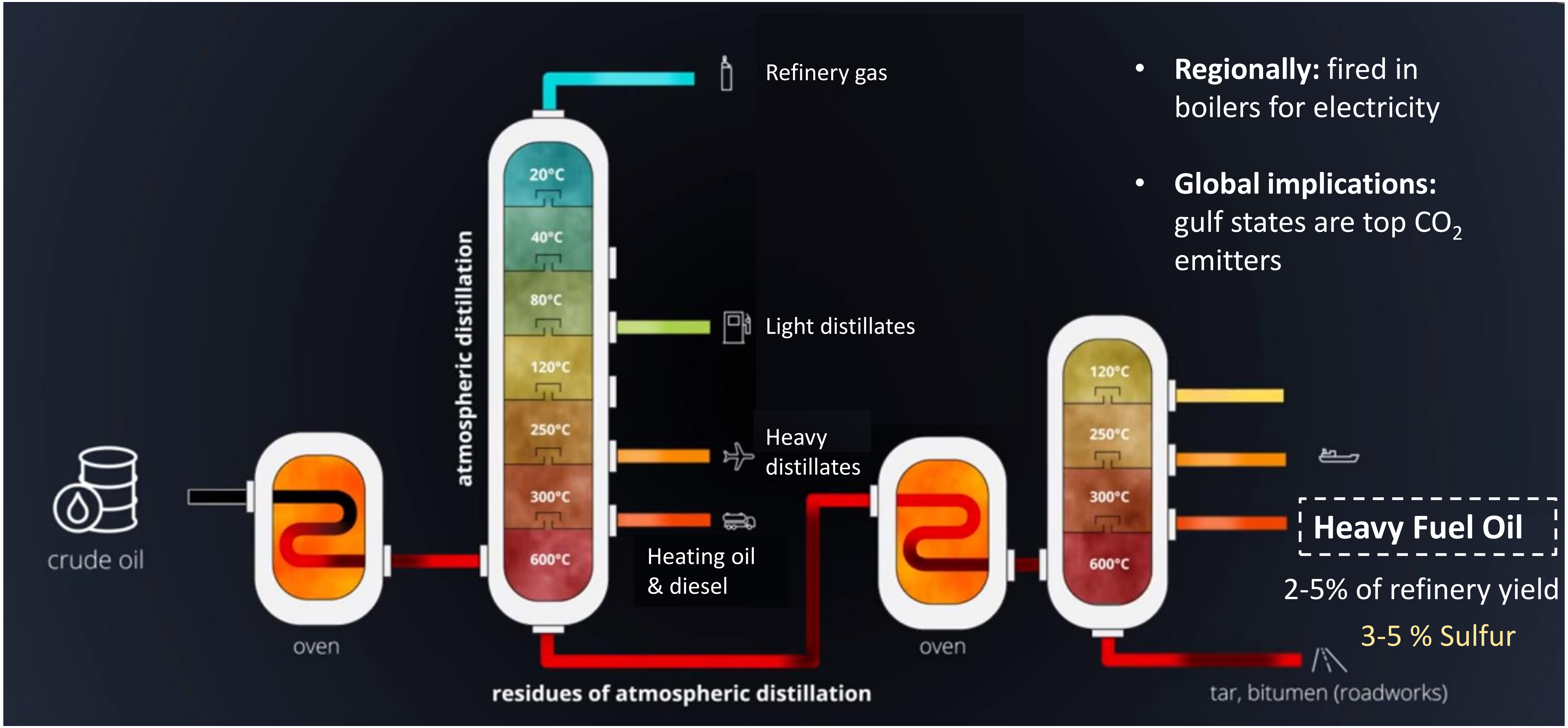
Calcium Looping Implementation at Heavy Fuel Oil-Fired Power Plants: The Effect of Calcination/Carbonation Cycles on SO_2 & CO_2 Co-Capture By Two Structurally Distinct Limestones

Sally L. Homsy & Robert W. Dibble

Heavy fuel oil (HFO) is a low cost residual petroleum distillation byproduct



- **Regionally:** fired in boilers for electricity
- **Global implications:** gulf states are top CO_2 emitters

Saudi Arabia is 8th in emissions (4th per capita)

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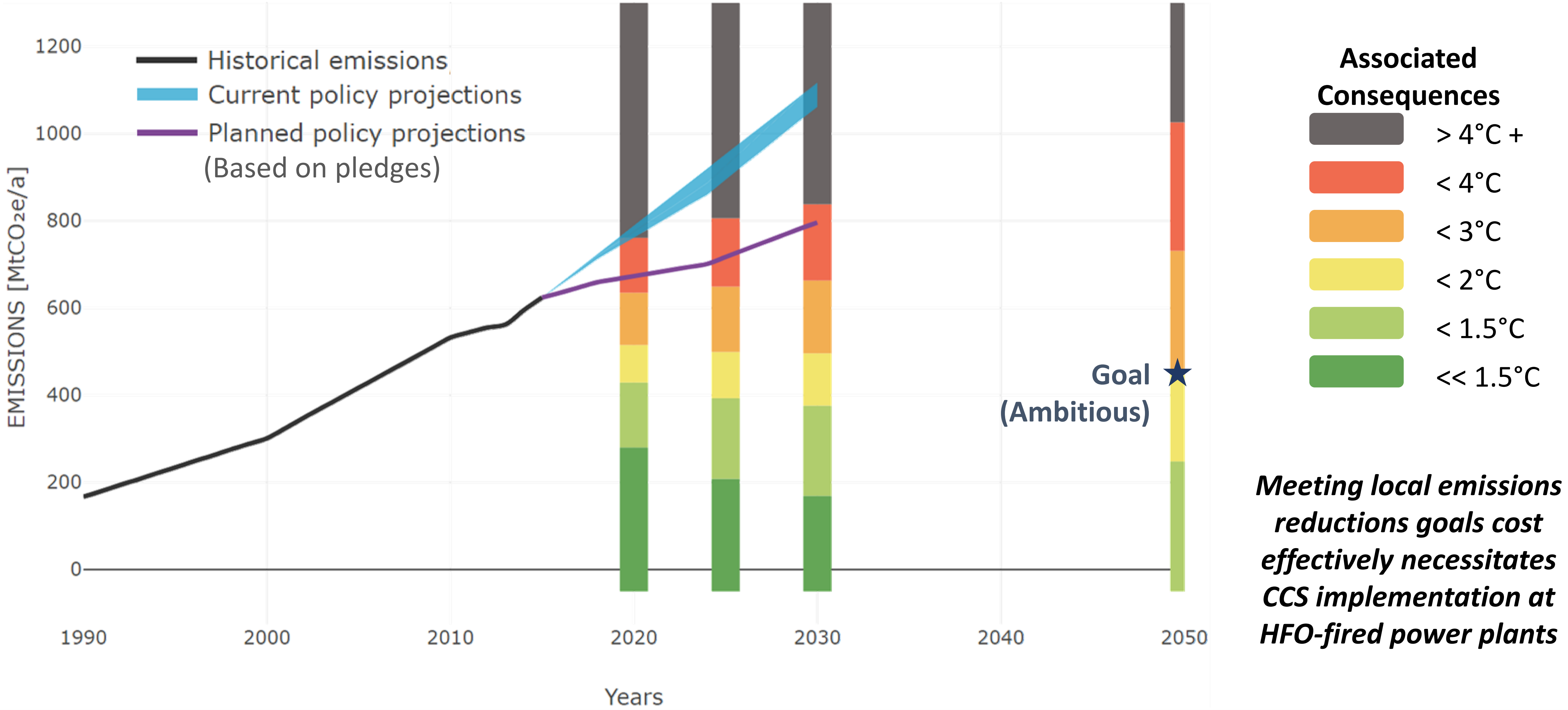

Meeting local emissions reductions goals cost effectively necessitates CCS implementation at HFO-fired power plants

Climate Action Tracker , 2018

Calcium Looping is a 2nd generation post combustion CO_2 capture technology

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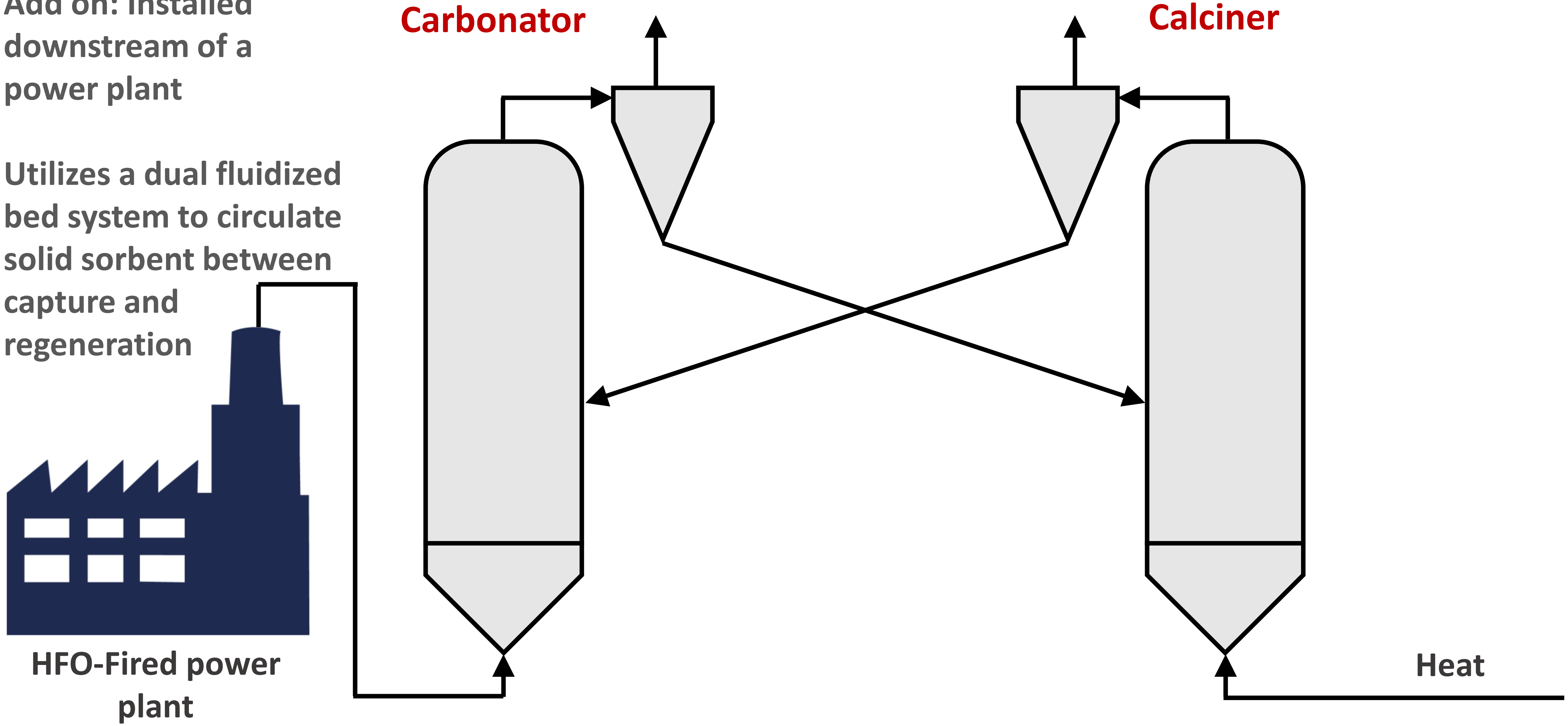
- **Add on: Installed downstream of a power plant**
- **Utilizes a dual fluidized bed system to circulate solid sorbent between capture and regeneration**



Calcium Looping is a 2nd generation post combustion CO_2 capture technology

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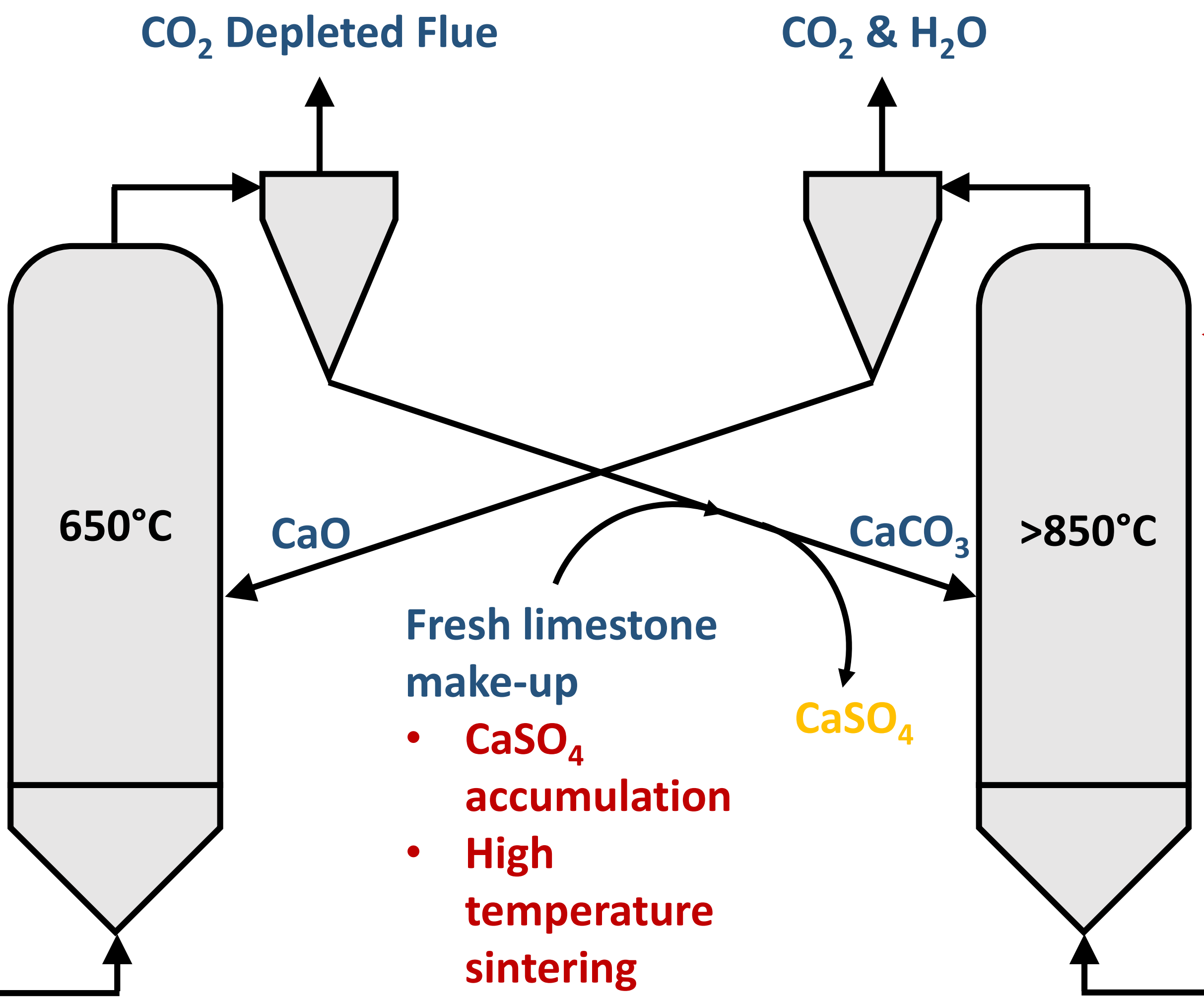
High temperature separation:

