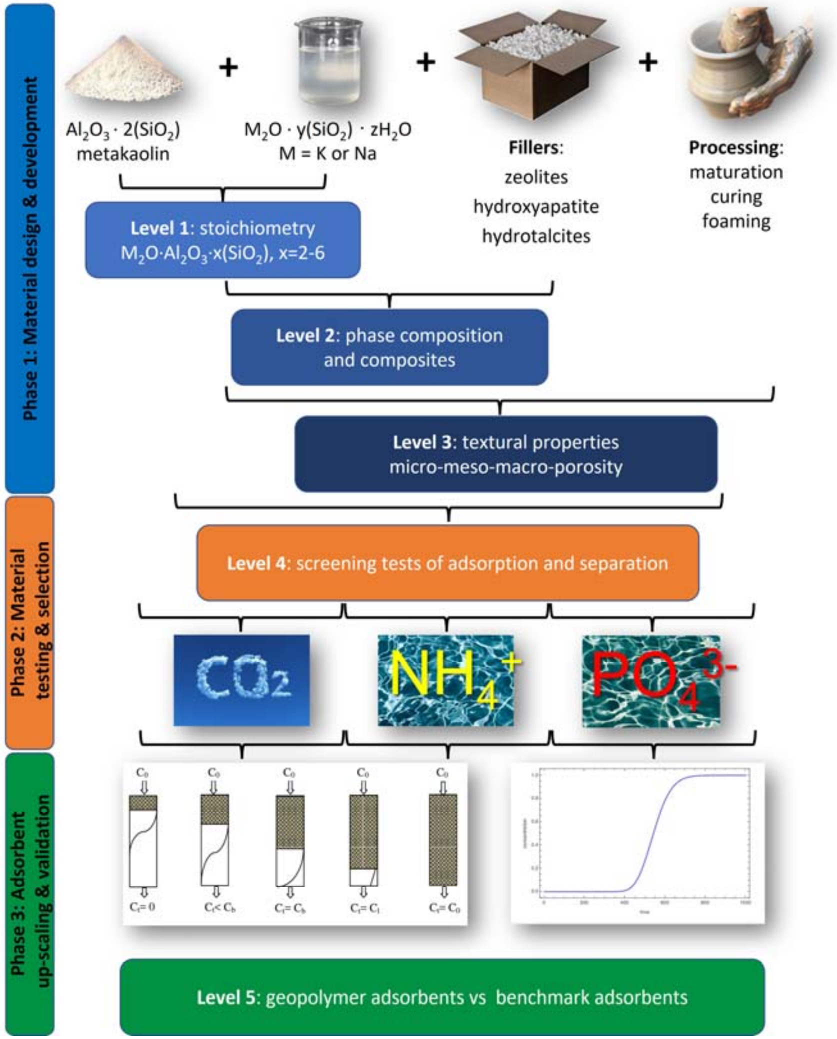

GEA PHASES

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Phase 1 - MATERIAL DESIGN & DEVELOPMENT

OUTPUT = geopolymer-based adsorbents with tuned stoichiometry, phase composition and textural properties → constituting the geopolymer-based materials platform.

Phase 2 - MATERIAL TESTING & SELECTION

OUTPUTS = 3 selected geopolymer-based adsorbents able to maximise adsorption and selectivity for selective separation of CO_2 and NH_4^+ and PO_4^{3-} ions in wastewater.

Phase 3 - ADSORBENT UP-SCALING & VALIDATION - COMPARISON WITH BENCHMARK ADSORBENTS

WP1 Synthesis and processing of geopolymer-based materials and composites
Task 1.1: Synthesis of geopolymer matrices with varied stoichiometries

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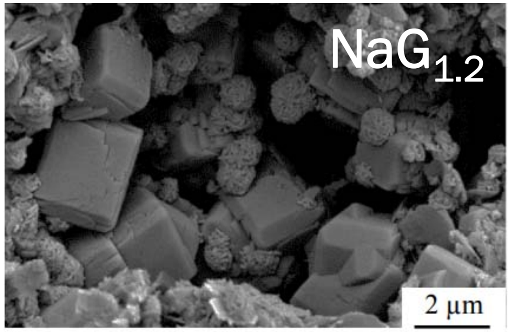
MATERIAL TESTING & SELECTION

All the different matrices were produced → selected on the basis of process reproducibility and on adsorption properties.

