

Textural Properties of Waste Marble Powder Samples Used as Cheap CaO-based Sorbents for Calcium Looping Cycle CO₂ Capture Process



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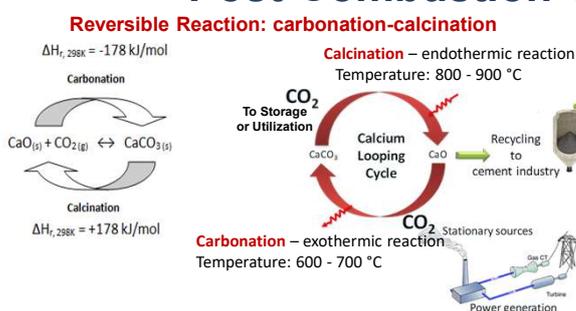
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Introduction

The high volume of marble production is associated with considerable amounts of **natural waste marble powder (WMP)** generated as by-product during cutting and polishing procedures, that negatively impacts the surrounding environment. We demonstrated recently the ability of WMP to be used as possible cheap and effective CaO-based sorbents with high carrying capacity efficiency upon Ca-looping cycle CO₂ post-combustion capture process.

Post-Combustion Calcium Looping Technology



- To investigate the evolution of the textural properties of WMP samples used as CaO-based sorbents in the Ca-looping cycle CO₂ capture, with multiple cycles of carbonation-calcination.

Efficient sorbents for Ca Looping: challenges!

- High adsorption capacity,
- High selectivity,
- High calcium oxide content,
- Non deactivating cyclic operation,
- Good mechanical resistance to attrition,
- Economically viable!

Marble is a CaCO₃-based rock and important natural resource in Portugal!



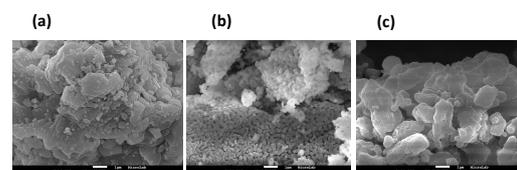
Nearly 20% of the total weight of the marble processed results into WMP!

WMP sorbents from 2 different portuguese marble producers

Chemical elemental composition of the fresh non calcined WMP_α and WMP_β sorbents dried at 120 °C

Fresh Sorbent	Element Content (weight %)					
	Si	Ca	Mg	Al	Fe	C
WMP _α	1.2	38	0.5	0.9	0.06	11.8
WMP _β	0.51	38.5	0.37	0.06	0.05	11.9

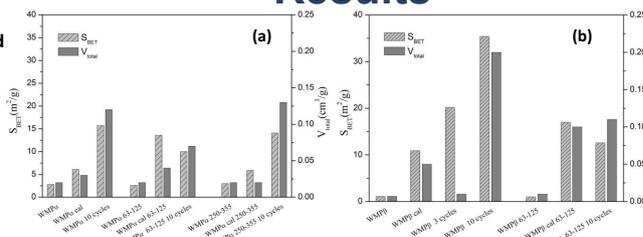
Marble powder is mainly a CaCO₃ based sorbent: Ca_{0.98}Mg_{0.02}CO₃
 Other components present in lower quantities: Fe₂O₃ + Al₂O₃ + SiO₂



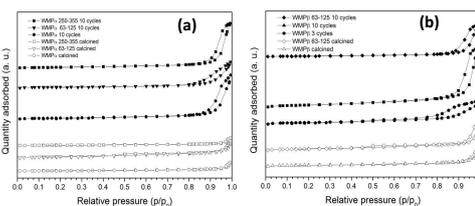
SEM images (in 1 μm scale) of sorbent WMP_α: (a) fresh dried at 120 °C, (b) fresh calcined at 850 °C, and (c) used after 10 cycles carbonation-calcination.

Samples of WMP CaO-based sorbents studied

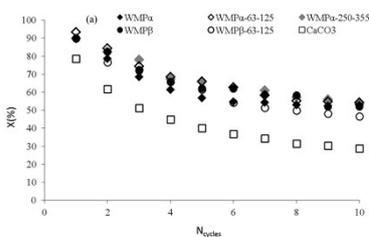
WMP _α	Non differentiated particle sizes
WMP _α 63-125	63 μm < Particle sizes < 125 μm
WMP _α 250-355	250 μm < Particle sizes < 355 μm
WMP _β	Non differentiated particle sizes
WMP _β 63-125	63 μm < Particle sizes < 125 μm



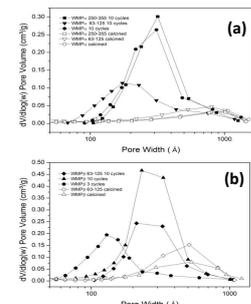
Comparison of the textural properties of the different samples of: (a) WMP_α sorbents, and (b) WMP_β sorbents.



N₂ sorption isotherms for the samples of fresh calcined and used sorbents: (a) WMP_α sorbents, and (b) WMP_β sorbents.



Carbonation conversion (X) of the WMP and commercial CaCO₃ sorbents with the number of cycles of carbonation-calcination (Ncycles).



PSD from BJH desorption branch for the samples of fresh calcined and used sorbents: (a) WMP_α and (b) WMP_β.

Conclusions

- During the carbonation-calcination cycling process of the WMP, there is an increase of the pore volume (V_p) (not including macropores) mainly because of the formation of mesopores with smaller pores average width (d_p) than in the initial fresh calcined sorbents, which can explain the unexpected result for WMP sorbents with non-differentiated particle sizes WMP_α and WMP_β and with the higher range particle sizes WMP_α-250-355: along with a significant increase of the BET surface area (S_{BET}) and mesopore volume with smaller pores, observed with the increasing number of cycles, there is a decrease of the CaO carbonation conversion.
- Possible explanation: there is a deactivation mechanism of blocking of the small narrow bottleneck pore mouths, by the formation of CaCO₃ with density significantly lower than that of CaO during the fast stage of the CaO carbonation step at a pore mouth, which makes the CaO sites inside the pores unavailable for the progress of the reaction with CO₂ during carbonation.

References

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- Carla I.C. Pinheiro, Auguste Fernandes, Cátia Freitas, Edgar T. Santos, Maria F. Ribeiro, *Ind. Eng. Chem. Res.* 55 (29) (2016) 7860-7872.

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