- heat recuperation post-separation
- Lower parasitic load

Carbonator

$CO_2 + CaO \rightarrow CaCO_3 + \Delta H$

$CaCO_3 + SO_2 \rightarrow CaSO_4 + \Delta H$



Calciner

$CaCO_3 + \Delta H \rightarrow CO_2 + CaO$

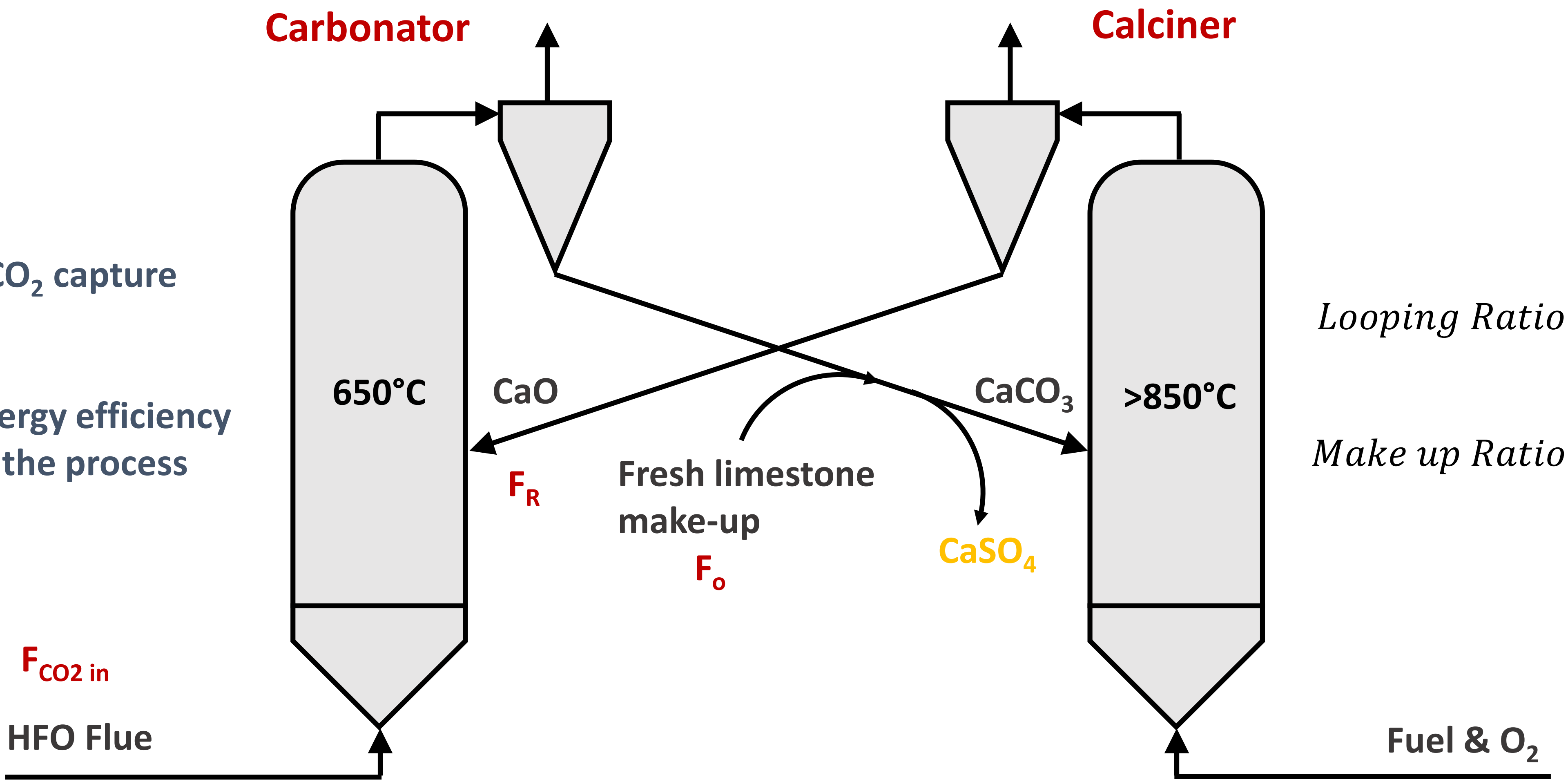
$CaCO_3 + SO_2 \rightarrow CaSO_4 + \Delta H$

HFO Flue gas:
12% CO_2
10% H_2O
2000 ppm SO_2

Fuel & O_2

Key process design parameters

- Maintain CO_2 capture efficiency
- Reduce energy efficiency penalty of the process



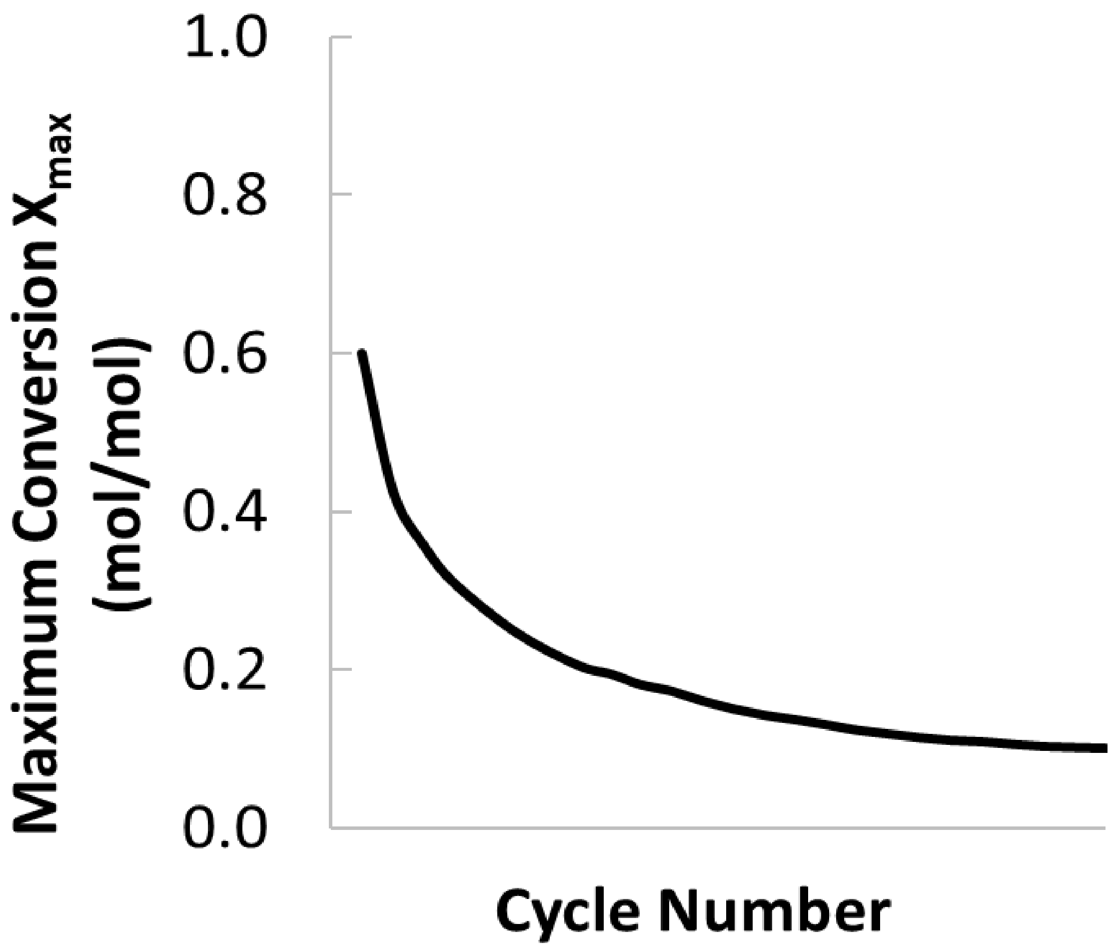
$$Looping\ Ratio = \frac{F_R}{F_{CO_2,\ in}}$$

$$Make\ up\ Ratio = \frac{F_o}{F_{CO_2,\ in}}$$

At typical optimal operation:

Sorbent inventory average "activity" typical maintained:

$0.6 > X_{max} > 0.1$



Presentation Overview

Examine the effect of Saudi limestone activity and $CaSO_4$ accumulation on CO_2 and SO_2 co-capture from synthetic HFO flue gas

Novelty:

1. Two structurally distinct limestone, from each of the two regions where Saudi limestone is mined: Further insight into the relationship between sorbent morphology and co-capture

2. Use of a fluidized bed system to study co-capture of SO_2 and CO_2 for limestone with different activities: Data is relevant for modeling a dual fluidized bed system

Saudi Arabian limestone

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Arabian Platform
“Riyadh” Limestone:

Red Sea Coastal Plain
“Saabar” Limestone:

SEM: Saudi Arabian limestone

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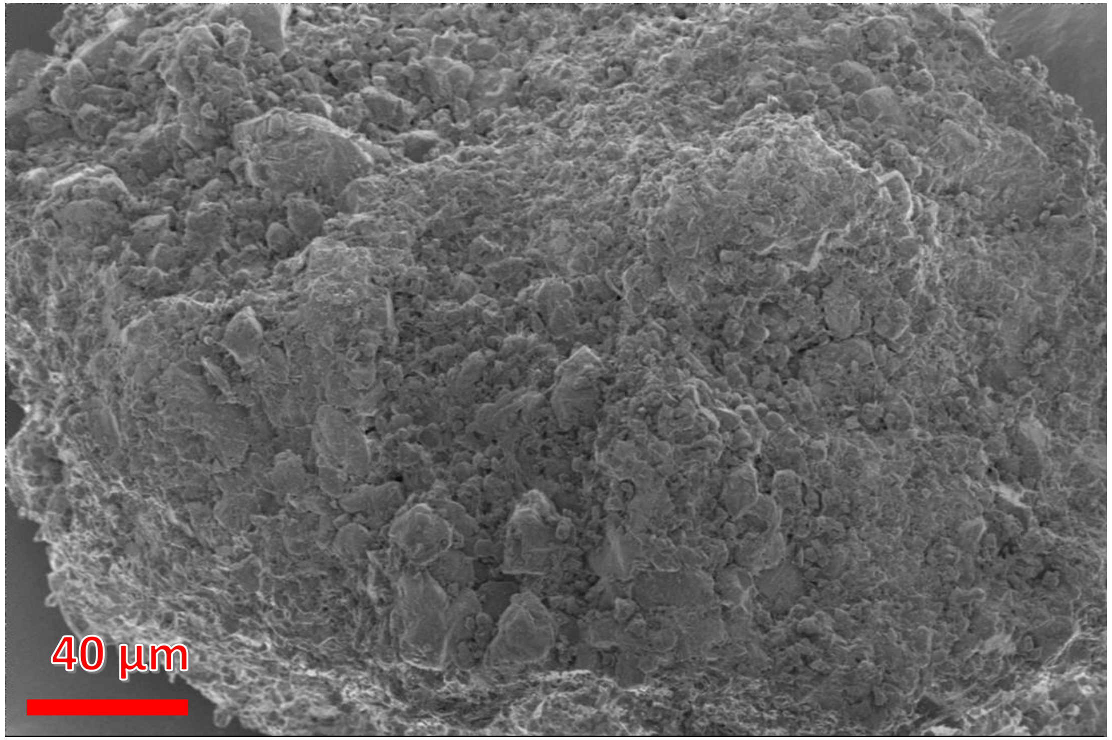
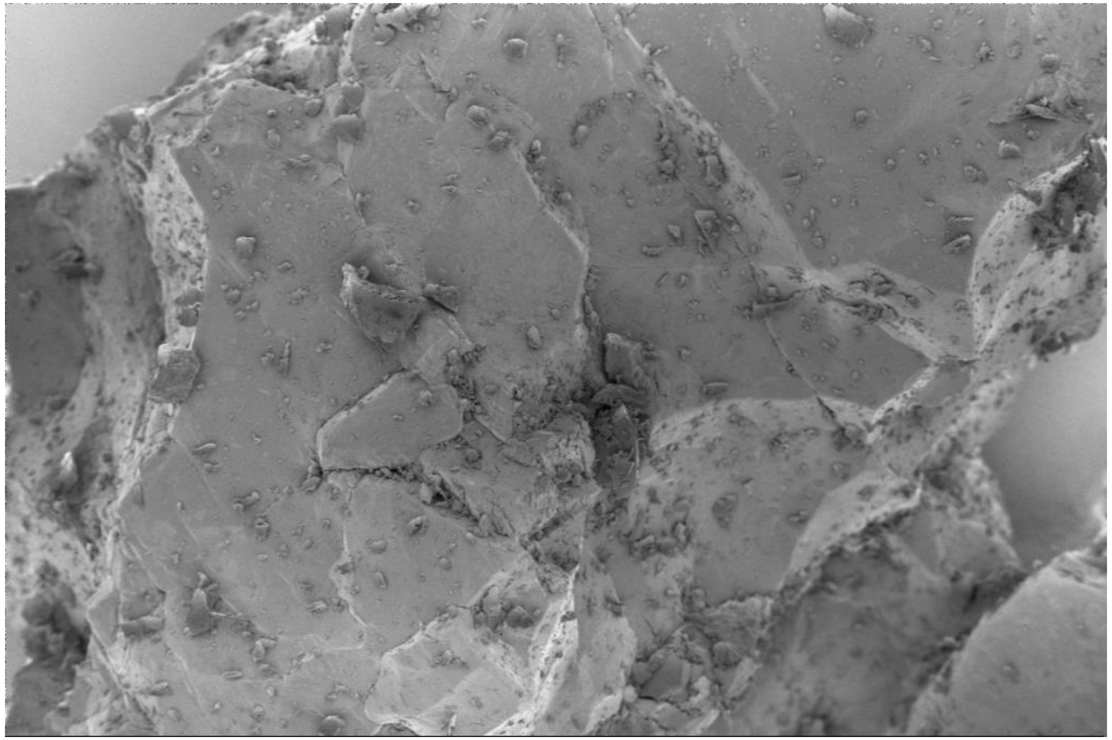
Riyadh Limestone:



Saabar Limestone:



XRF:

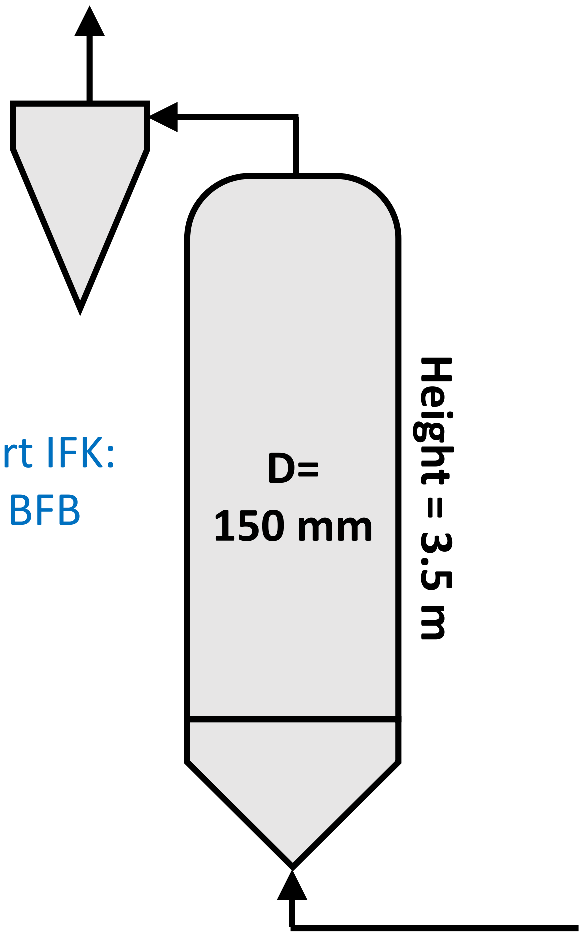
Riyadh: ~53.2% CaO, 2.0% SiO_2
~ 0.7% MgO, 0.55% Al_2O_3, 0.5% Fe_2O_3