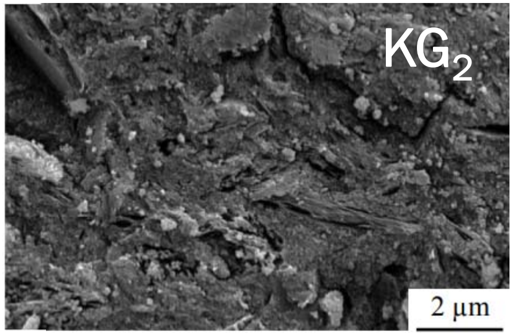
- Synthesis of geopolymer matrices with different stoichiometry (**Si/Al = 1.2 , 2 , 3**)
- Alkali cation **Na^+** or **K^+**



Metakaolin Na-based geopolymer
Si:Al=1.2

Degree of conversion into zeolite NaA (RIR method) ≈ 81%
Modal pore Ø = 0.71 µm

- **Good CO_2 capacity but low selectivity**
- **Ammonium adsorption capacities similar to those of zeolite NaA**



Metakaolin K-based geopolymer
Si:Al=2

Modal pore Ø = 0.01 µm
Compact matrix → 27 Mpa

- **Good CO_2 selectivity but low capacity**
- **High performances in terms of ammonium selectivity**

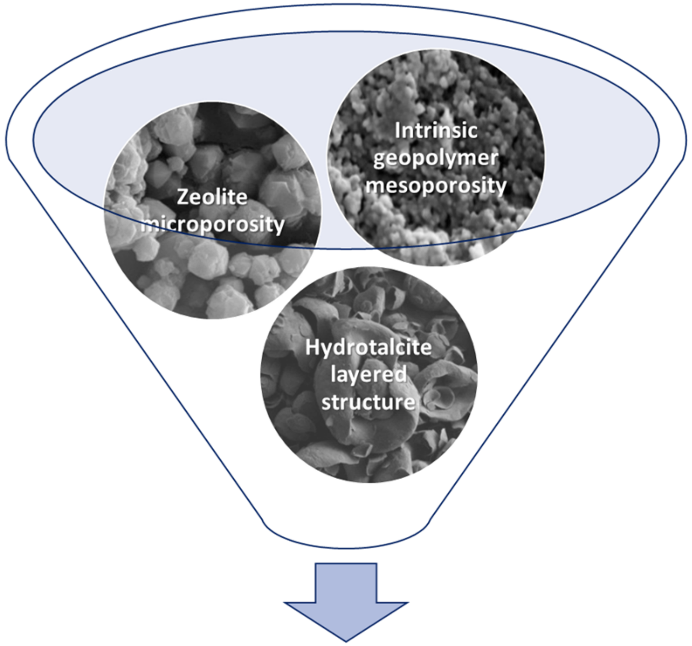
Medri et al., "Ammonium removal and recovery from municipal wastewater by ion exchange using a metakaolin K-based geopolymer ", Water Research 225 (2022) 119203

Task 1.2: Synthesis of geopolymer-based composites

Adsorbing phases such synthetic zeolites (NaA and Na13X), hydrotalcites are used as fillers, ranging from a minimum 20 vol.% up to a maximum value depending on the slurry workability.

