CO_2 Sorption Capacity and Cyclic Performance of Quicklime (CaO) Under Gasification conditions

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Introduction

Sorption-enhanced gasification (SEG) is a promising technology based on the use of Ca-based sorbents (e.g., limestone, $CaCO_3$) to selectively remove CO_2 from the gasification environment for production of H_2-rich syngas.[1]

- Steam is used as the gasification agent, and
- *In situ* removal of CO_2, both leading to a H_2-rich syngas production *via* WGS reaction.[2]

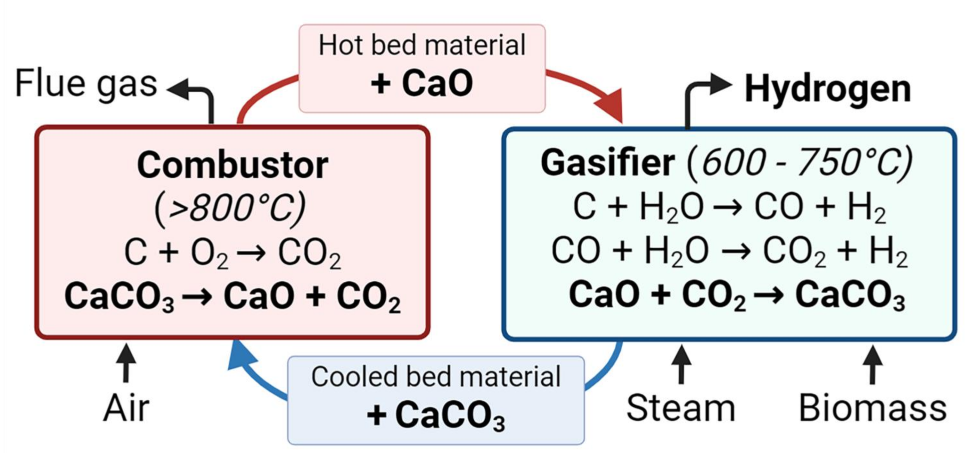


Fig 1. Simplified scheme for SEG in dual fluidized bed.

Experimental

Table 1. Key operating parameters for carbonation at simulated gasification conditions.

Carbonation of CaO (calcination at 950°C in 100% N_2)					
	Feed gas composition (*vol. %*)				
Condition	N_2	CO_2	Steam	CO	H_2
dry	80	20	-	-	-
dry CO	70	20	-	10	-
dry H_2	70	20	-	-	10
wet	30	20	50	-	-
wet CO	20	20	50	10	-
wet H_2	20	20	50	-	10

