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PIANO NAZIONALE DI RIPRESA E RESILIENZA

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CO_2 adsorption in geopolymers and geopolymer composites for post-combustion CO_2 capture

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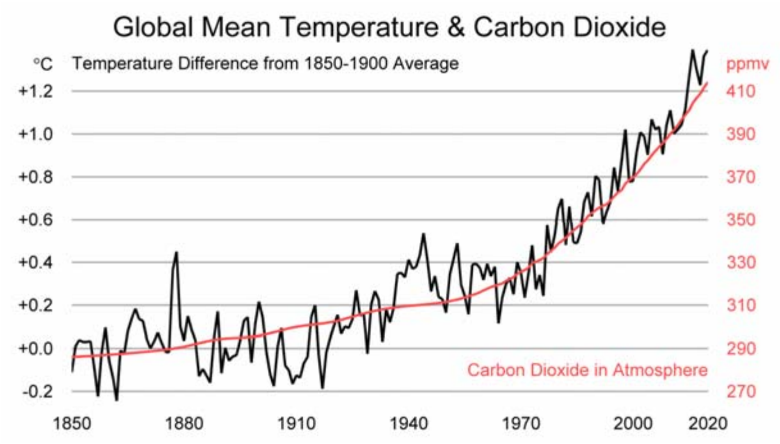
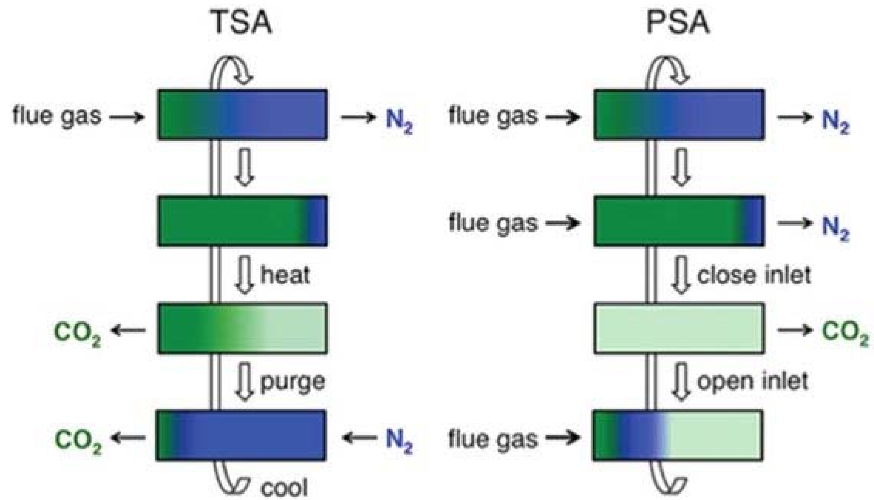
GEA
GEopolymer based Adsorbents

motivation: CO_2 capture

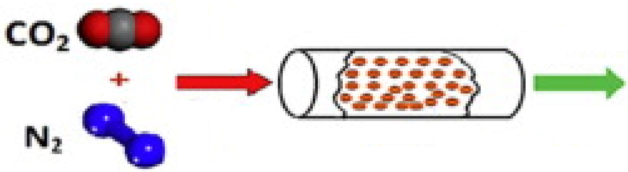


global warming is becoming a real issue, but energy from fossil fuels is still predominant, and situation will not change over the next few decades

carbon capture and storage (CCS) is the promising strategy to readily reduce CO_2 emissions to a significant extent



CO_2 removal from flue gases (N_2/CO_2 mixture) can be obtained by means of **solid adsorbents**:



GEopolymer based Adsorbents

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metakaolin-based geopolymers

✓highly tunable
(chemistry, composition, microstructure, final shape...)