Saabar: ~53.6% CaO, 2.1% SiO_2
~ 1.0% MgO, 0.23% Al_2O_3, 0.38% Fe_2O_3

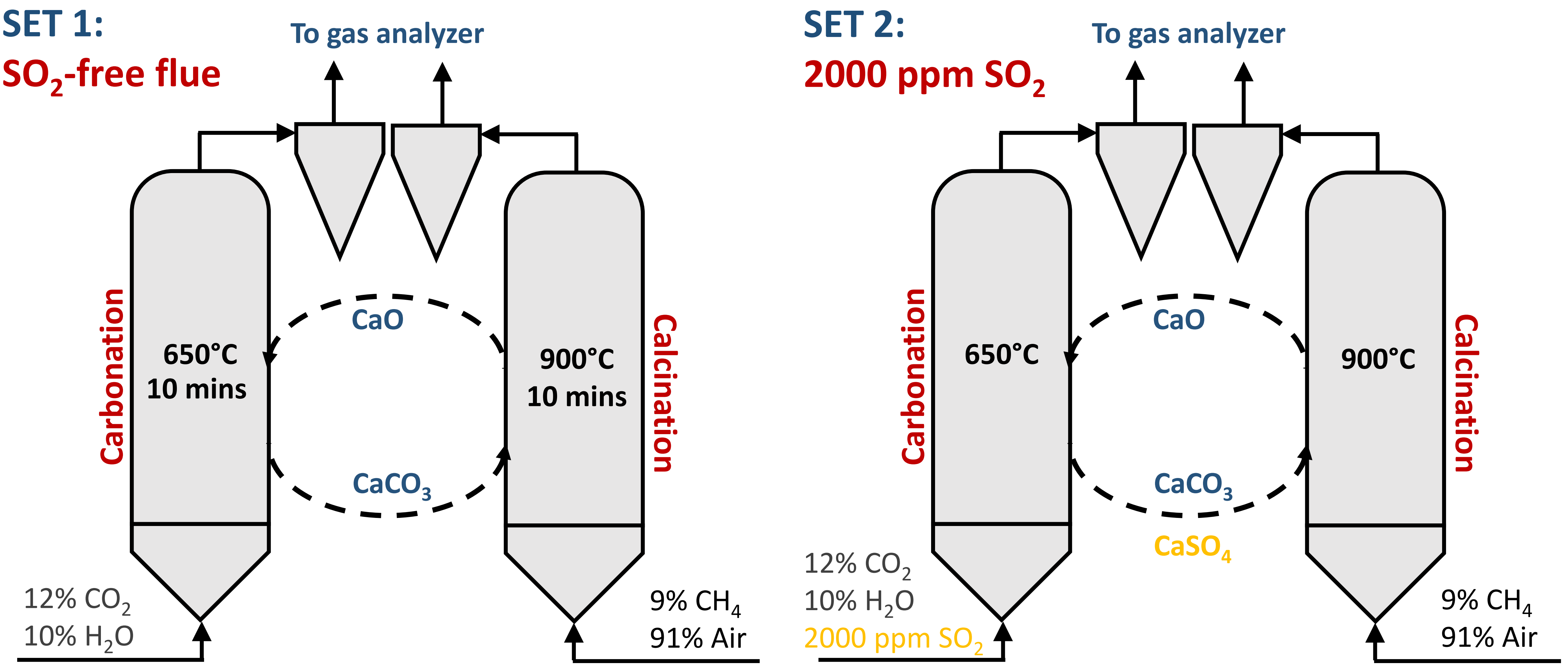
Similar CaO purity & impurity composition

Experimental Design: To obtain sorbent with different activities and $CaSO_4$ content

University of Stuttgart IFK:
electrically heated BFB



Experimental Design: To obtain sorbent with different activities and $CaSO_4$ content



Experimental Design:

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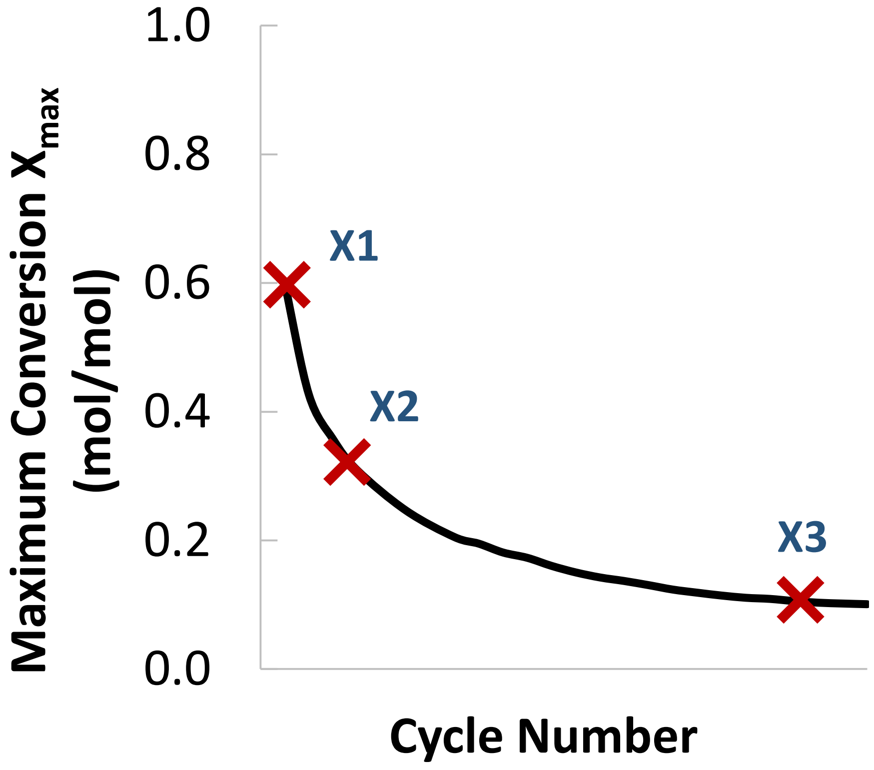
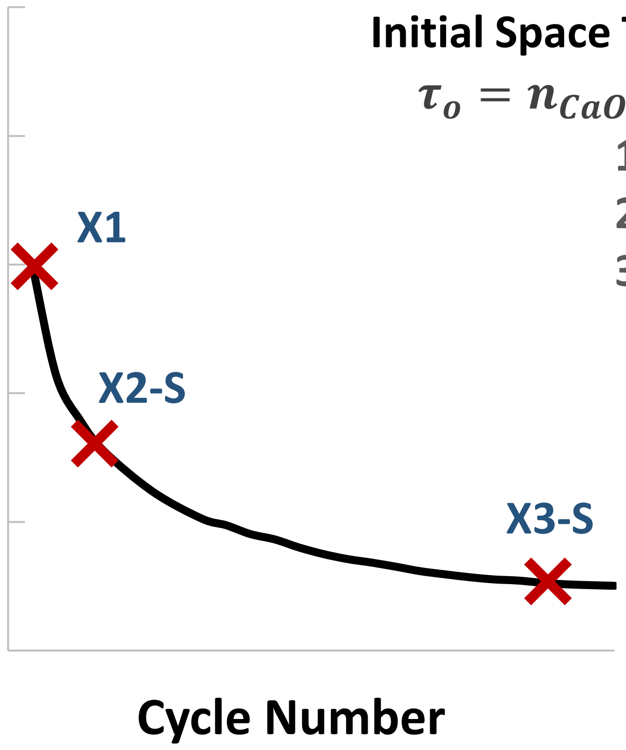
SET 1: SO_2-free flue



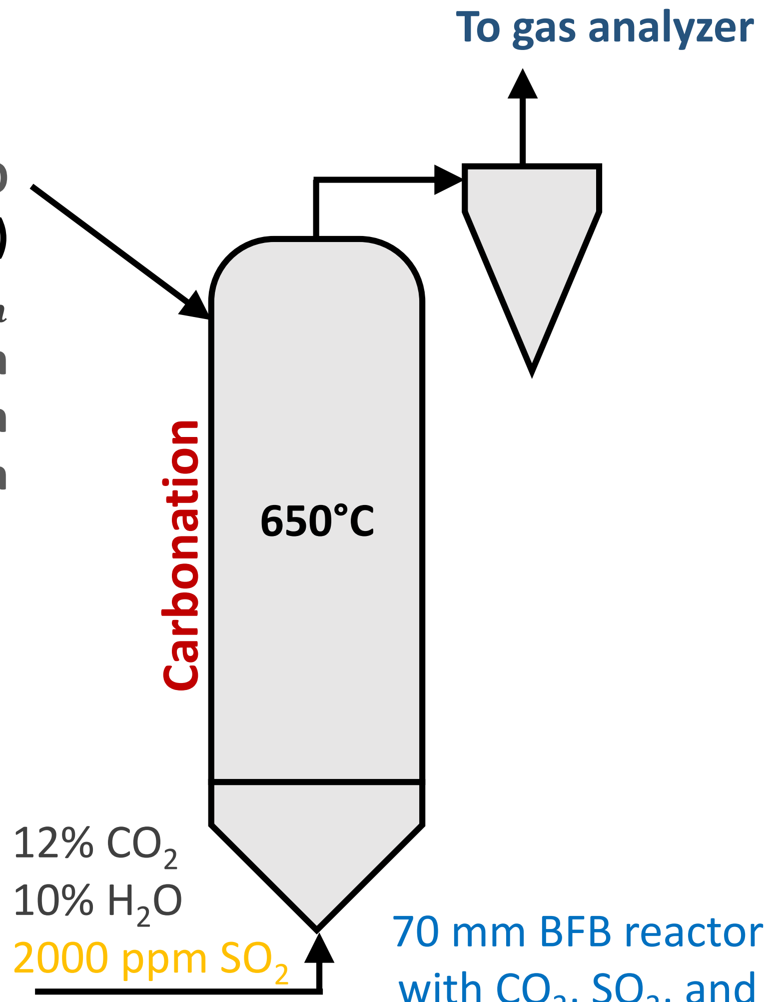
SET 2: With SO_2



Initial Space Time (min)

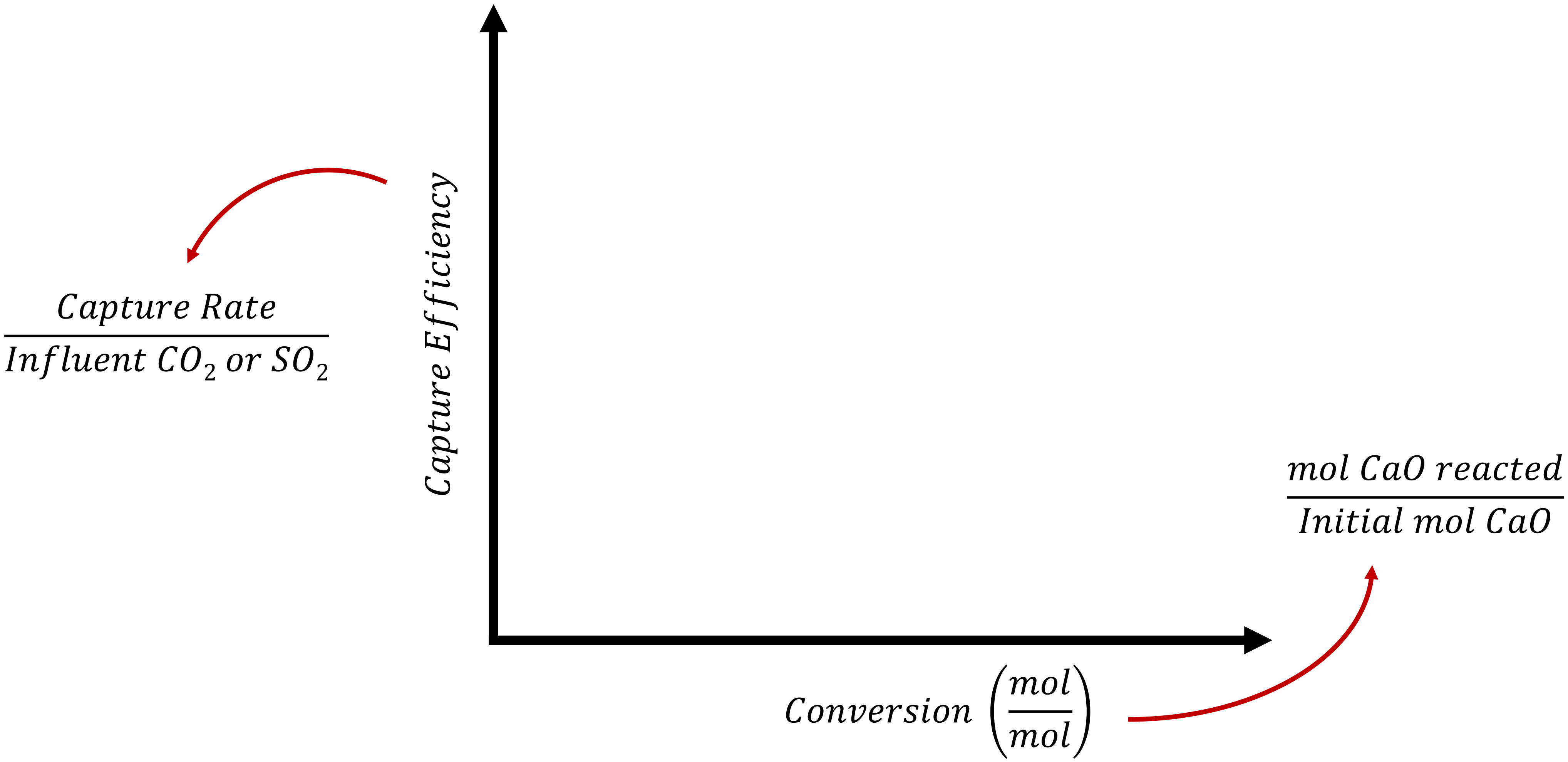
$$\tau_o = n_{CaO,in}/\dot{F}_{CO_2,in}$$

1- 0.90 min
2- 4.65 min
3- 9.30 min



70 mm BFB reactor with CO_2, SO_2, and O_2 gas analysis

Results: Visualizing the impact on capture rate relative to CaO Consumption



X1 Results: Riyadh sorbent exhibited greater overall conversion superior “fast” capture rate