Synergetic effect of the two composite components:

- Increase of the porosity dimensional range
- **Easy casting and shaping** (geopolymer binder): structuring a porous powder, enables to obtain an optimized structure with high mass transfer, low pressure drop and high mechanical and chemical stability
- Functionalization



Addition of Fillers → to increase adsorption capacity

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Zeolite composites – geopolymer matrices + Na13X or NaA

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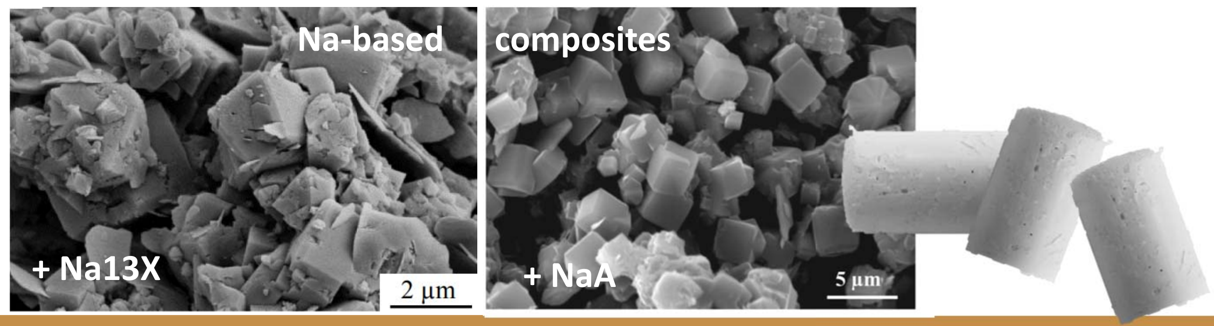
Na-$G_{1.2}$-Z

- Metakaolin Na-based geopolymer matrix (Si:Al=1.2) → Nucleation of zeolite NaA
- Composites: addition of zeolite Na13X and NaA (27 wt.%)
- Low mechanical strength (3 MPa)
- Modal pore Ø = 1.47 µm
- Synergistic effect: nucleated NaA + fillers
- Good CO_2 capacity → comparable with that of pure zeolites but selectivity is lower

K-G_2-Z

- Metakaolin K-based geopolymer matrix (Si:Al=2)
- Filler Na13X (22 e 36 wt.%), NaA (22 wt.%)
- Selectivity basically equal to that of the geopolymer matrix, with a CO_2 capacity enhanced in the case of Na13X addition
- Compact matrix and good mechanical strenght (17 MPa), modal pore Ø = 0.03 µm



Papa et al., "Zeolite-geopolymer composite materials: Production and characterization", Journal of Cleaner Production 171 (2018) 76-84
Minelli et al., "Characterization of novel geopolymer – Zeolite composites as solid adsorbents for CO2 capture", Chemical Engineering Journal 341 (2018) 505-515

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Hydrotalcite composites

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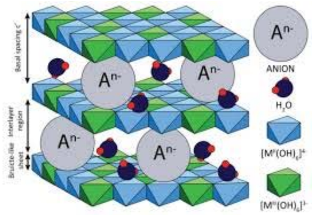
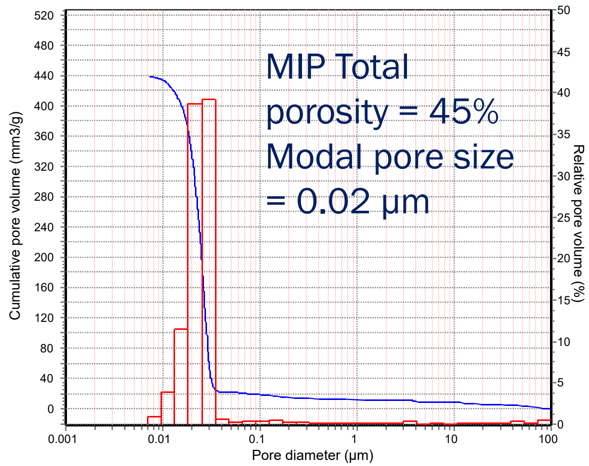
Hydrotalcites: well-developed pore size, various functional groups, and a large specific surface area → good adsorption properties for many pollutants.