Si/Al atomic ratio
(stoichiometry range 1.2–3)

alkaline cations
(K^+ or Na^+)

synthesis and processing
(consolidation at low T and p)

composites with zeolites (or other fillers)

material optimization to the desired application: (**CO_2 capture**)

GEopolymer based Adsorbents

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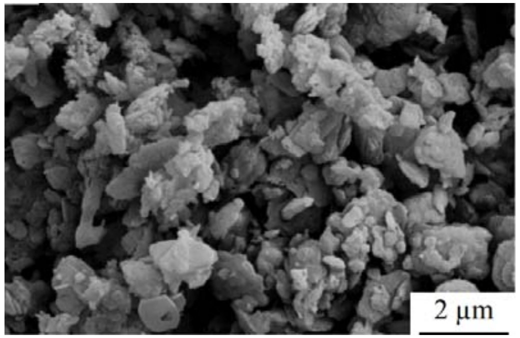
effect of chemistry and stochiometry

geop. phases can be easily shaped in moliths or pellets → no relevant differences in adsorption properties

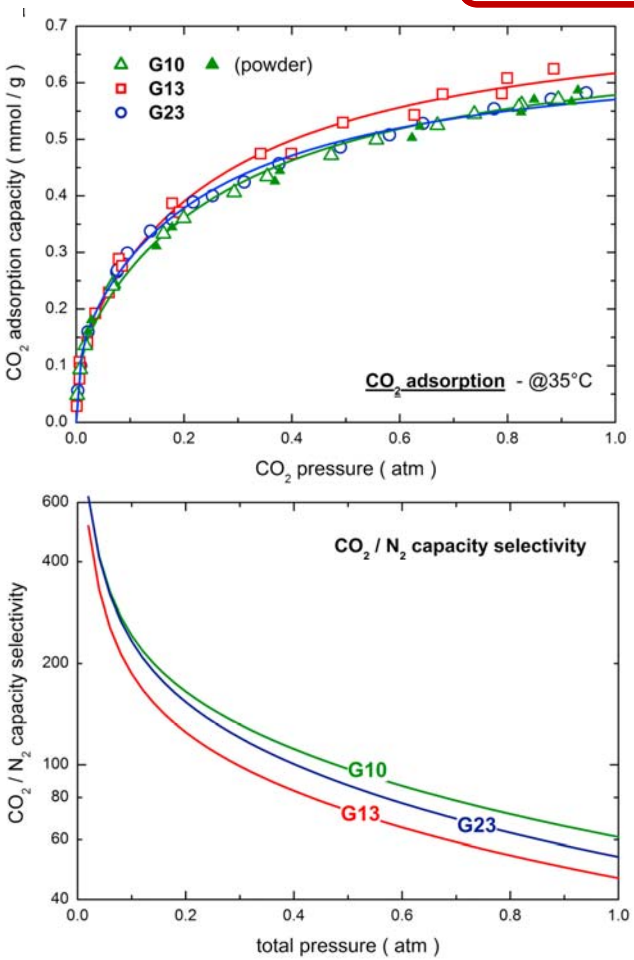
potassium based geop.

$KG_{1.2}$

Si/Al ratio 1.2



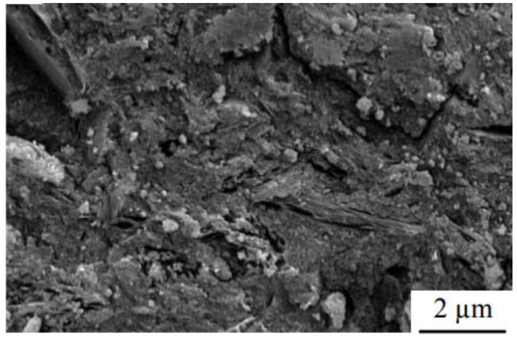
- loosely packed
- very low BET surface area
- no measurable CO_2 adsorption



potassium based geop.