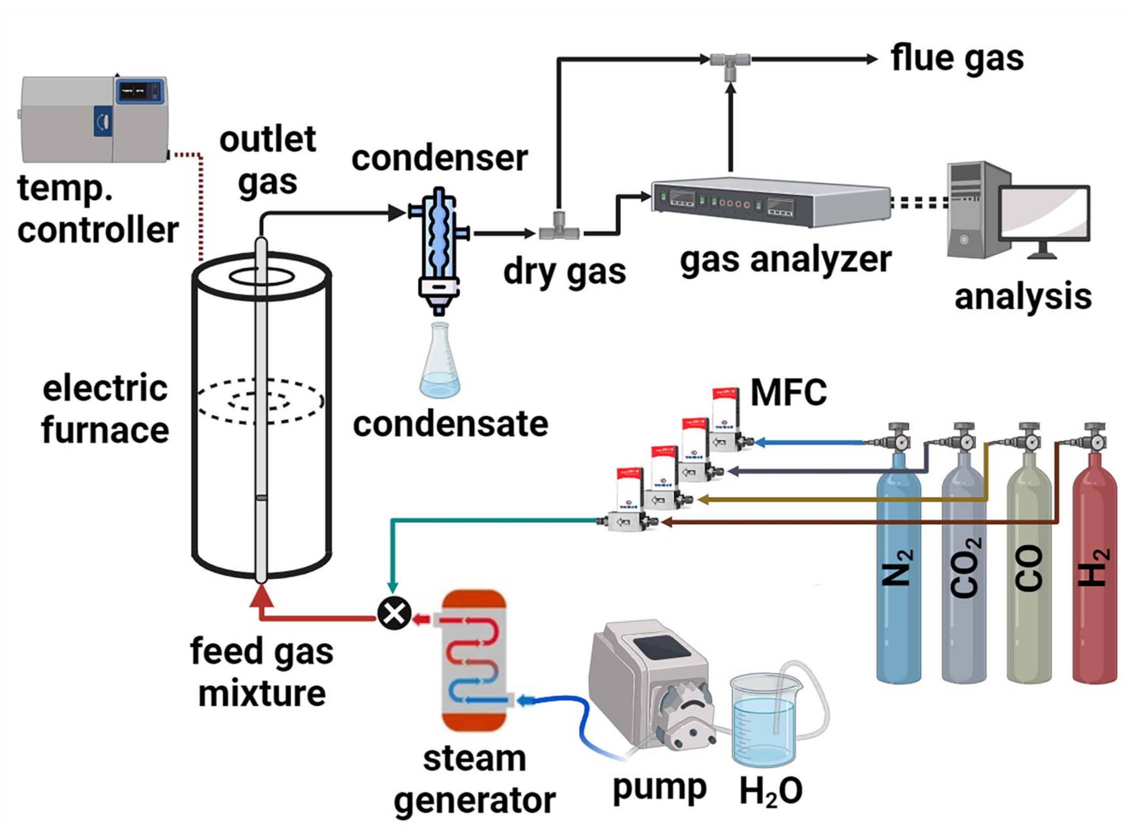


Fig 2. Schematic illustration of the experimental setup.

Results : CO_2 sorption tests and Characterizations

Effects of Carbonation Temperature

- CO_2 sorption performance increases with T up to a certain limit (Fig. 3 A & B).
- Further increase drives decarbonation due to thermodynamic limitations.
- At a given T, if $P_{CO_2} > P_{eq}$: carbonation takes place and vice versa.[3]
- Due to equilibrium of CaO-CO_2, gasification temperature is limited to 720°C for SEG.[4]

Effects of Steam Addition

- Steam enhances CO_2 sorption performance, both in steam-added carbonation or with *ex situ* steam hydration (Fig. 3 C & D).
- Steam enhances carbonation rate during slow diffusion-controlled regime, with no apparent effect on fast reaction-controlled regime.[5]
- This beneficial effect of steam on CaO reactivity can be mostly attributed to more open microstructures (Fig. 5) and increased pore volume, leading to an improved solid-state diffusion of CO_2 through carbonate layer.[6-7]
- Steam increases residual activity, but also promotes sorbent decay due to sintering,[8] and elutriated fines/ fragmentation.