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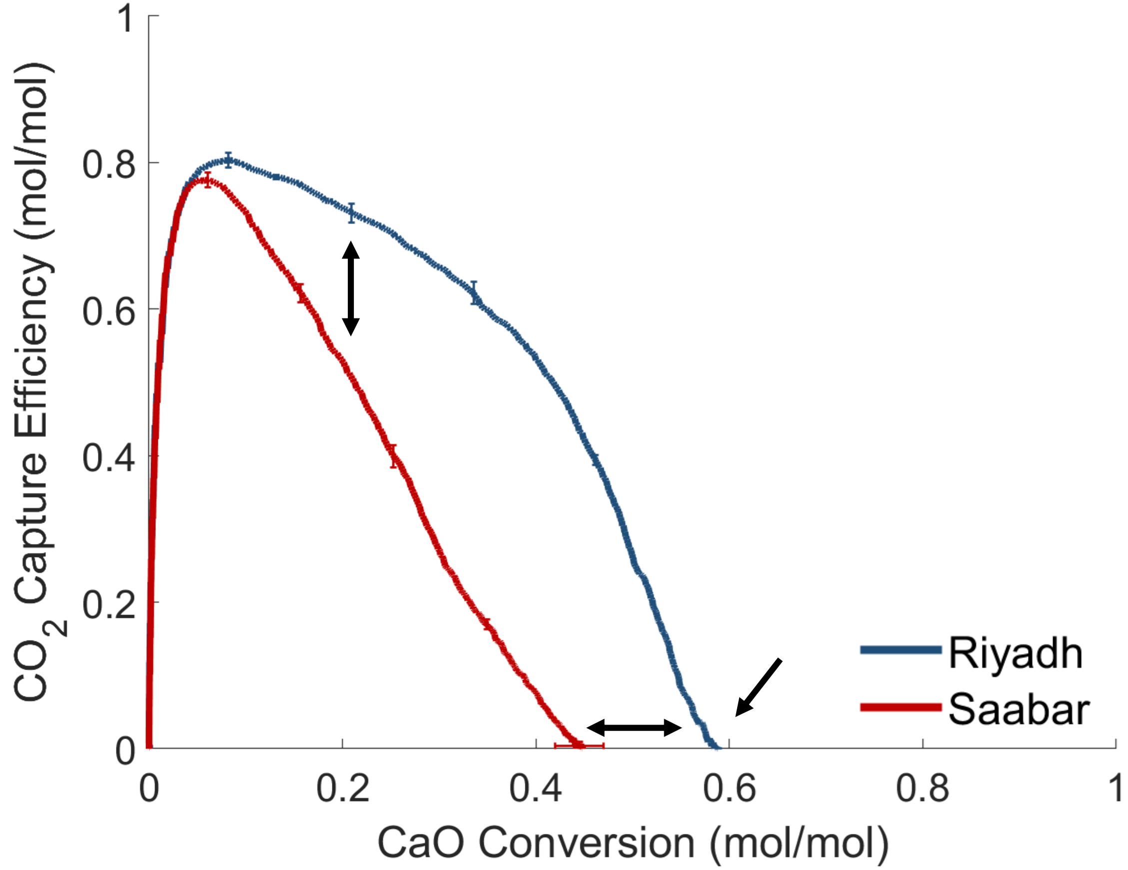
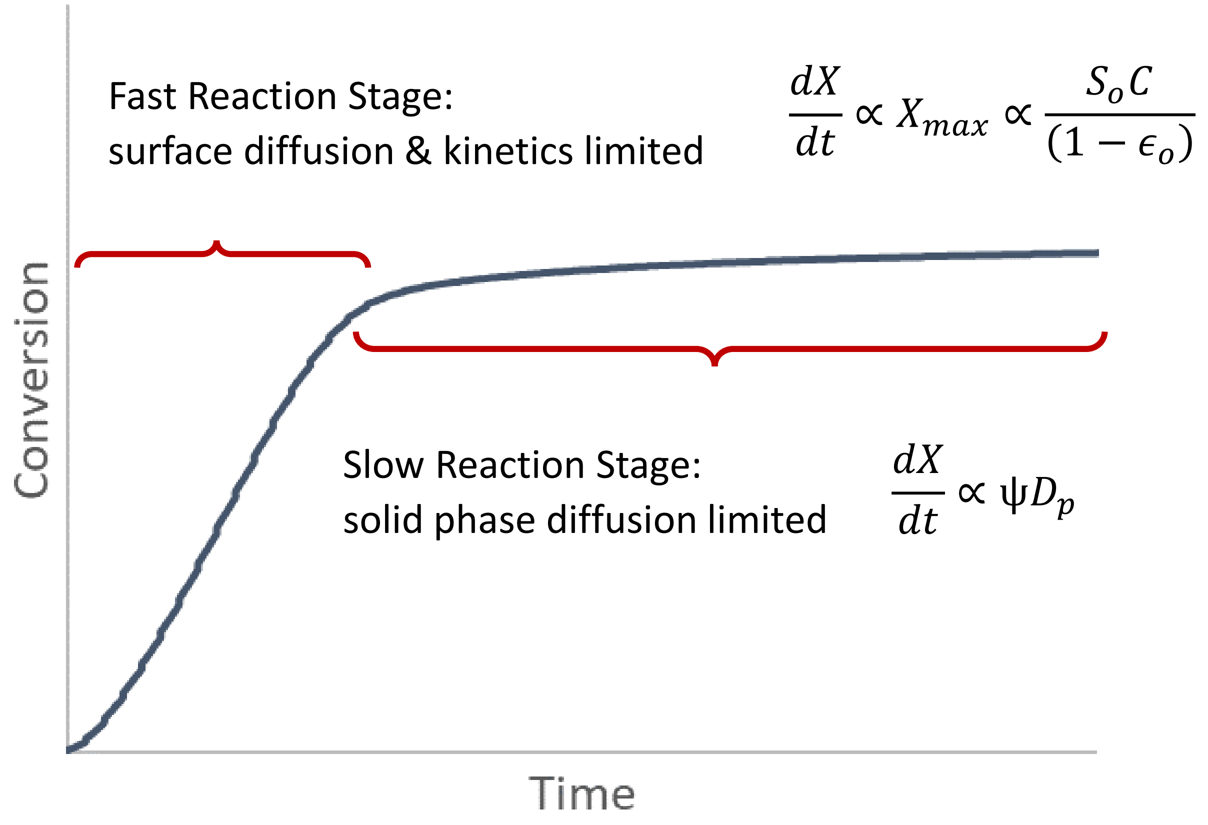
Relative CO_2 capture performance after one Calcination

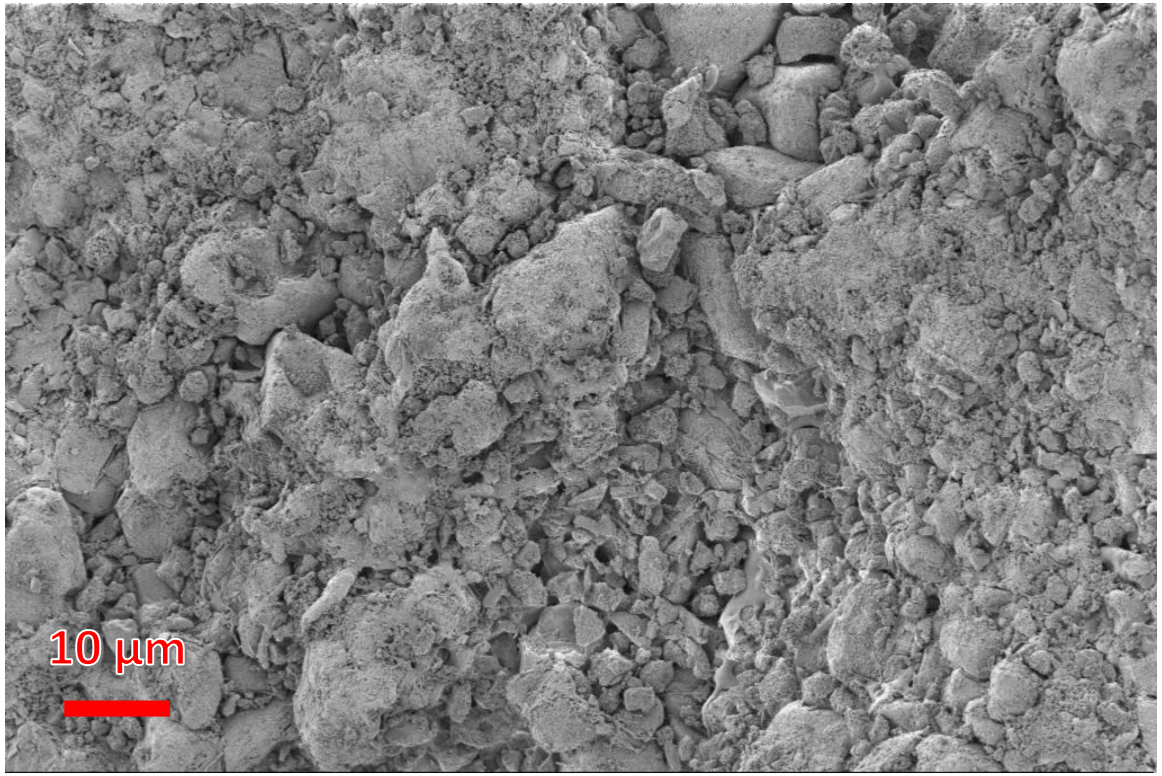


During CaL, residence times are maintained to ensure operation under fast reaction conditions

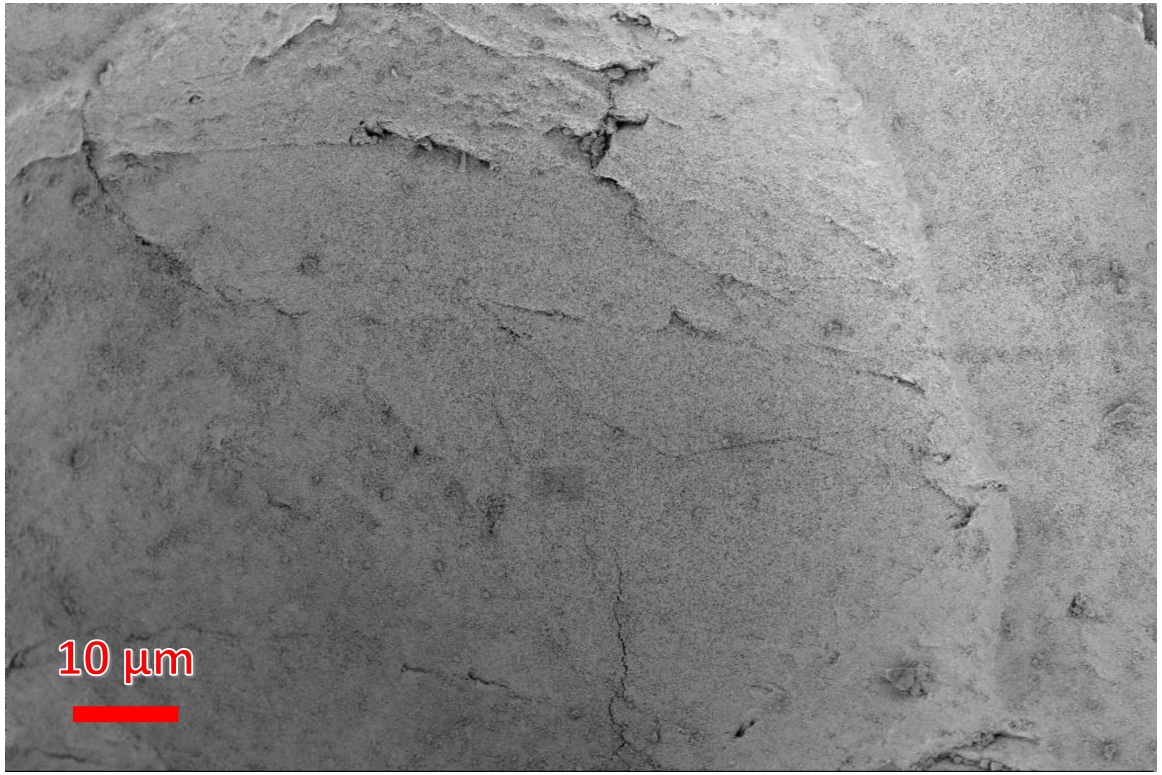


SEM: Riyadh sorbent has more structural defects & enhanced surface diffusion

X1 Riyadh Sorbent:



X1 Saabar Sorbent:



SET 1 Results: Both sorbents exhibit reduced CO_2 capture capacity and efficiency due to cycling

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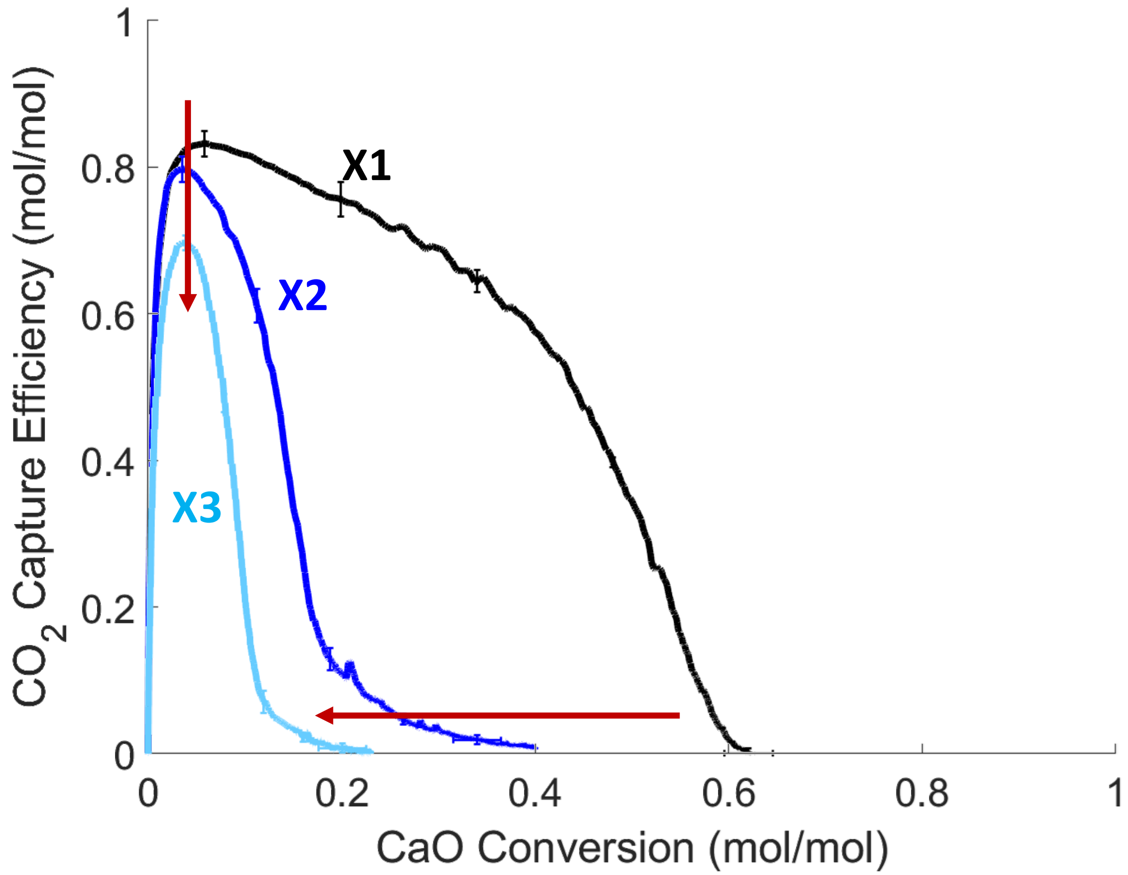
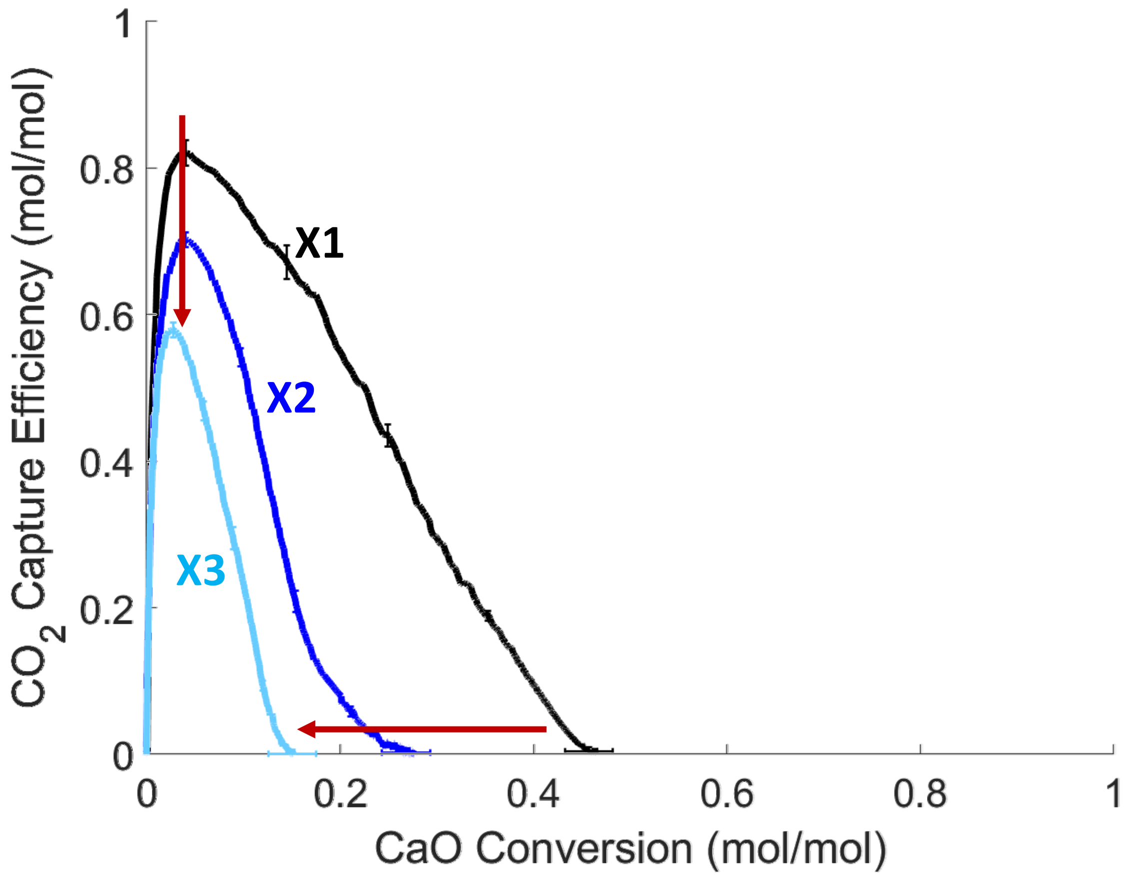
Riyadh Sorbent



Saabar Sorbent



SET 2 Results: Both sorbents exhibit reduced CO_2 capture capacity and efficiency due to cycling