KG_2

Si/Al ratio 2



- compact matrix → 27 Mpa
- modal pore Ø = 0.01 μm

- very large CO_2/N_2 selectivity
- poor CO_2 capacity

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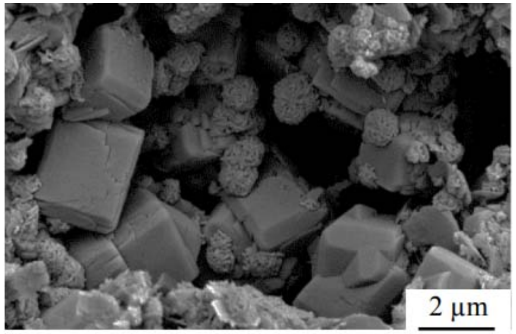
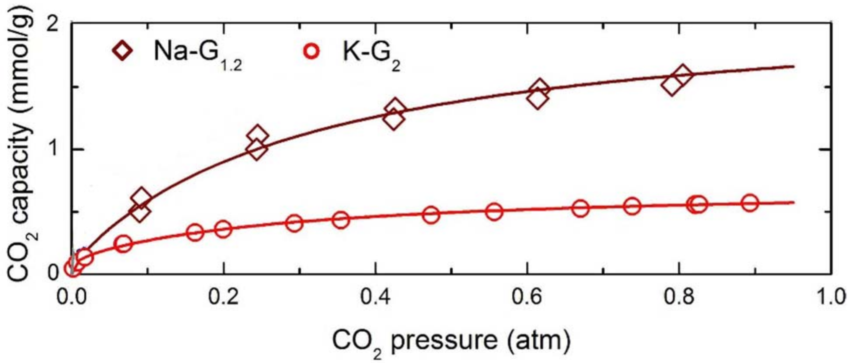
effect of chemistry and stochiometry

sodium based geop.
$NaG_{1.2}$
Si/Al ratio 1.2



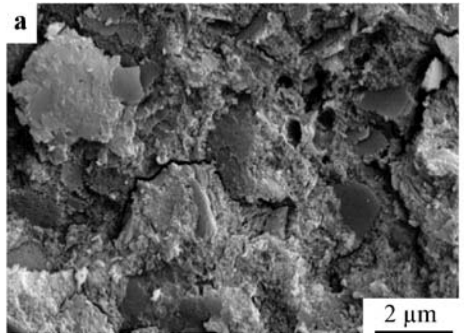
- nucleation of NaA
- modal pore Ø = 0.71 μm
- improved CO_2 capacity

T=35°C



	porosity	BET area
$KG_{1.2}$	38%	13 m^2/g
KG_2	42%	88 m^2/g
$NaG_{1.2}$	41%	14 m^2/g
NaG_2	-	-

sodium based geop.
NaG_2
Si/Al ratio 2



- processing and geop. fabrication issues
- microstructure similar to KG_2

GEopolymer based Adsorbents

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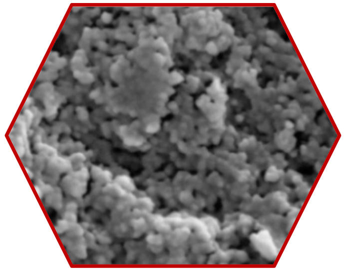
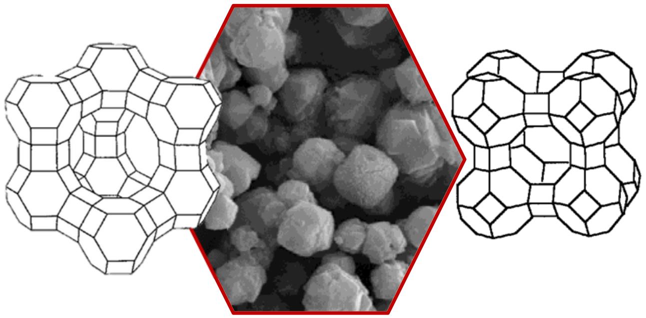
geopolymer-based composites

geopolymer (mesoporosity)



+

zeolite (microporosity)



- ✓ geopolymer microstructure is intrinsically **meso-porous** (nano-particulates separated by pores)
- ✓ geopolymers can also incorporate other moieties forming **composites**

geopolymer-zeolite composites

→ synergetic effect between the 2 components

- ✓ increase of pore size distribution range: (**micro** + **meso-macro**)
- ✓ easy casting and shaping (binder)
- ✓ functionalization (zeolite properties + geopolymer properties)