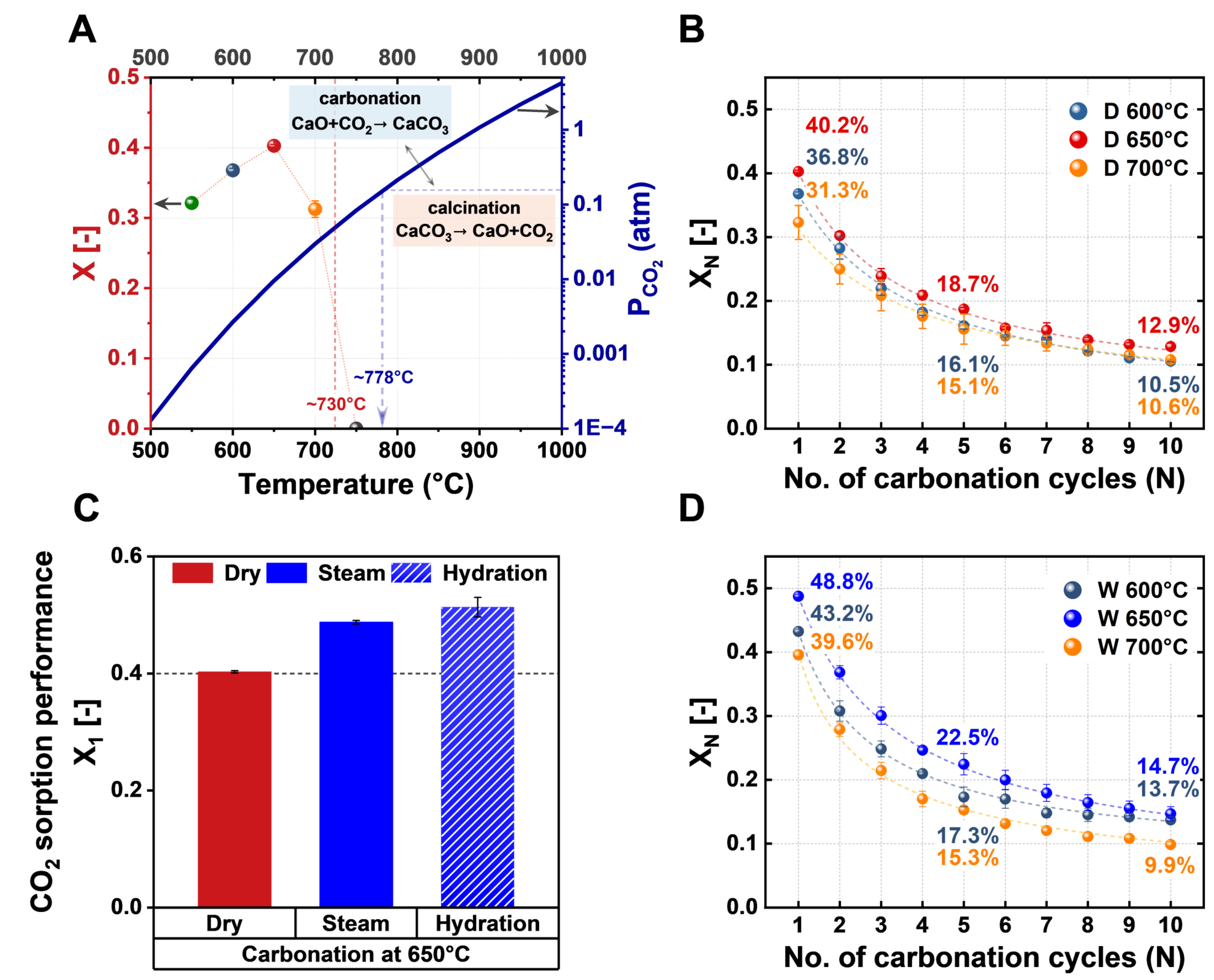


Fig 3. A) Effects of temperature on CO_2 sorption performance with respect to CaO-CO_2 equilibrium; **B)** Multicyclic carbonation at different temperatures at dry condition; **C)** Effects of steam addition and *ex situ* steam hydration on carbonation extent of CaO; **D)** Multicyclic carbonation at different temperatures at wet conditions.