Calcination at 500 °C for 5 hours to promote the thermal evolution of the HyT

- Metakaolin K-based geopolymer matrix (Si:Al=2)
- Different commercial hydrotalcites as filler: Pural 50, Pural 70, Pural 61, Sorbacid 911 → previously tested for the removal of phosphates in water
- Sorbacid 911 found to be the best performant
- Optimization of the production process to obtain composites with 23 and 30 wt% of Sorbacid 911 → production of granules



Papa et al., "CO2 adsorption at intermediate and low temperature by geopolymer-hydrotalcite composites ", Open Ceramics 5 (2021) 100048
Papa et al., "Geopolymer-hydrotalcite composites for CO2 capture", Journal of Cleaner Production 237 (2019) 117738

Task 1.3: Tailoring of textural characteristics in geopolymer-based materials and composites

Cold sintering process

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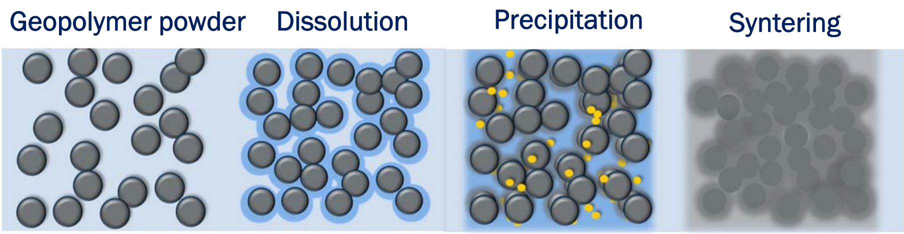

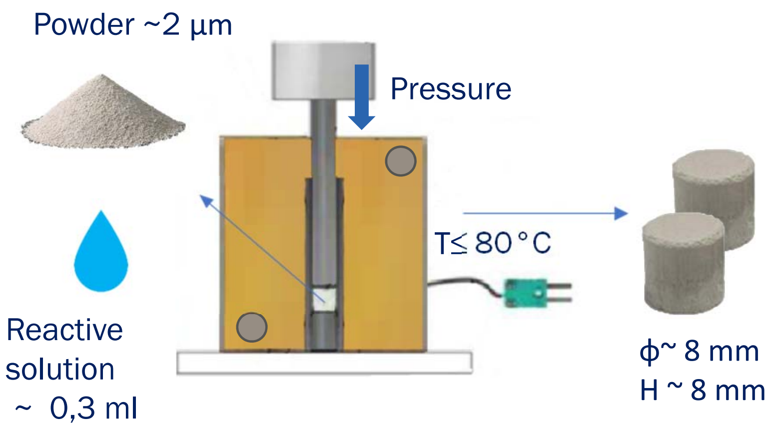

- The porosities in matrices and composites are varied to maximize adsorption performances
- Cold sintering process (CSP) ⟶ alternative production processes with lower environmental impact
- In CSP ⟶ inorganic powder humidified with a transient liquid phase (reactive solution) ⟶ placed in a mould and then heated and simultaneously densified through the application of a uniaxial pressure
- Possibility to use all the matrices and composites powders produced
- Recycle geopolymer wastes, arising from the production of geopolymer granules

Medri et al., "Development of membranes based on recycled geopolymer and zeolite through a cold sintering process", Journal of the European Ceramic Society 44 (2024) 7778-7790

Cold sintering process - CSP

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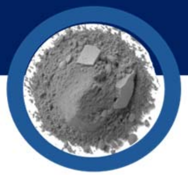
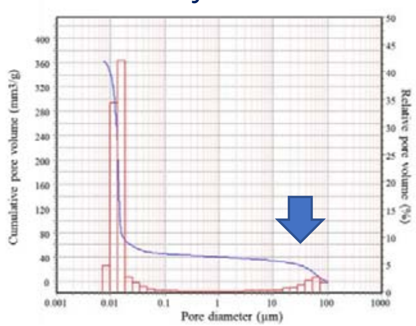