GEopolymer based Adsorbents

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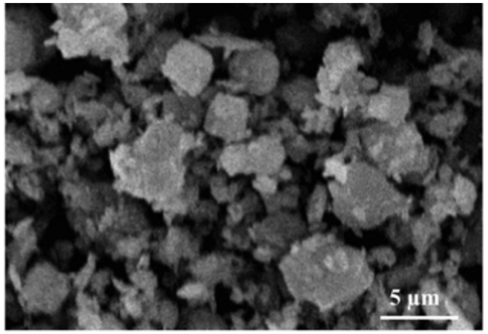
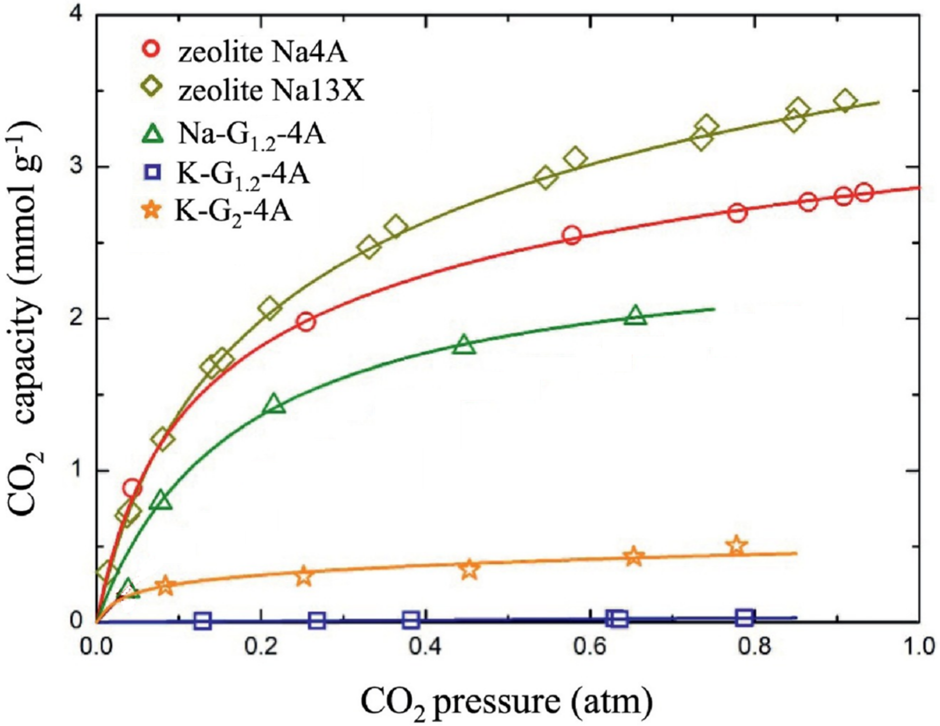
geopolymer-based composites

potassium based
geop. composite
KG_2+Na4A

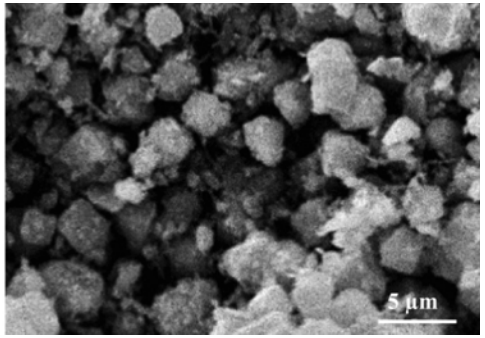


- filler Na4A (22 wt.%)
- KG_2 matrix remains pretty much amorphous
- modal pore Ø = 0.06 µm
- weak CO_2 capacity

T=35°C



sodium based geop.
composite
$NaG_{1.2}$+Na4A



- filler Na4A (27 wt.%)
- large nucleation of NaA (up to about 80% from RIR)
- modal pore Ø = 1.8 µm

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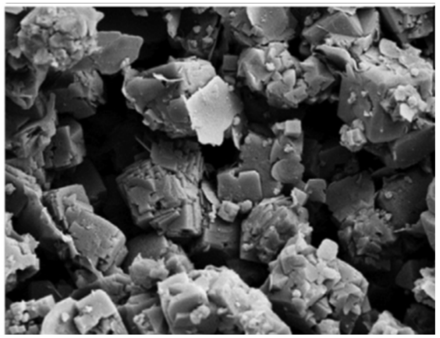
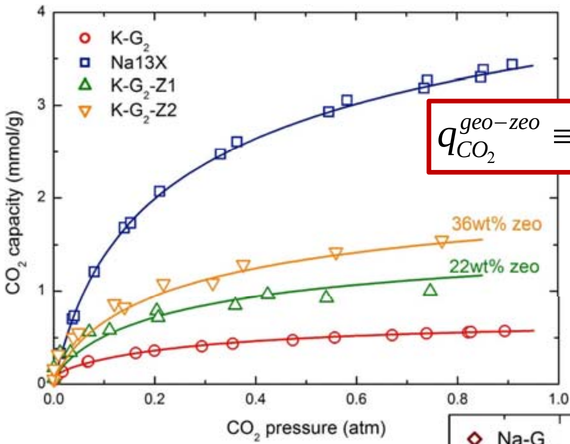
geopolymer-based composites