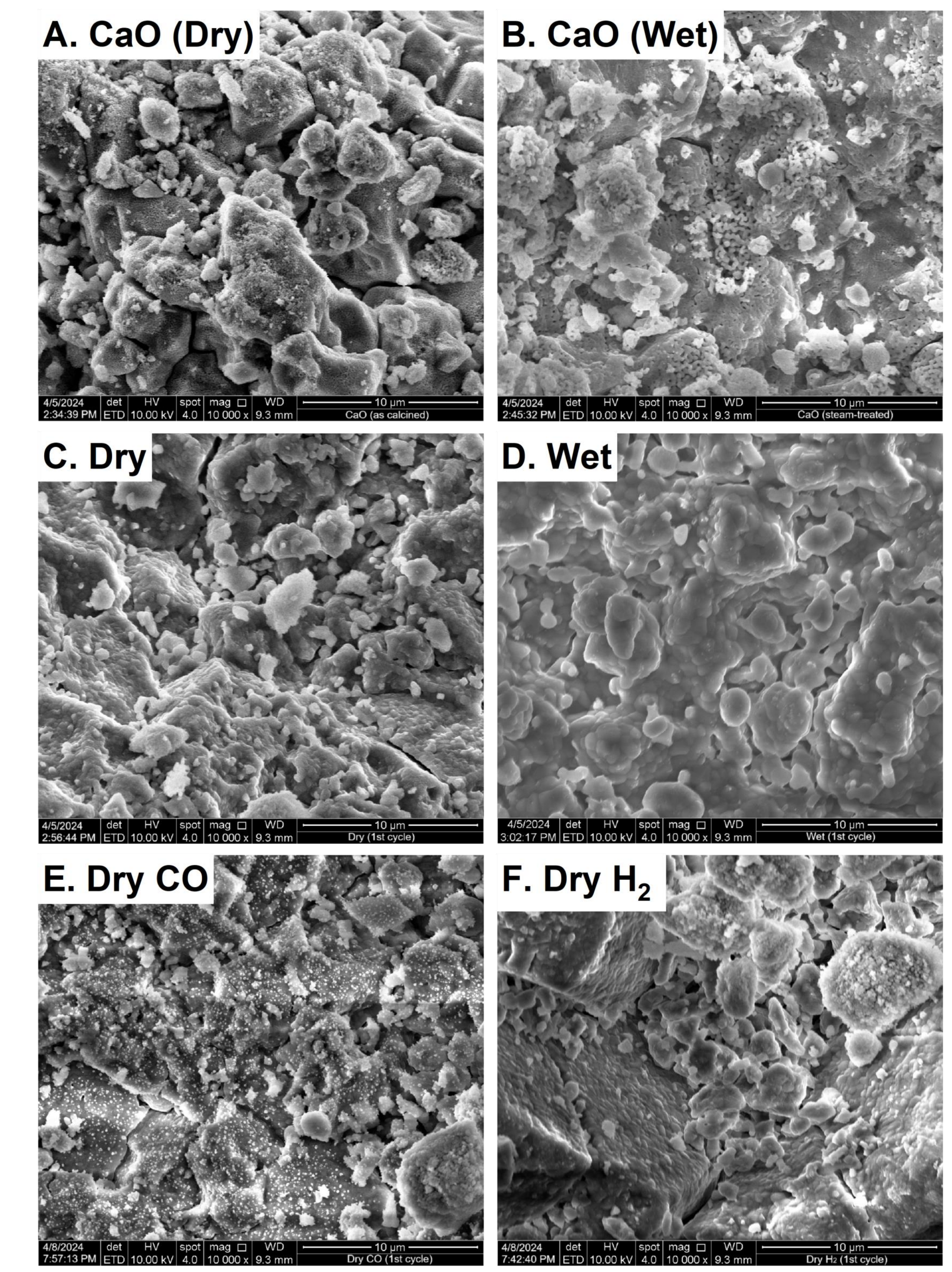
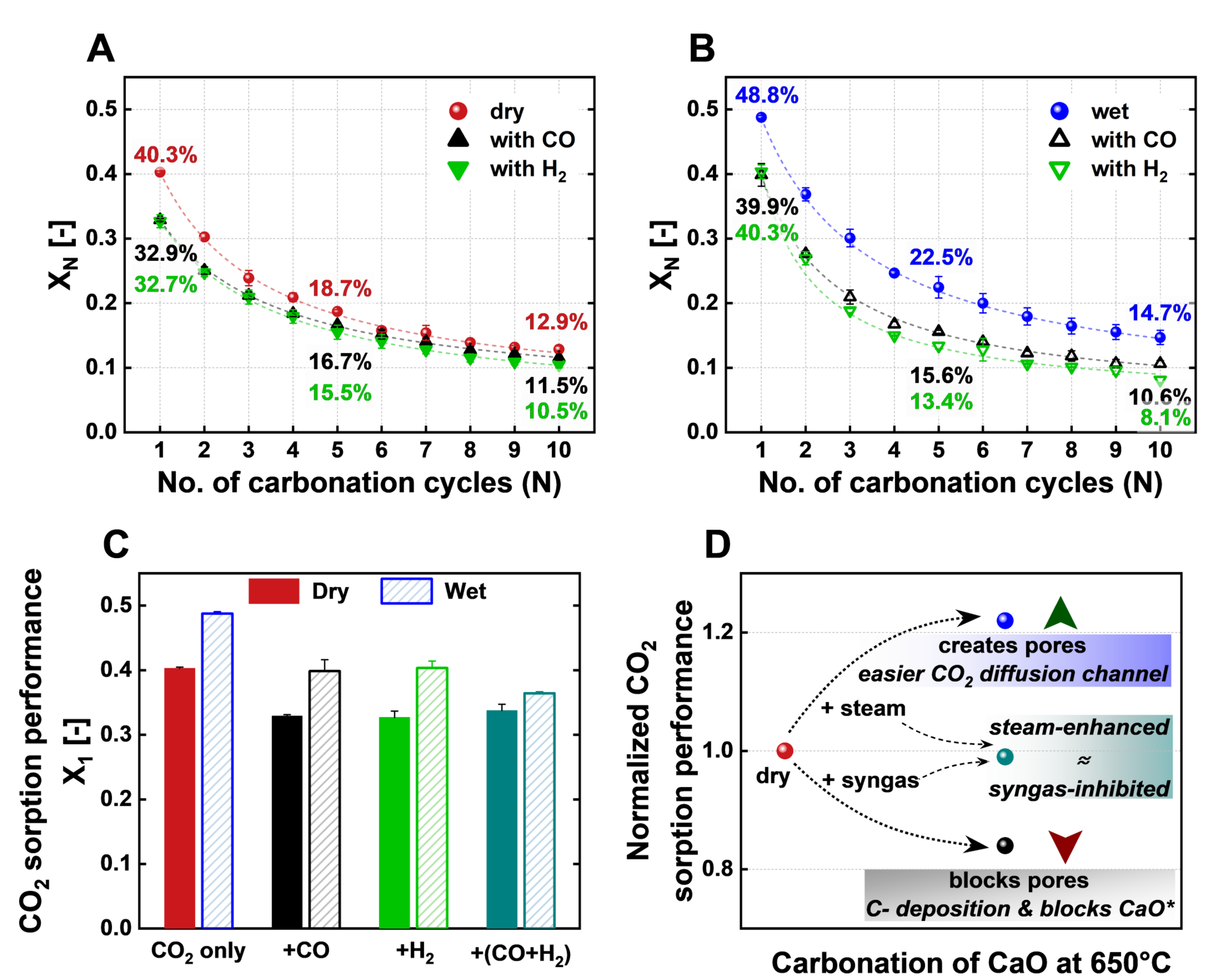