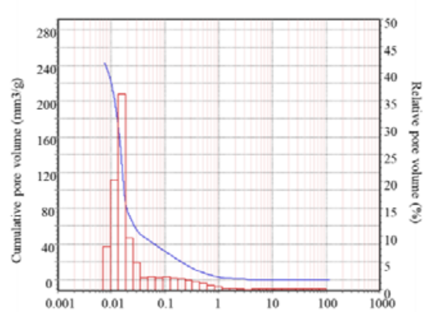

The role of the CSP parameters on densification, textural and mechanical properties were studied varying temperature (25, 40 and 80 °C), applied pressure (10, 30 bar) and reactive solution (H_2O, KOH or NaOH 2, 4, 6, 8M)

Optimization and selection of the production process parameters

Slurry route



CSP



100% of recycled KG_2
P=30 Bar, T=40 °C, KOH 2 M; 4 M; 6 M

90 wt.% $NaG_{1.2}$ (containig 81 vol% of NaA) and 10 wt.% of KG_2 as binder
P=10 Bar, T=40 °C, NaOH 4 M

CSP allows to:

- densify and fully recycle geopolymer wastes
- Remove macroporosities due to the slurry route
- Produce membranes (i.e. for ultrafiltration)

Medri et al., “Development of membranes based on recycled geopolymer and zeolite through a cold sintering process“, Journal of the European Ceramic Society 44 (2024) 7778-7790

Cold sintering process – Zeolite 13X composites

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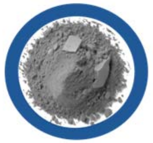


- CSP samples produced with commercial Na13X zeolite and KG_2
- Geopolymer matrix in different 5,10, 20, 30 wt.% used as binder
- Relative density ≈ 60%
- Mechanical strenght ≈ 5MPa
- Monoliths for CO_2 adsorption processes