potassium based geop. composite
KG_2+Na13X



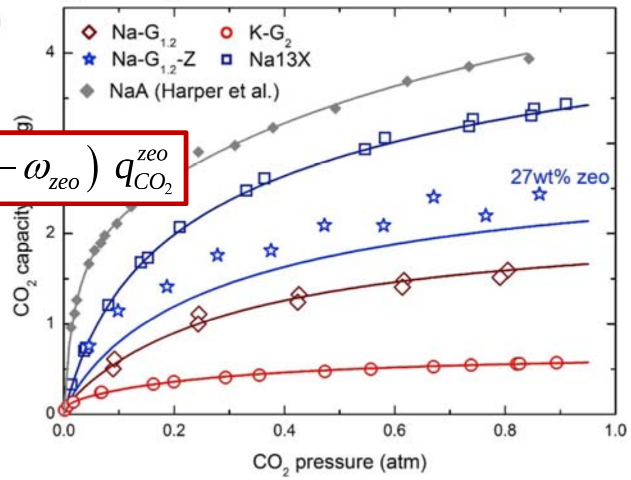
- Filler Na13X (22 e 36 wt.%)
- Compact matrix and good mechanical strenght (17 MPa)
- Modal pore Ø = 0.03 µm



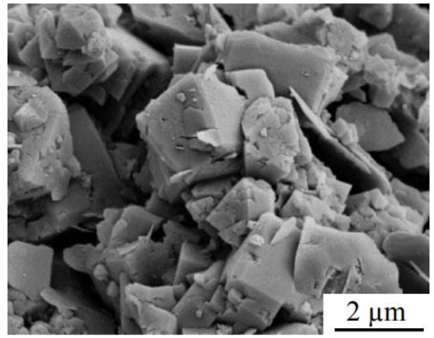
$$q_{CO_2}^{geo-zeo} \equiv \omega_{zeo}\ q_{CO_2}^{geo} + (1-\omega_{zeo})\ q_{CO_2}^{zeo}$$

T=35°C

$$q_{CO_2}^{geo-zeo} > \omega_{zeo}\ q_{CO_2}^{geo} + (1-\omega_{zeo})\ q_{CO_2}^{zeo}$$



sodium based geop. composite
$NaG_{1.2}$+Na13X



- Nucleation of NaA + filler Na13X (27 wt.%)

Lower mechanical strength

- Modal pore Ø = 1.47 µm

GEopolymer based Adsorbents

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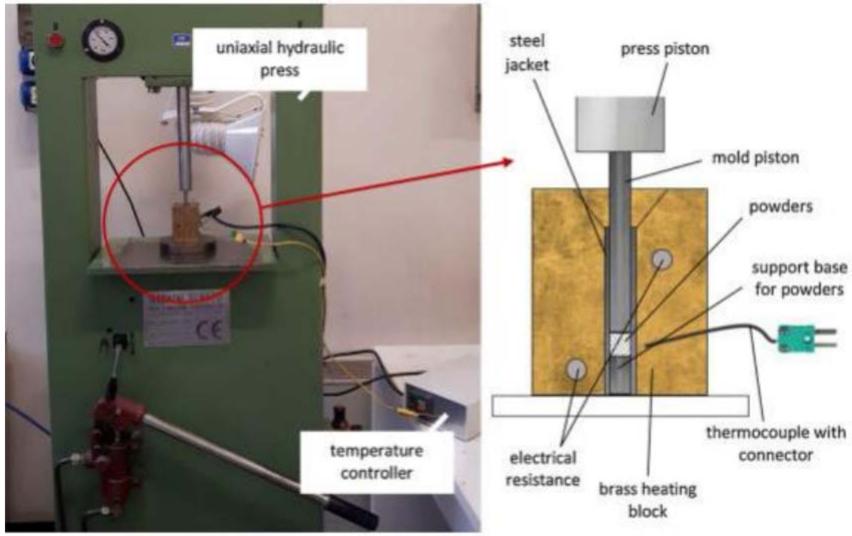
geopolymer composites (cold sintered - CSP)

composite monoliths are also obtained by **cold sintering** geopolymer and zeolite powders:

- ✓ compression @ P = 56 or 168 MPa and T= 40°C
- ✓ re-activation with **KOH or NaOH 4M**



K-G_2 (<200 μm)

+

commercial Na13X
or
Na$G_{1.2}$ (81% NaA)

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geopolymer composites (cold sintered - CSP)

K-G_2 (<200 μm)

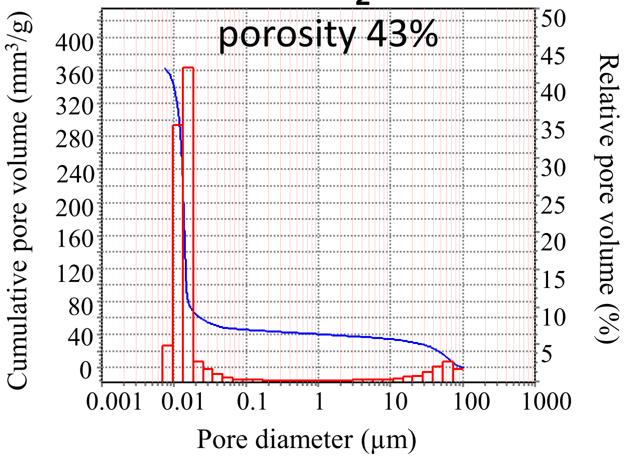
+

commercial Na13X

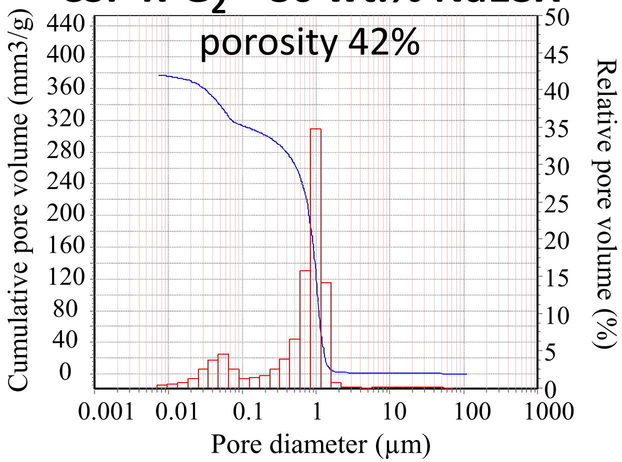
56 MPa
40°C
NaOH 4M

- ✓ disappearance of the ultra macropores
- ✓ bimodal distribution

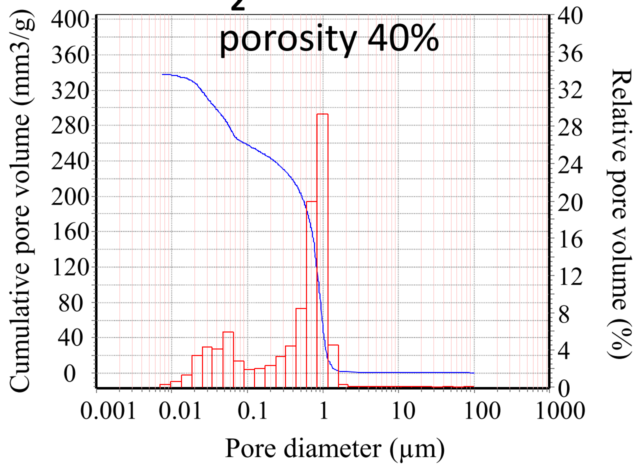
K-G_2



CSP K-G_2 + 80 wt.% Na13X



CSP K-G_2 + 70 wt.% Na13X



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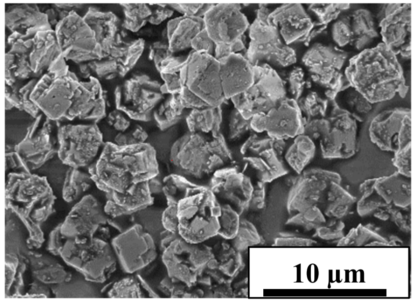
geopolymer composites (cold sintered - CSP)