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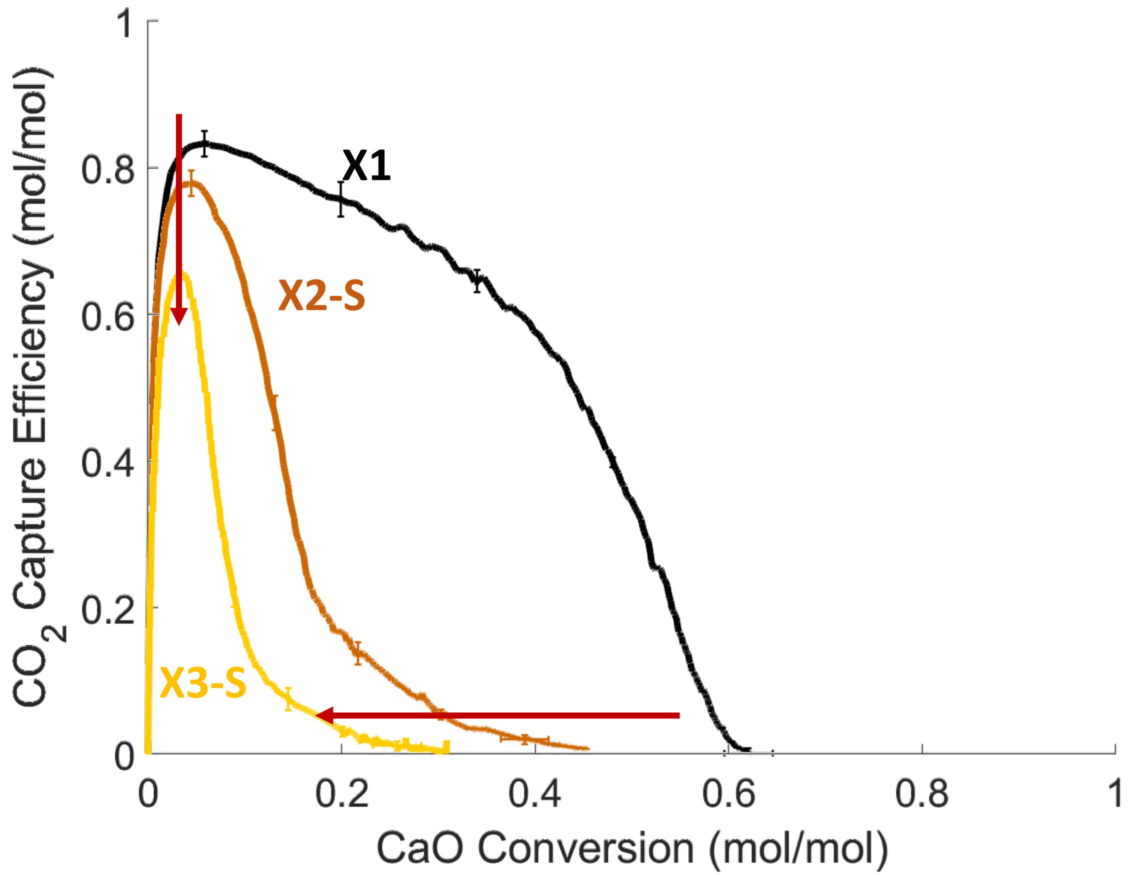
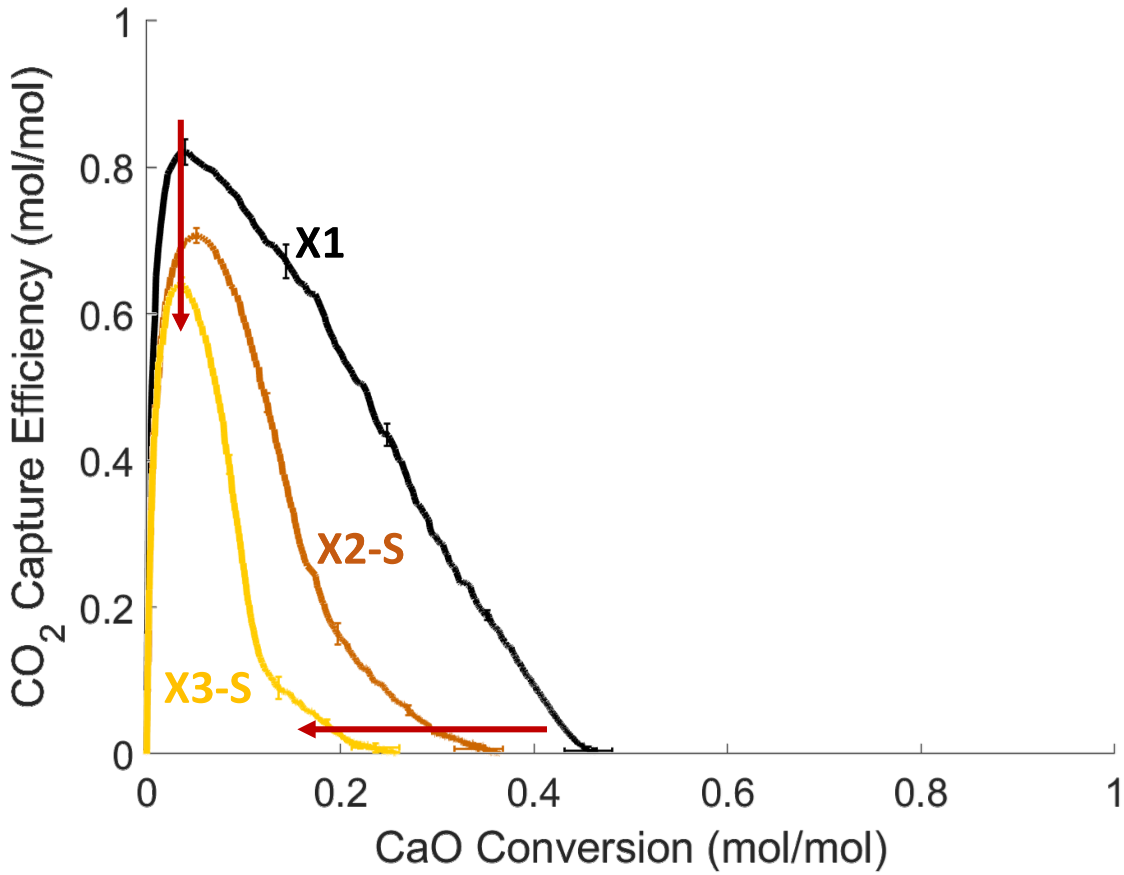
Riyadh Sorbent



Saabar Sorbent



Results: Cycling with SO_2 affects Riyadh and Saabar sorbent carbonation differently

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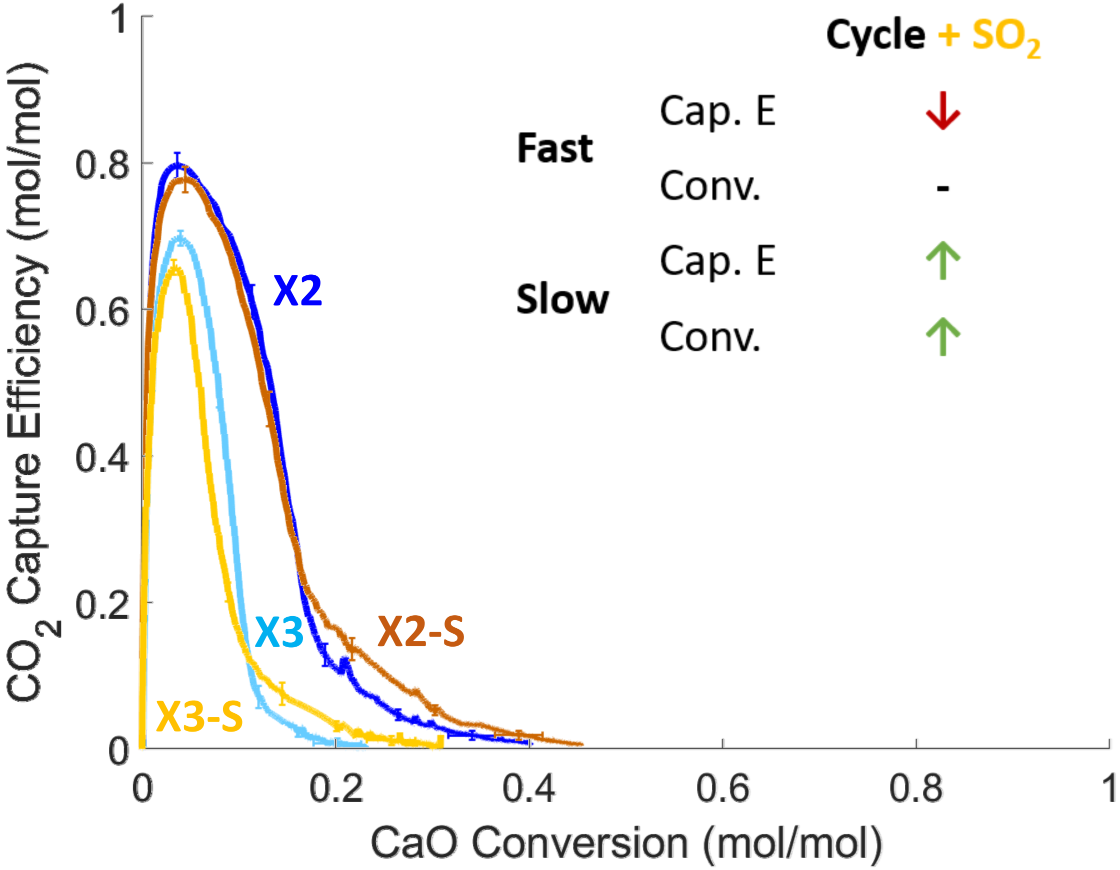
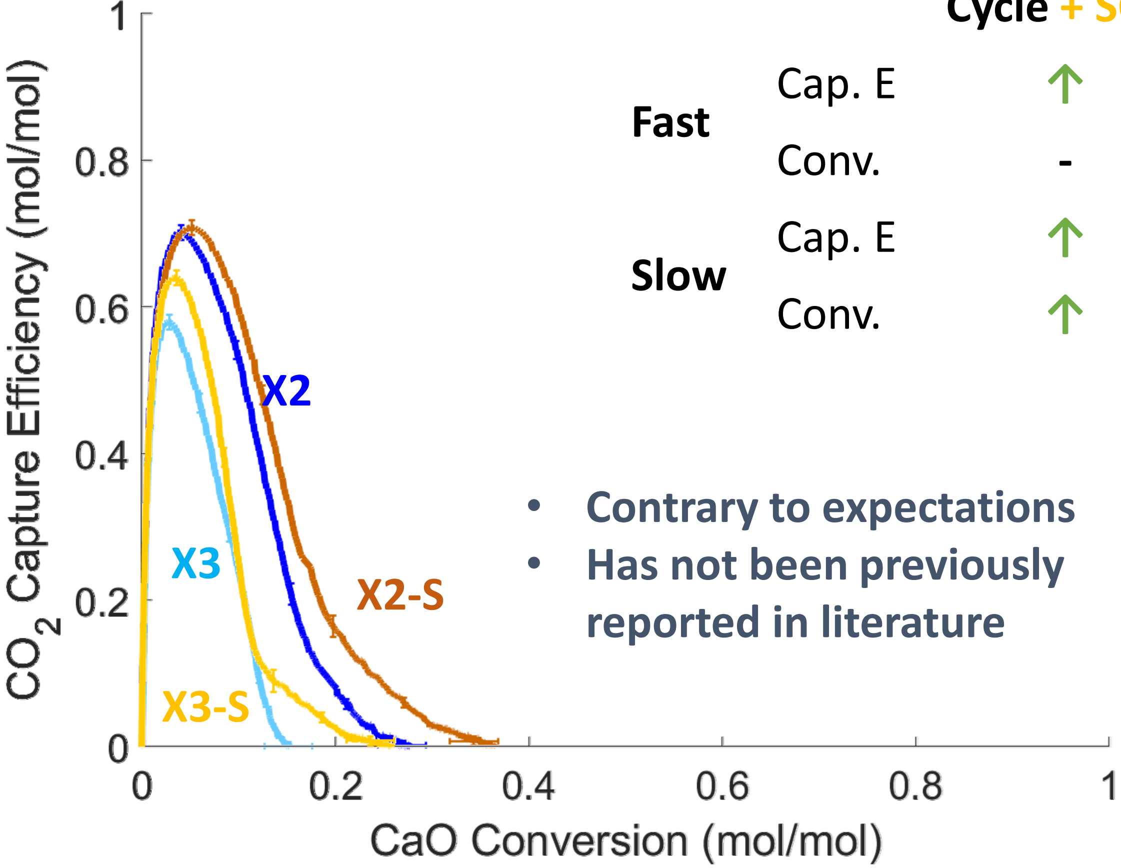
Riyadh Sorbent



		Cycle + SO_2
Fast	Cap. E	↓
	Conv.	-
Slow	Cap. E	↑
	Conv.	↑

Saabar Sorbent



		Cycle + SO_2
Fast	Cap. E	↑
	Conv.	-
Slow	Cap. E	↑
	Conv.	↑

- Contrary to expectations
- Has not been previously reported in literature

Results: Cycling with SO_2 affects Riyadh and Saabar sorbent sulfation differently

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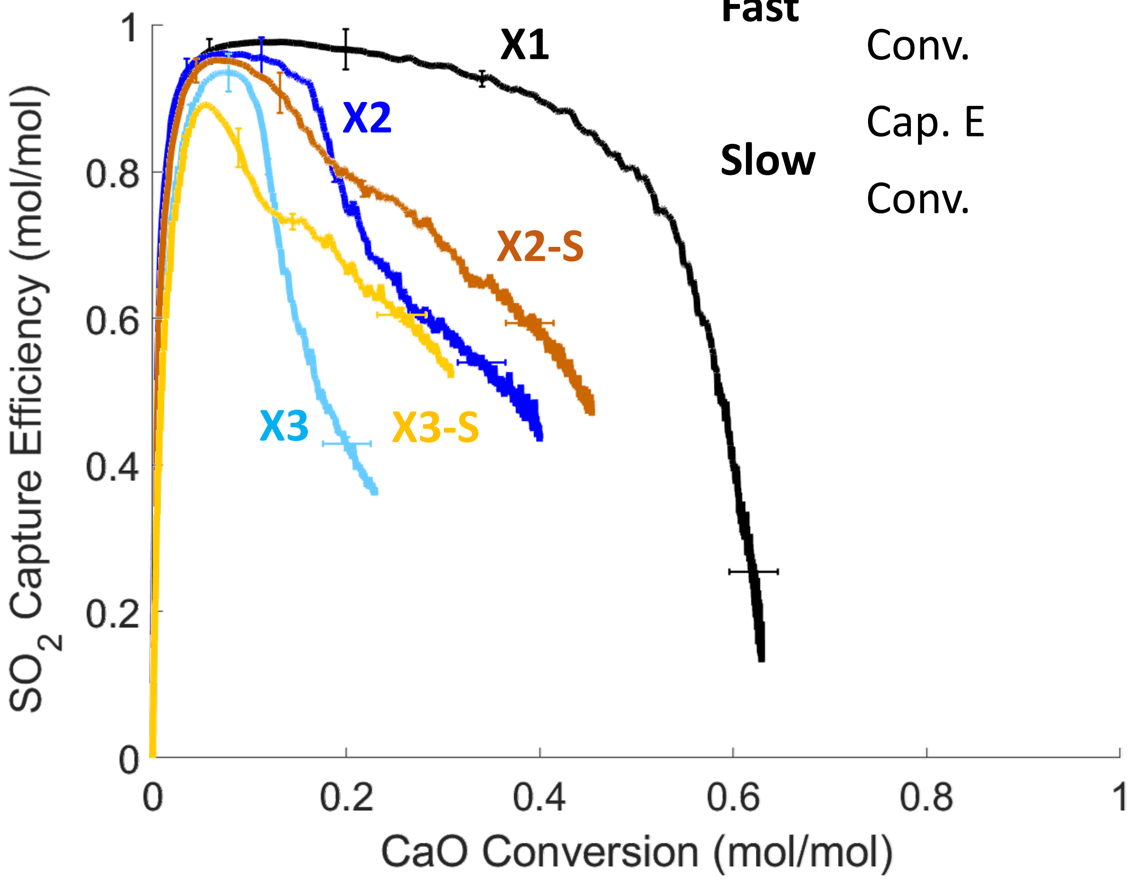
Riyadh Limestone