Fig 5. SEM micrographs **A)** calcined CaO; **B)** steam-treated CaO; after 1[st] carbonation with **C)** 20% CO_2; **D)** 20% CO_2, 50% steam; **E)** 20% CO_2, 10% CO; **F)** 20% CO_2, 10% H_2, balance N_2

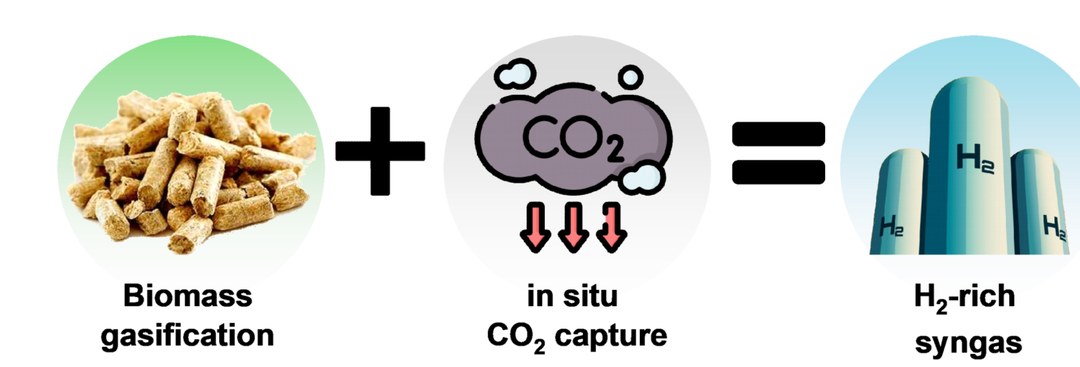


Effects of Syngas (CO/H_2) Addition

- CO_2 sorption performance decreases significantly with CO/H_2 addition (Fig. 4).
- Competitive adsorption of CO/H_2 at available CaO active sites (CaO*).
- Visible carbon deposits (2CO → C + CO_2), leading to possible CaO* and pore blockage.
- Particles formed aggregates, resulting in a loss of surface area for CO_2 adsorption (Fig. 5).
- Steam-enhanced and syngas-inhibitory effects balance out in presence of both.

Fig 4. Multicyclic carbonation performance in presence of CO and H_2 at **A)** dry conditions and **B)** wet conditions at 650°C; **C)** Comparison of initial CO_2 sorption activity of CaO at different conditions; **D)** Illustration of combined effect(s) of steam and syngas (CO & H_2) addition during carbonation.

Conclusions



- Carbonation temperature needs to be limited to 700°C to enhance CO_2 sorption performance.
- CO_2 sorption is positively affected by steam, which improves micropore structures of CaO and increases pore volume, thereby facilitating solid-state CO_2 diffusion.
- Syngas limits CO_2 sorption due to competitive adsorption and sorbent coking, leading to CaO* and pore blockage.
- Sorbent decay is more pronounced with steam, which is further intensified in the presence of syngas.

References

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Acknowledgments

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