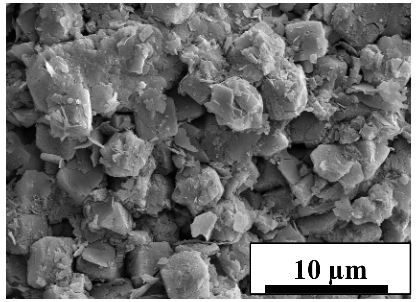
K-G_2 (<200 µm)

+

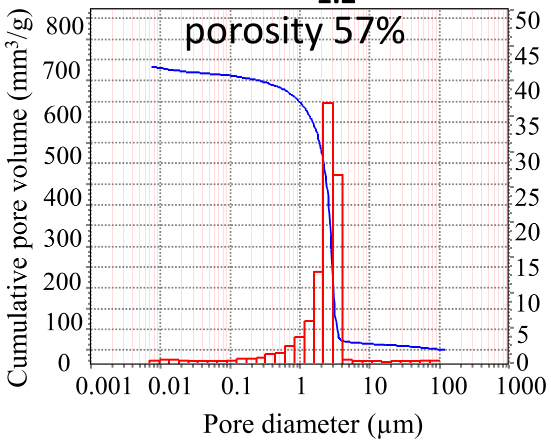


$NaG_{1.2}$ (81% NaA) (<200 µm)

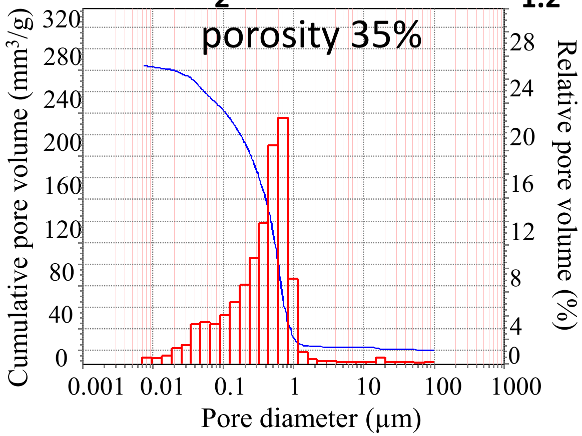
56 MPa
40°C
NaOH 4M



$NaG_{1.2}$



CSP K-G_2 + 90 wt.% $NaG_{1.2}$



- ✓ the geopolymer matrix, in the CSP composite, is more cohesive
- ✓ decrease of total porosity
- ✓ decrease of the average pore size
- ✓ broad pore size distribution

GEopolymer based Adsorbents

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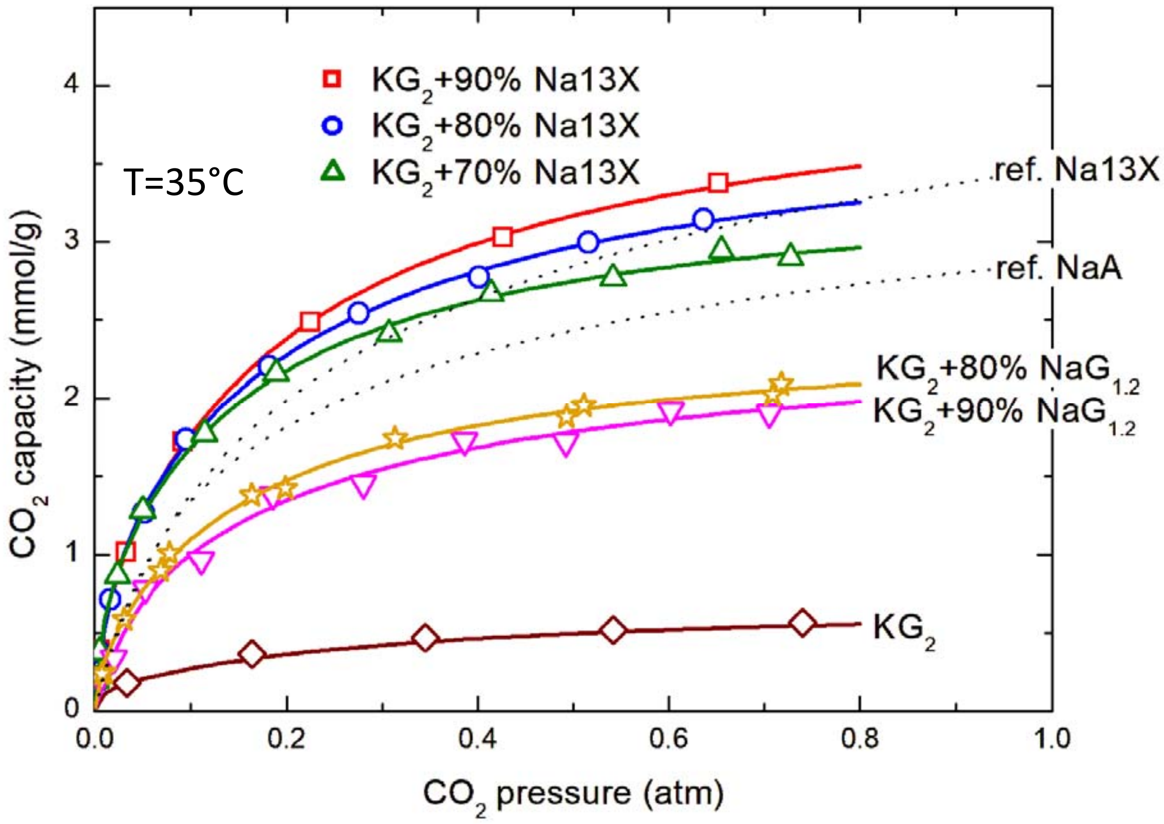
geopolymer composites (cold sintered - CSP)