		Cycle + SO_2
Fast	Cap. E	↓
	Conv.	-
Slow	Cap. E	↑
	Conv.	↑

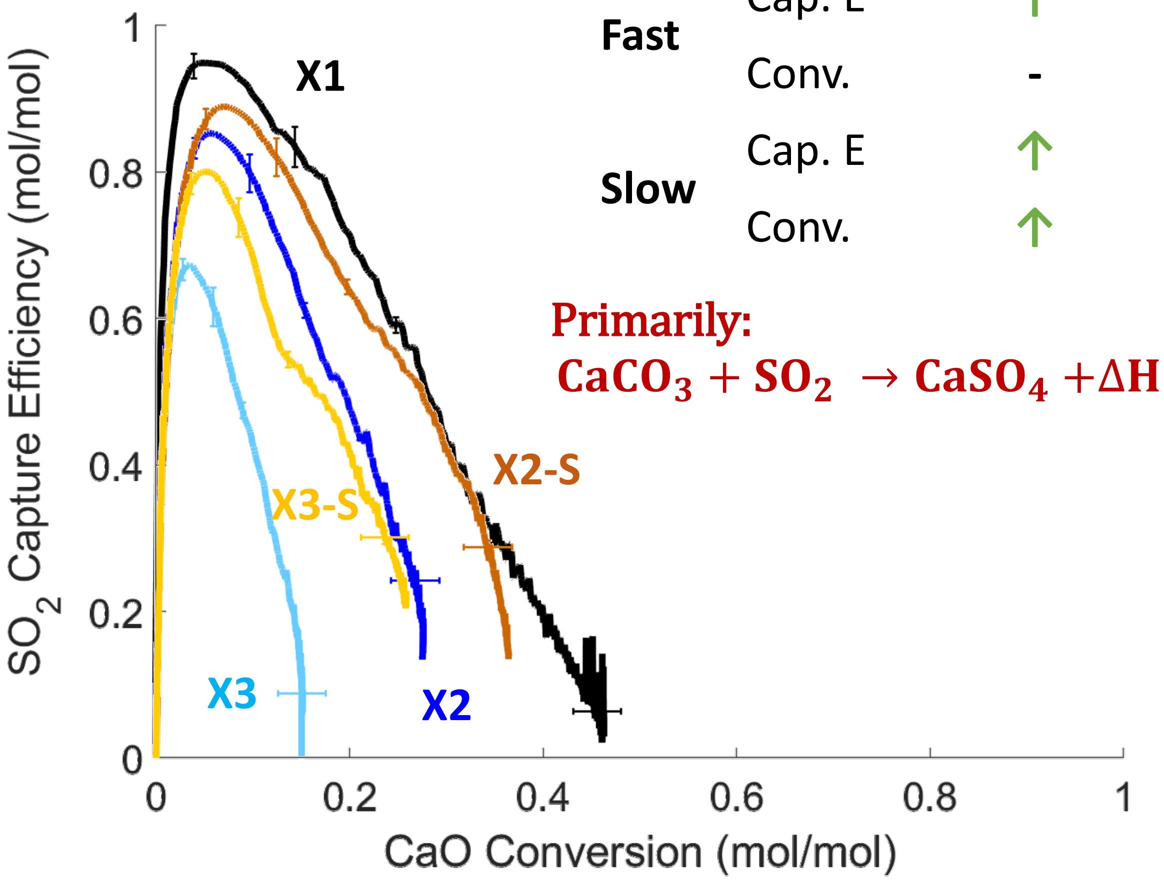


Saabar Limestone

		Cycle + SO_2
Fast	Cap. E	↑
	Conv.	-
Slow	Cap. E	↑
	Conv.	↑

Primarily:

$$CaCO_3 + SO_2 \rightarrow CaSO_4 + \Delta H$$



SEM-EDS:
Attribute capture discrepancy to distribution of impurities

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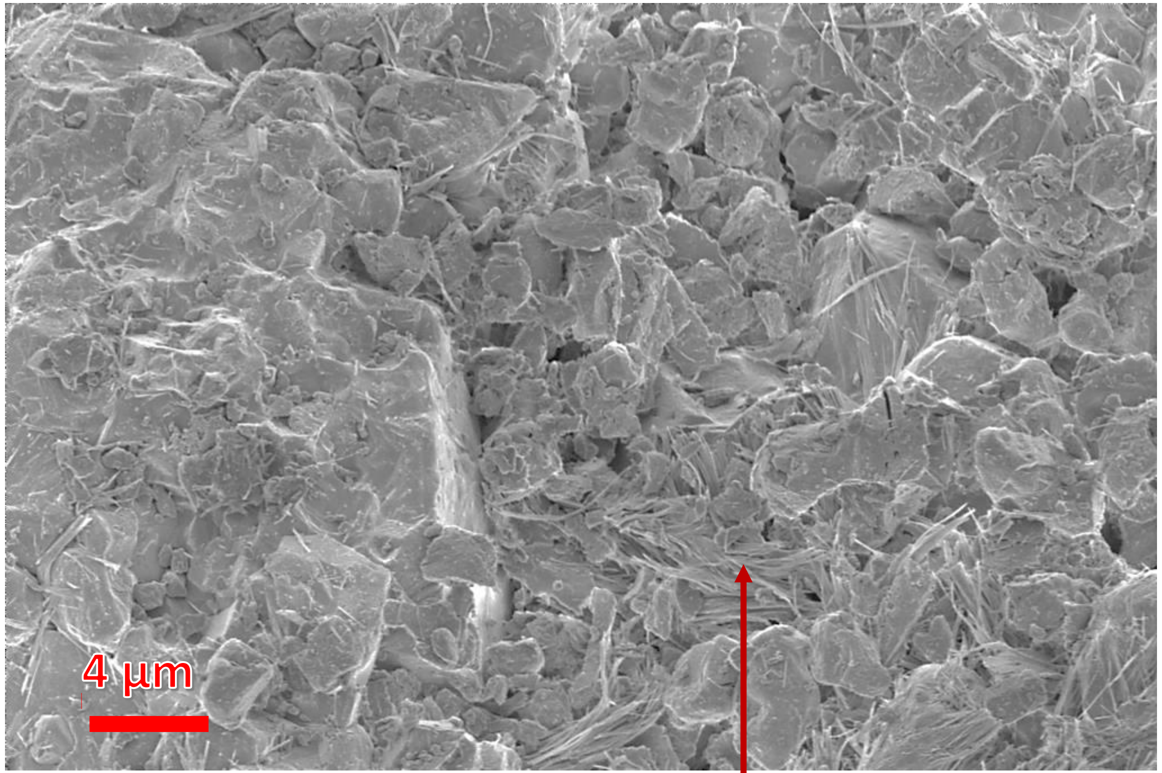
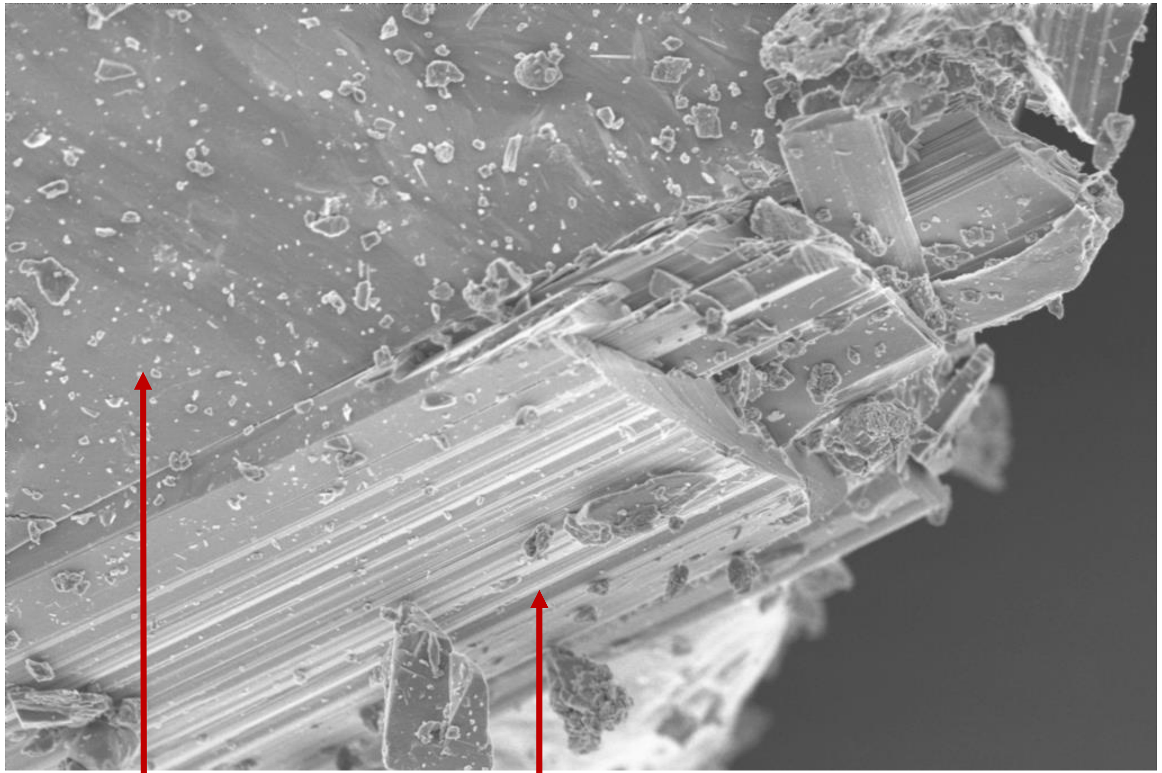
Riyadh Limestone:



Need-like structure: Si/Al/Mg oxide

Saabar Limestone:



$CaCO_3$

Si/Mg oxide

SEM-EDS: Saabar monomineralic CaO phases more susceptible to sintering

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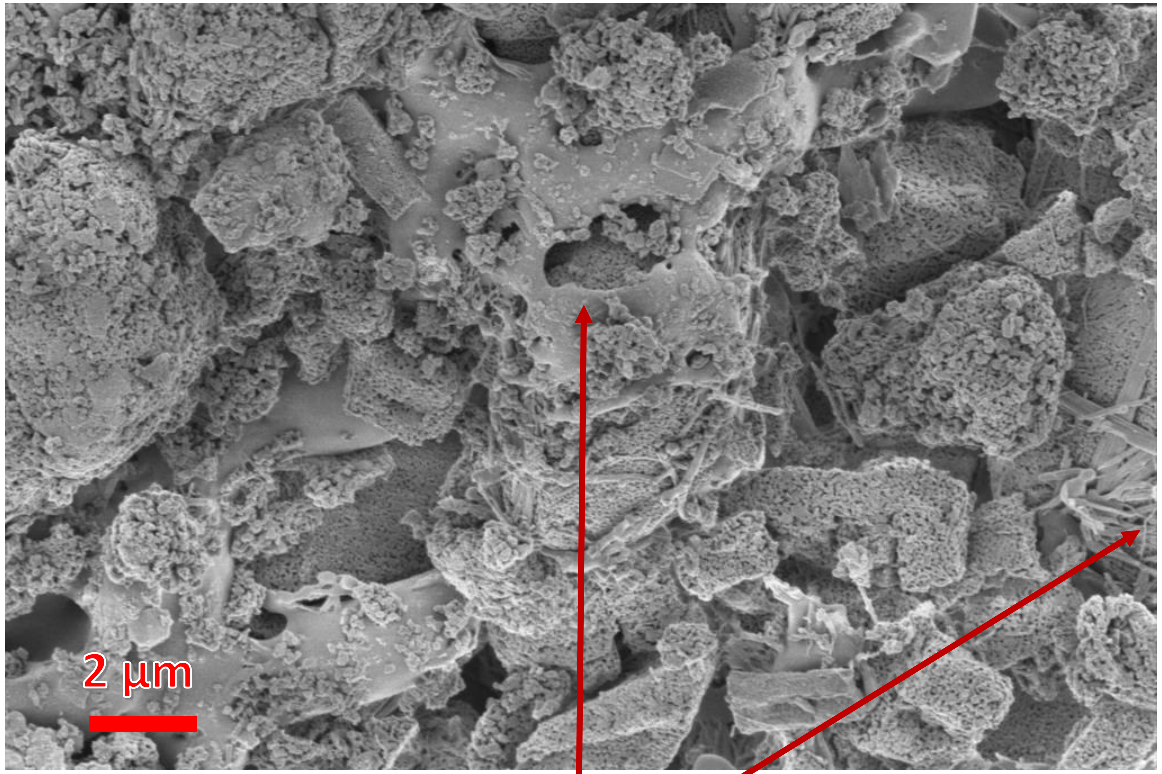
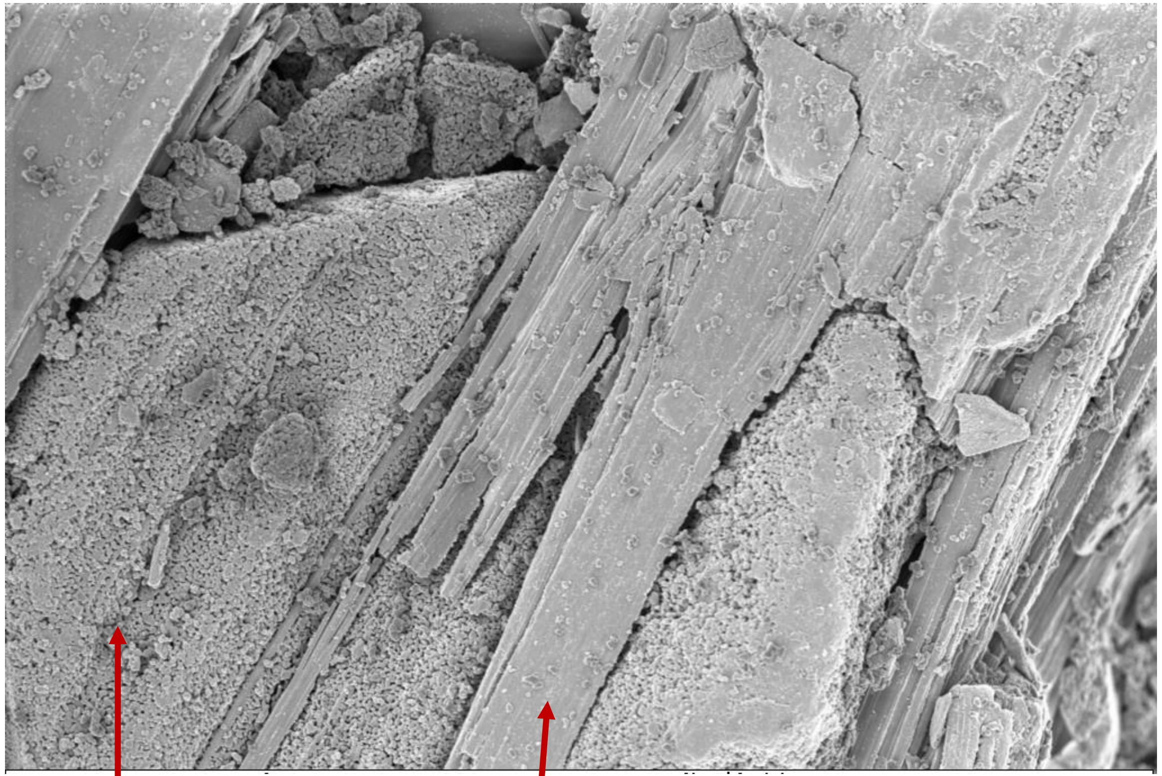
X1: Riyadh Sorbent:



Si/Al/Mg oxide

X1: Saabar Sorbent:



CaO

Si/Mg oxide

SEM-EDS:

Saabar sorbent cycled without SO_2 has smaller grain size

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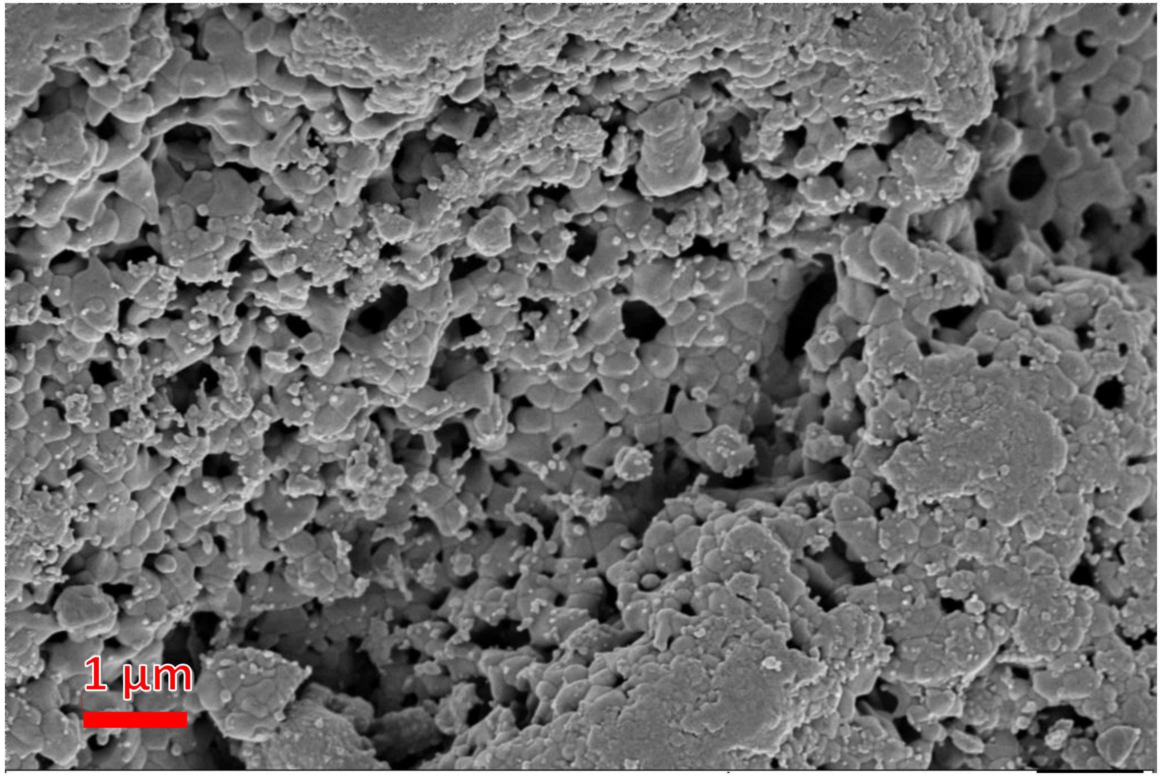
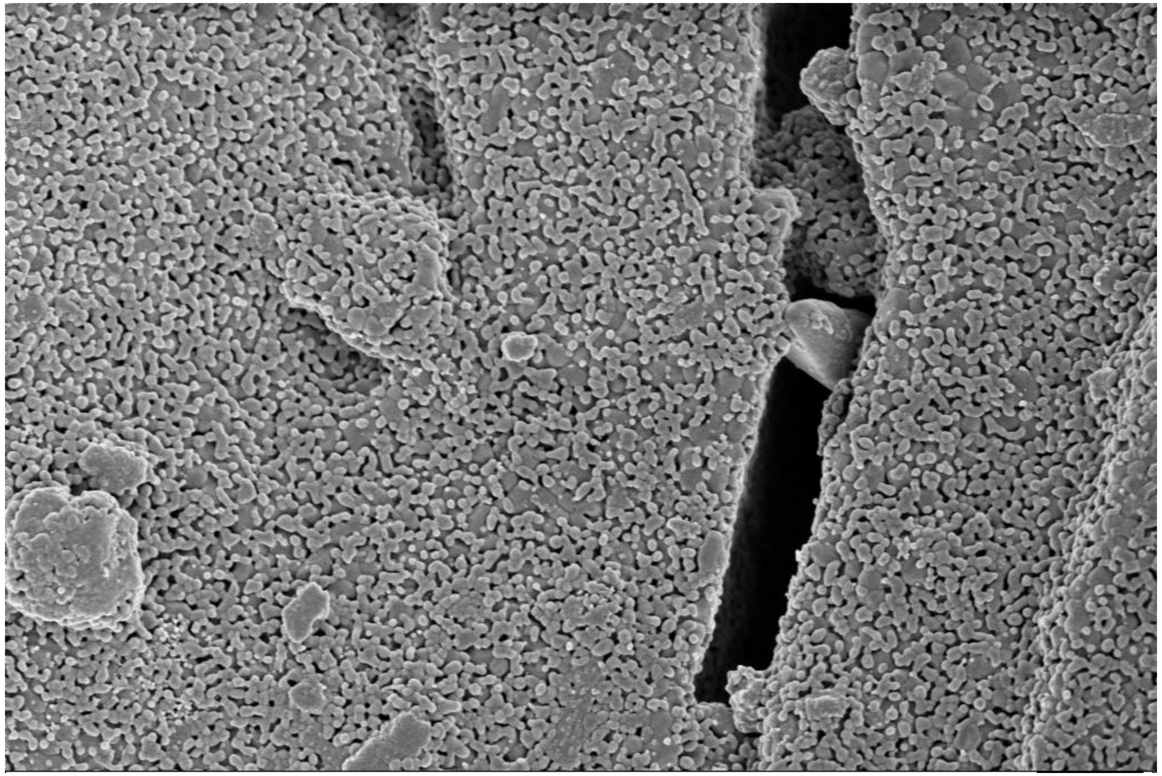
X3 Riyadh Sorbent:



X3 Saabar Sorbent:



SEM-EDS:
Sorbent cycled with SO_2 has similar grain size

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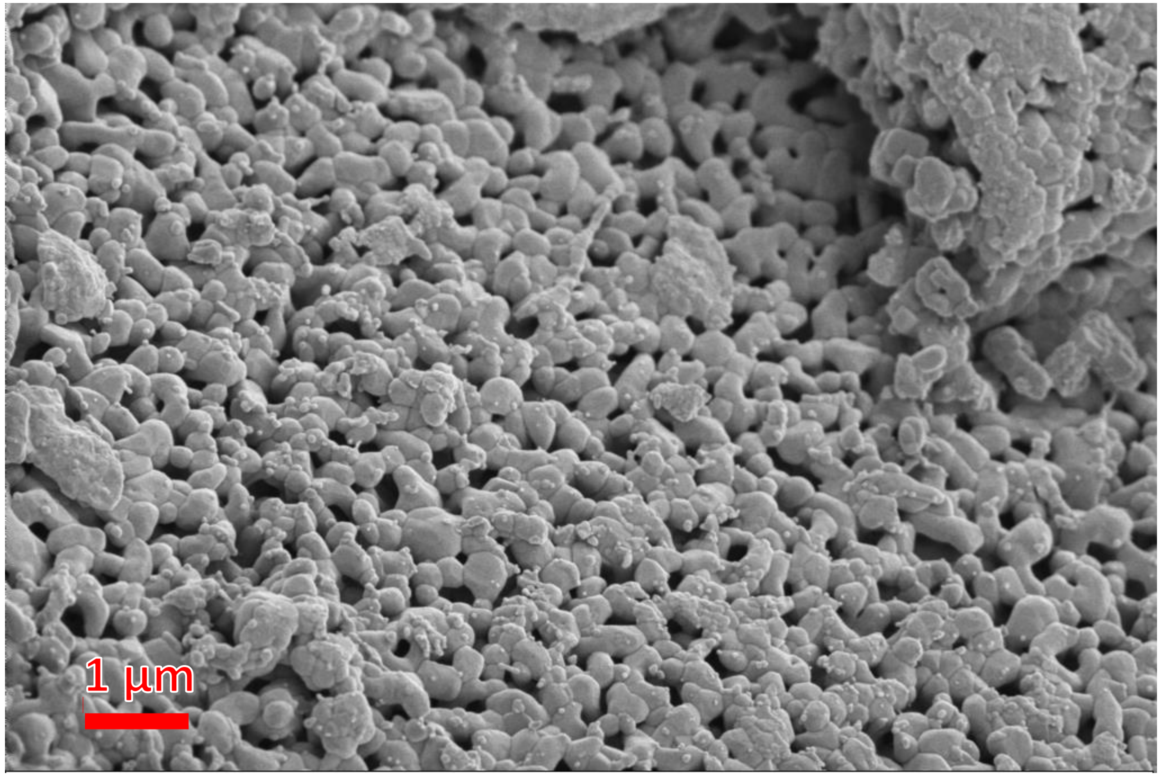
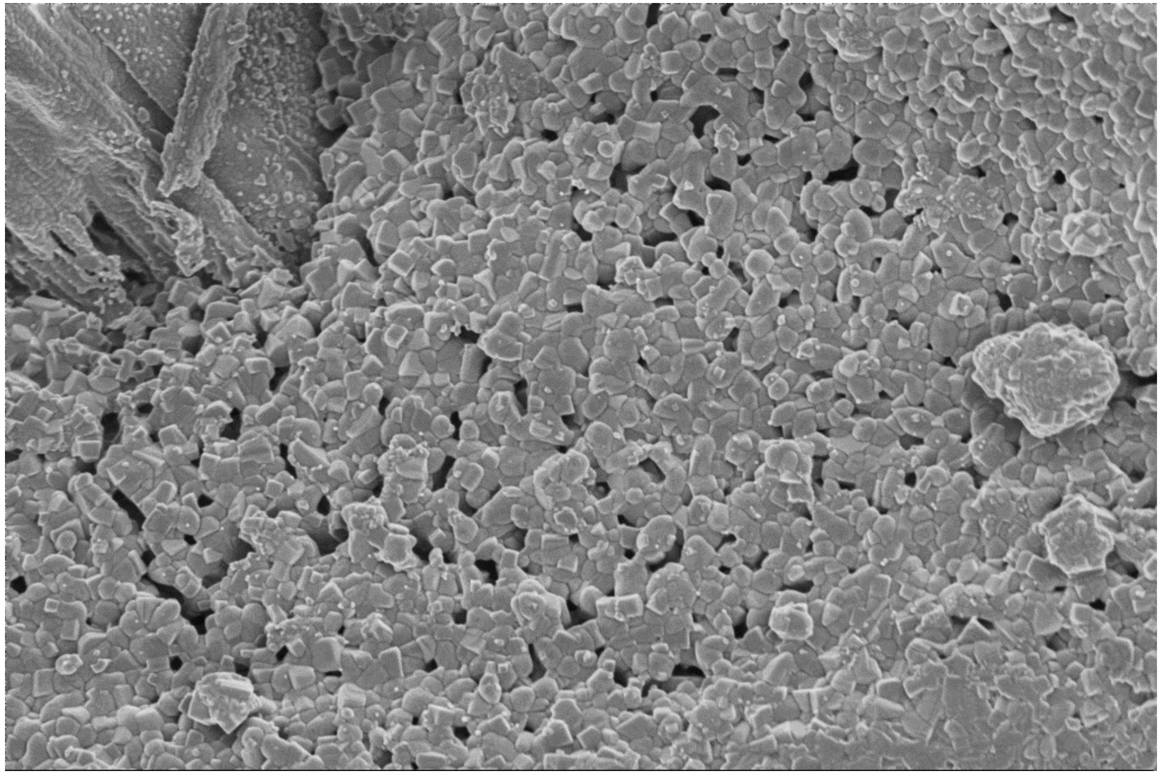
X3-S Riyadh Sorbent



X3-S Saabar Sorbent



Mercury Porosymetry & N_2 Adsorption:

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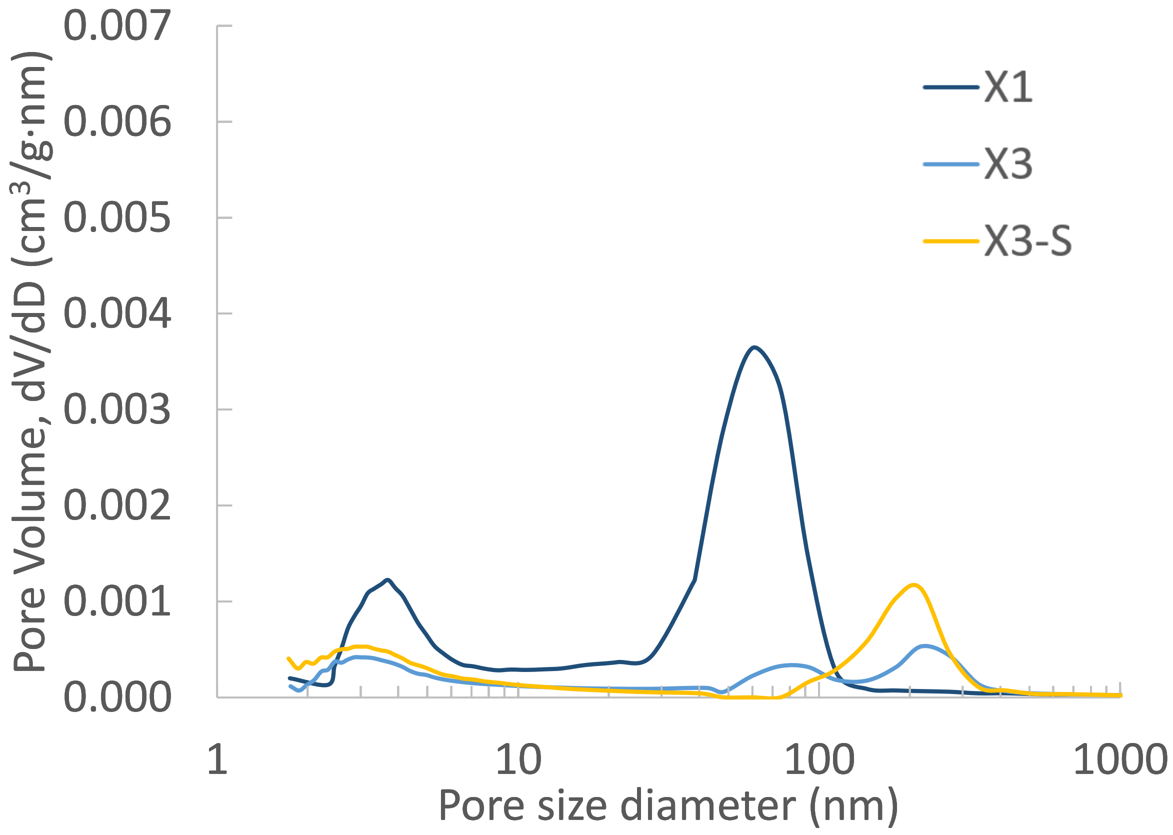
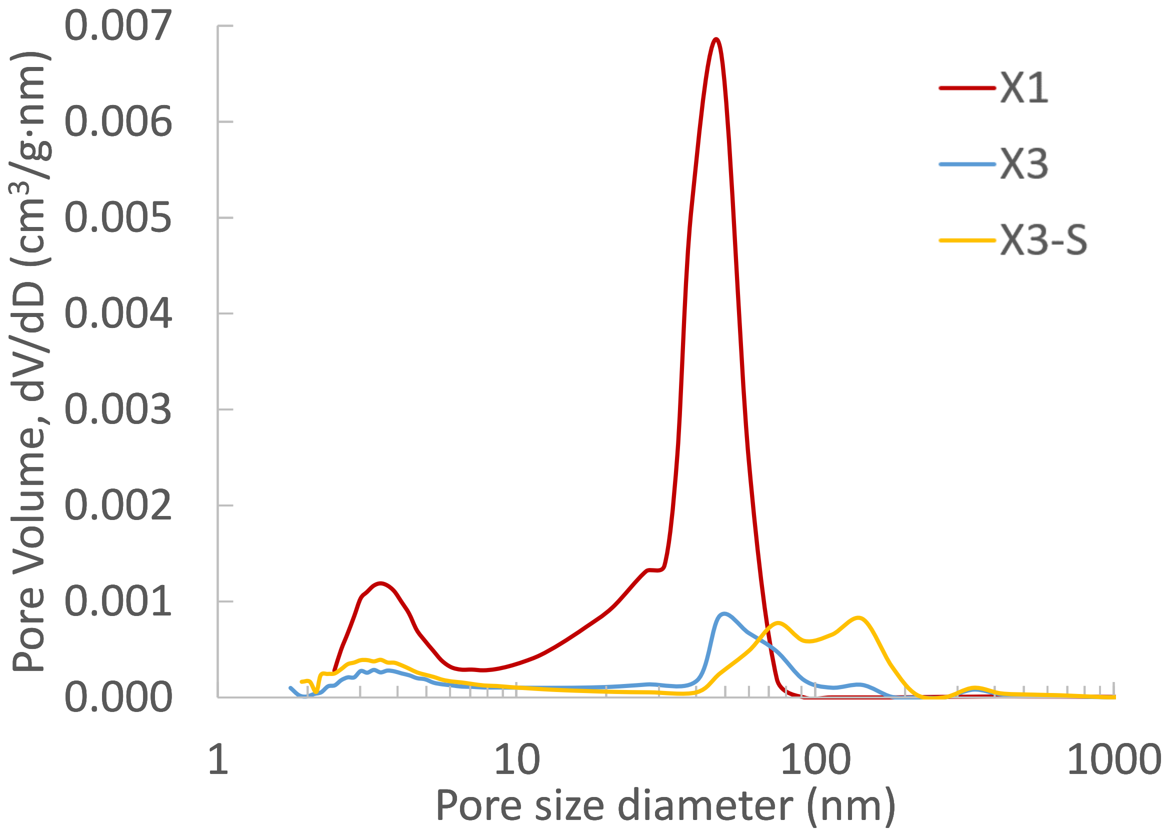
Riyadh:



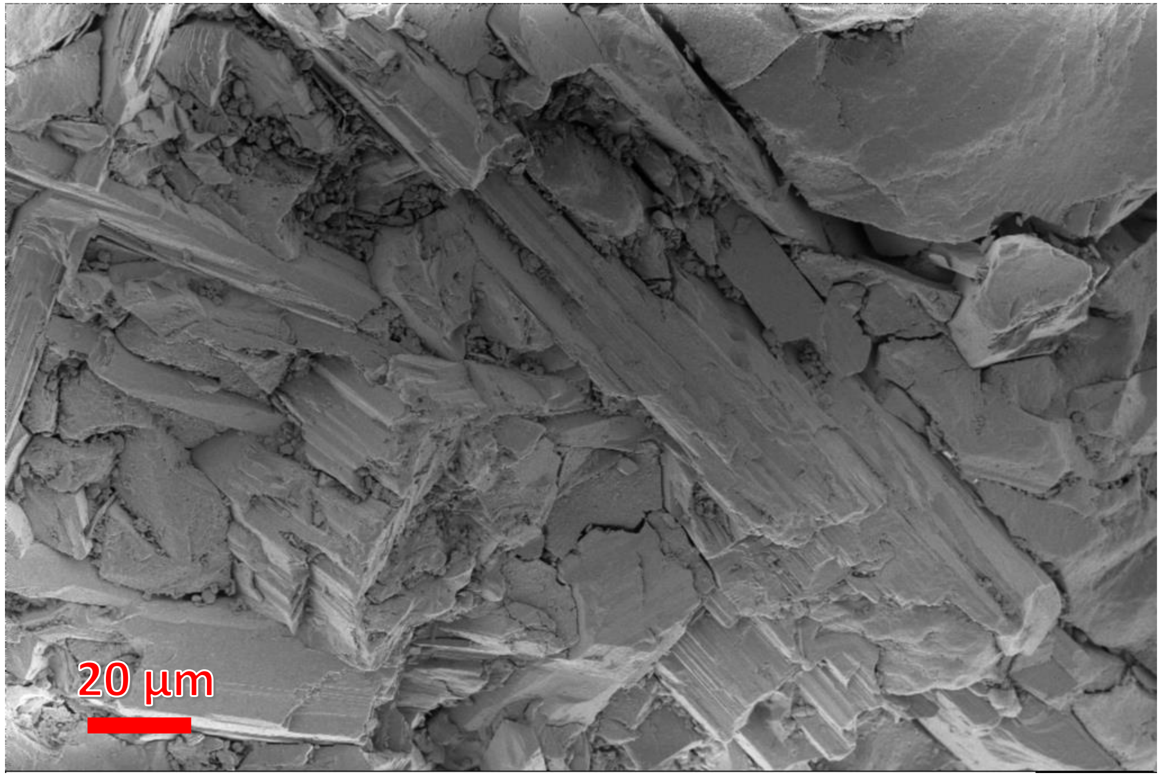
Saabar:



"Mild" sulfation of Saabar limestone reduces the monomineralic nature of this sorbent & increases the Tamman temperature of the sorbent thereby reducing susceptibility to heat induced sintering

SEM-EDS:
Saabar grain size disruption leads to structural defects

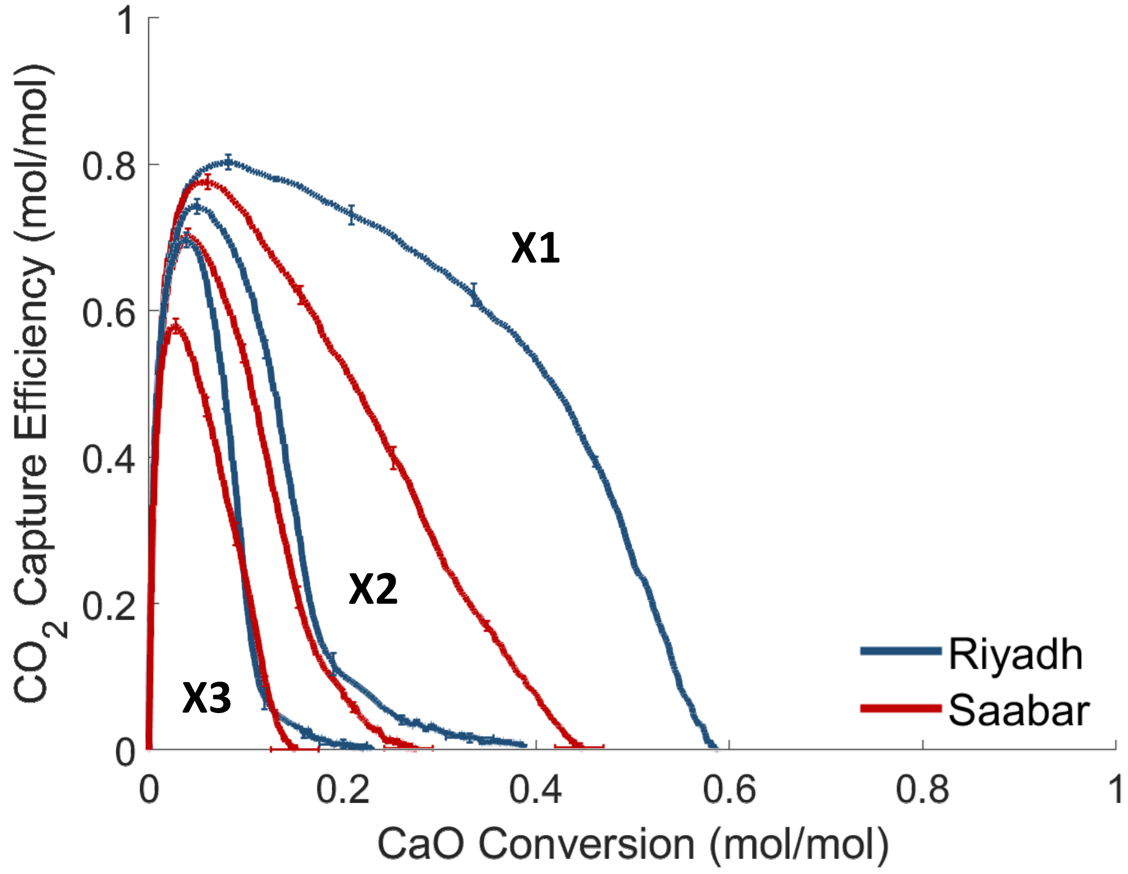
Saabar X3 Recarbonated



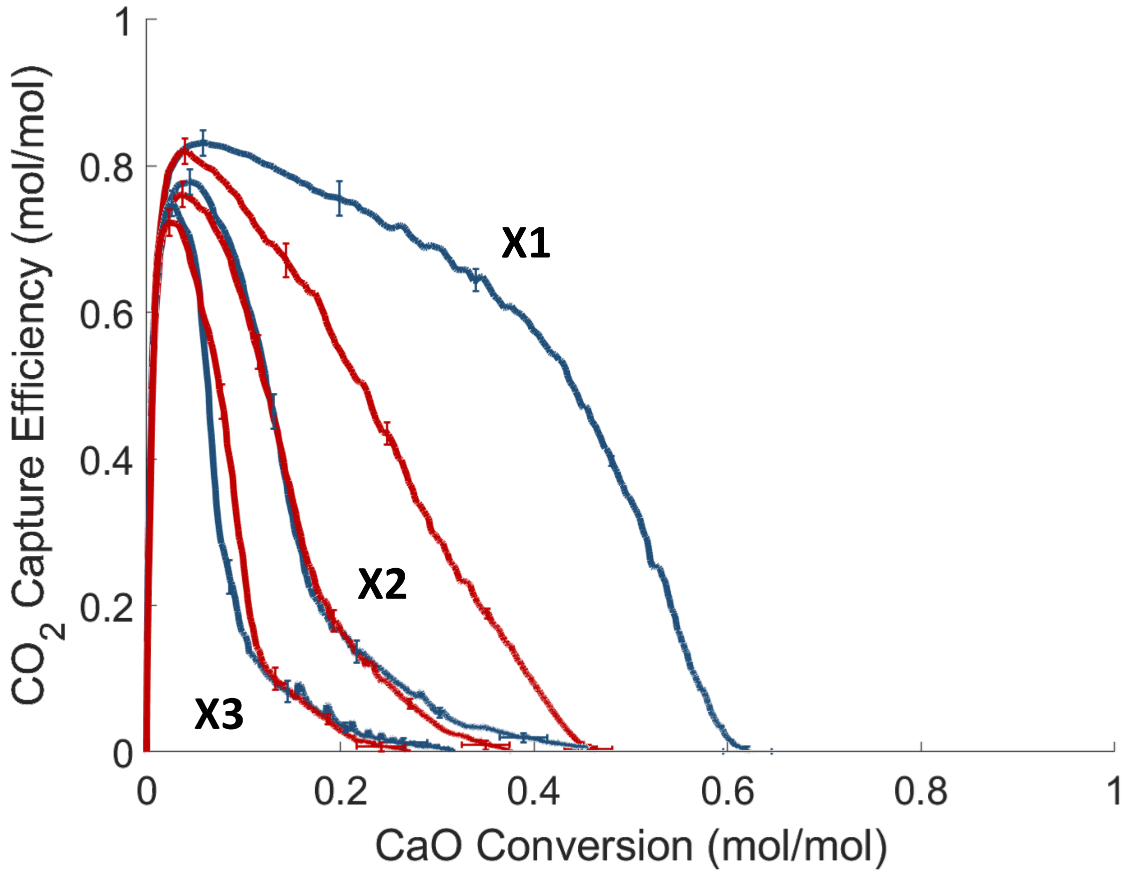
Saabar X3-S Recarbonated

Results: Sorbents cycled in SO_2 exhibit similar CO_2 capture performance

Cycled Without SO_2



Cycled with SO_2

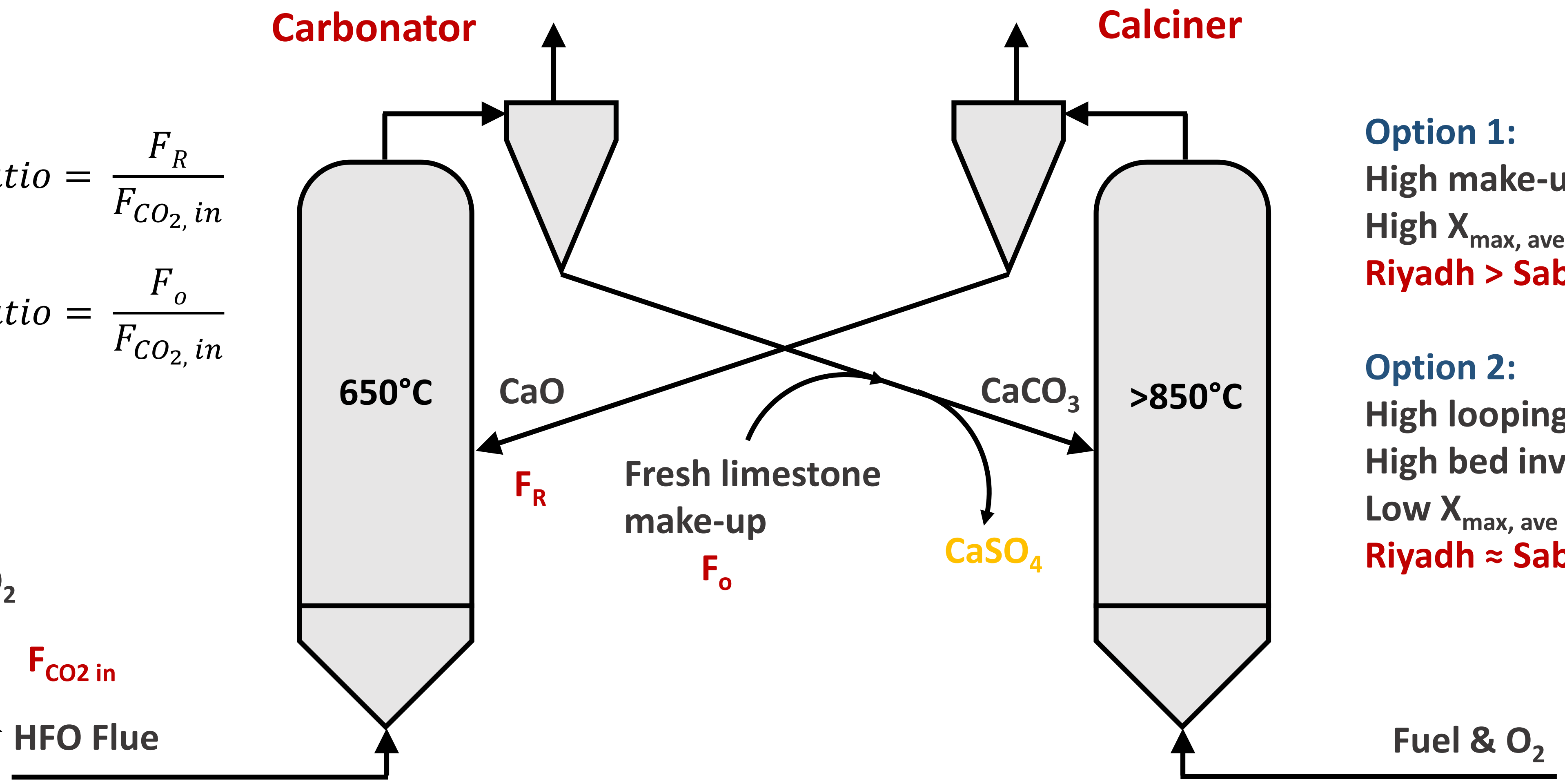


Big Picture: Influence on key process design parameters

$$Looping\ Ratio = \frac{F_R}{F_{CO_2,\ in}}$$

$$Make\ up\ Ratio = \frac{F_o}{F_{CO_2,\ in}}$$

Case 2:
flue w/ SO_2



Option 1:
High make-up ratio
High $X_{max,\ ave}$
Riyadh > Sabaar

Option 2:
High looping ratio
High bed inventory
Low $X_{max,\ ave}$
Riyadh ≈ Sabaar

Conclusions and Progress

Conclusions:

1. This data, along with limestone deactivation rates, can be used to model a CaL system: reasonable limits on operating parameters for CaL implementation at HFO-fired power plants
2. Distribution of impurities in limestone plays an important role
3. Limestone with non-homogeneously distributed impurities is more susceptible to sintering & less susceptible to deactivation when cycled in flue gas with SO_2

Progress:

1. Assessing limestone deactivation rates due to cycling at different looping rates in relevant gas atmospheres
2. Modeling CaL system using collected data

THANK YOU!

CARBON
MANAGEMENT
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