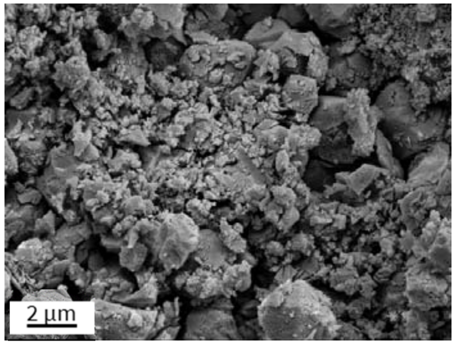
Optimized process parameters

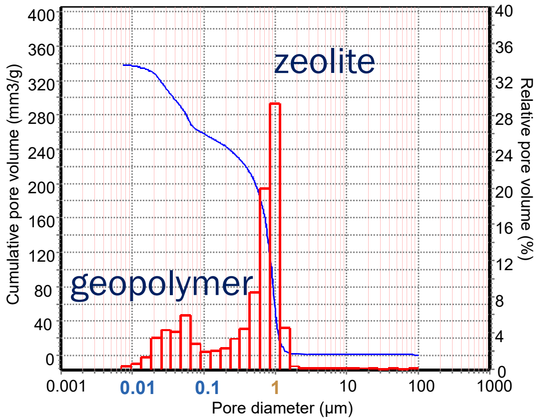
NaOH 4M

P = 10 Bar

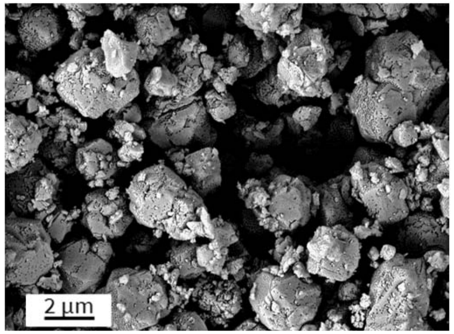
T = 40 °C

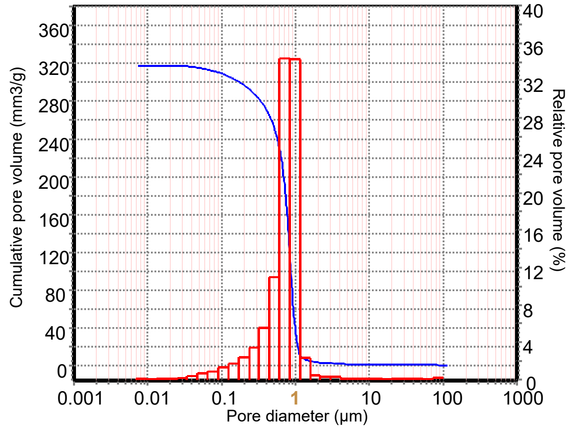
Na13X + 30 wt.% of $K\text{-}G_2$





100 wt.% Na13X





Task 1.3: Tailoring of textural characteristics in geopolymer-based materials and composites

Cold sintering process

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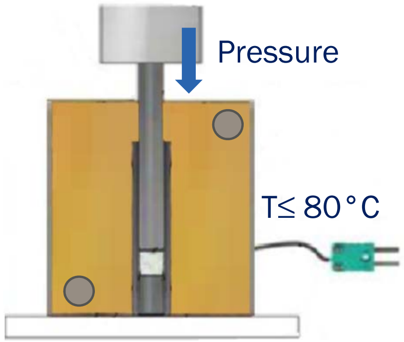
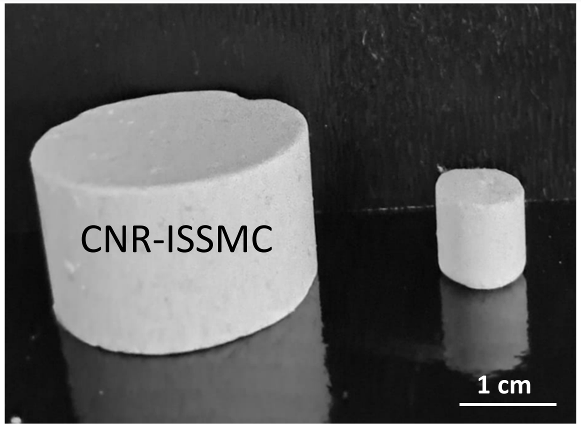
- **Up-scaling**
- Production of bigger samples → From Ø 0.8 cm, H 0.8 cm to Ø 2.5 cm, H 1.5 cm
- CSP suitable for the production of membranes with different dimension and geometries





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Task 1.3: Tailoring of textural characteristics in geopolymer-based materials and composites