cold sintering process allows:

- ✓ the re-use of waste material (e.g. KG_2 powder)
- ✓ the formation of monoliths to be used in adsorption processes (geop. as **binders**)
- ✓ the enhancement of the overall gas adsorption, thanks to **basic re-activation**



GEopolymer based Adsorbents

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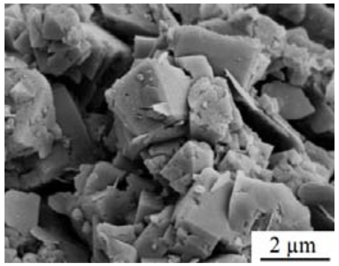
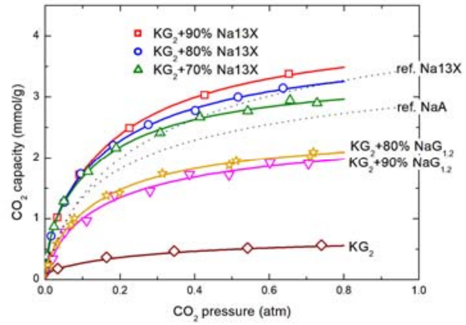
conclusions

geopolymers are characterized by an interesting potential for CO_2 capture application:

- ✓ ease of fabrication and processing (mild conditions synthesis);
- ✓ they can be readily shaped in **monoliths** or pellets;



- ✓ gas adsorption properties are **tunable**, playing with chemistry or fabricating composites, reaching good performances



- ✓ **cold sintering process** is a promising pathway to produce composites with improved sorption capacity.

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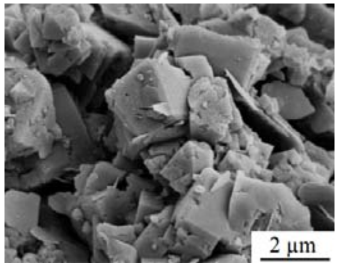

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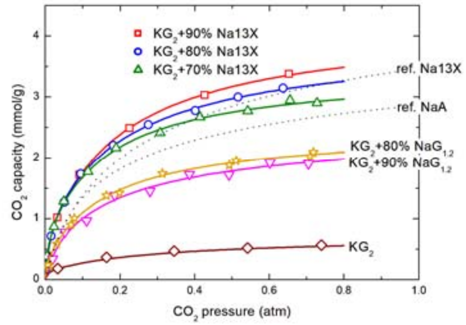

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GEopolymer based Adsorbents

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acknowledgments

National Recovery and Resilience Plan
PNRR

Mission 4 “Education and Research” - Component C2

Investment 1.1 “Fund for the National Research Program and Projects of Significant National Interest (PRIN)”

Ministero dell'Università e della Ricerca

Bando PRIN 2022

GEopolymer based Adsorbents

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

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Thank you

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