Foams

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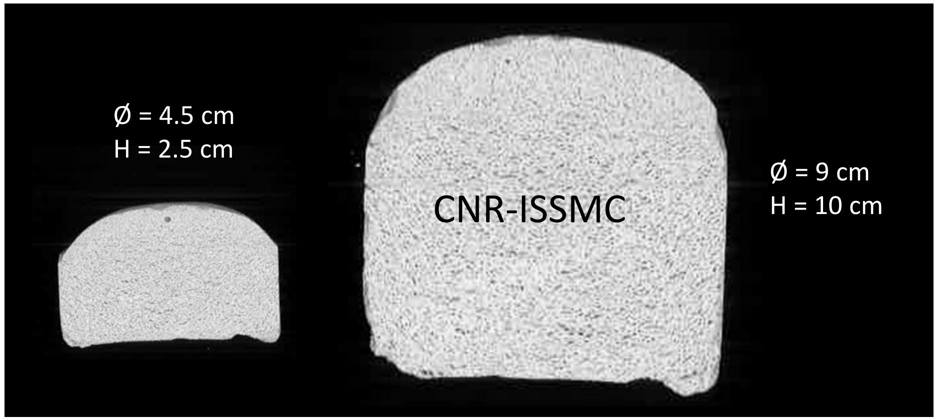
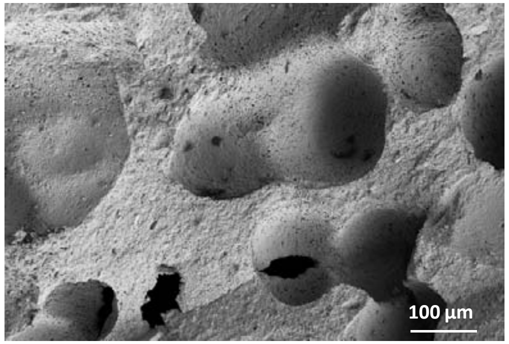
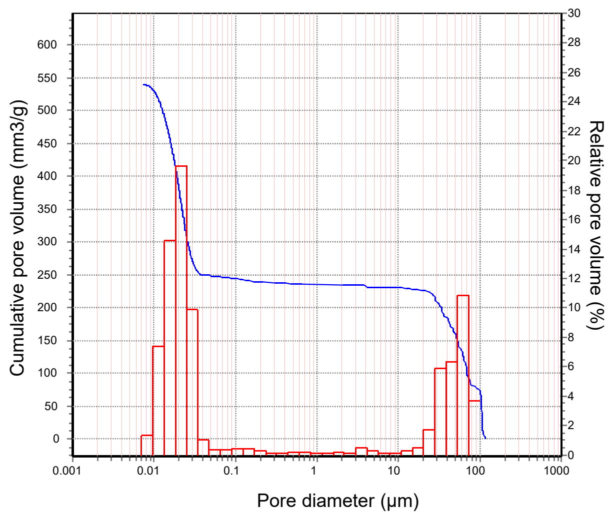
- Porosities in matrices and composites → varied to maximize adsorption performances
- Use of blowing agents as metallic silicon and H_2O_2 in order to induce different level of macroporosity
- Production of granules or monoliths





MIP Total porosity = 51%
Modal pore size = 0.03 µm
Density = 0.8 g cm^{-3}



Scale up of the process ⟶ reproducibility of the macroporosity ⟶ production of granules at large scale

Task 1.3: Tailoring of textural characteristics in geopolymer-based materials and composites

Composite Foams

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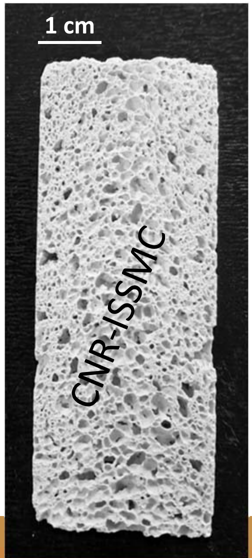
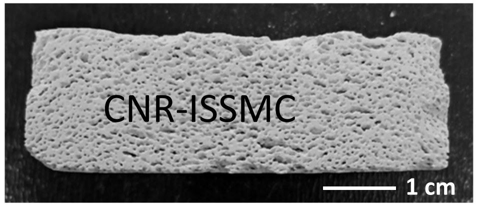
- Same composite composition: KG_2 + 22 wt.% Na13X
- Metallic silicon or H_2O_2 in different amount → production of monoliths or granules

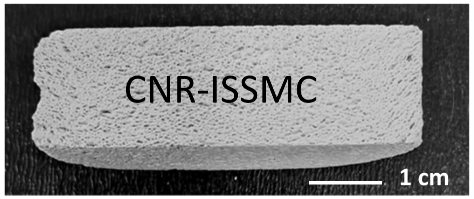
- Fine macropores for the production of granules ⟶ wastewater treatment.



- Monolith ⟶ 3 wt.% H_2O_2 to induce high level of macroporosity
- MIP total porosity = 56%, modal pore size = 0.05 μm
- Density = 0.5 g cm^{-3}
- Preliminary permeability test with H_2 and N_2 ⟶ foams will be used for CO_2 adsorption test



- 0.03 wt.% Si
- MIP total porosity = 41%, modal pore size = 0.03 μm
- Density = 0.8 g cm^{-3}



- 0.5 wt.% H_2O_2
- MIP total porosity = 54%, modal pore size = 0.05 μm
- Density = 0.6 g cm^{-3}

Future developments…

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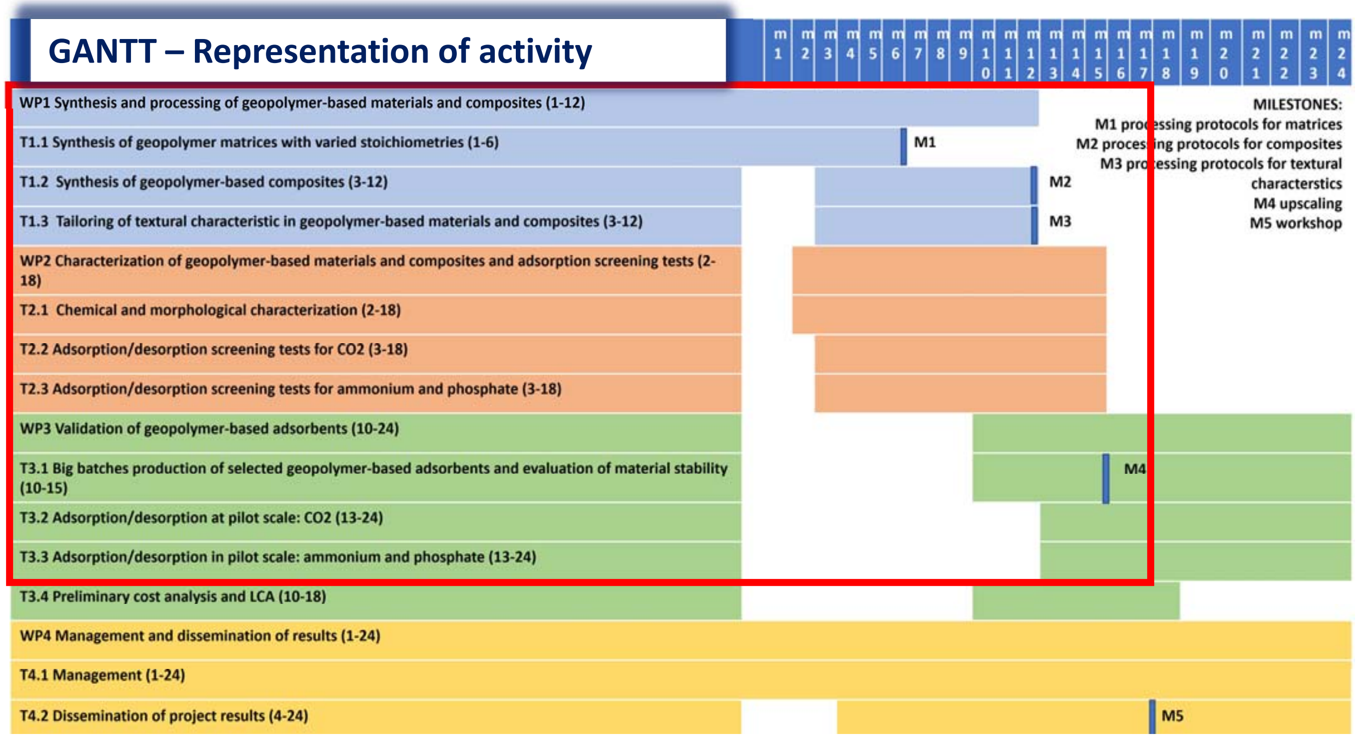

ON GOING

- Further characterization of synthesized samples (CNR-ISSMC)
- Adsorption tests for removal of pollutants (DICAM)

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Thanks to all the Project colleagues:
Valentina Medri, Francesco Miccio,
Cristina Di Pietro
(CNR - ISSMC)

Dario Frascari, Davide Pinelli, Matteo Minelli,
Walter Cossio Guzman
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PRIN: PROGETTI DI RICERCA DI RILEVANTE INTERESSE NAZIONALE – Bando 2022
Prot. 20229THRM2
CUP B53D23015240006
Starting date: 16-10-2023

Thank you for your attention!