



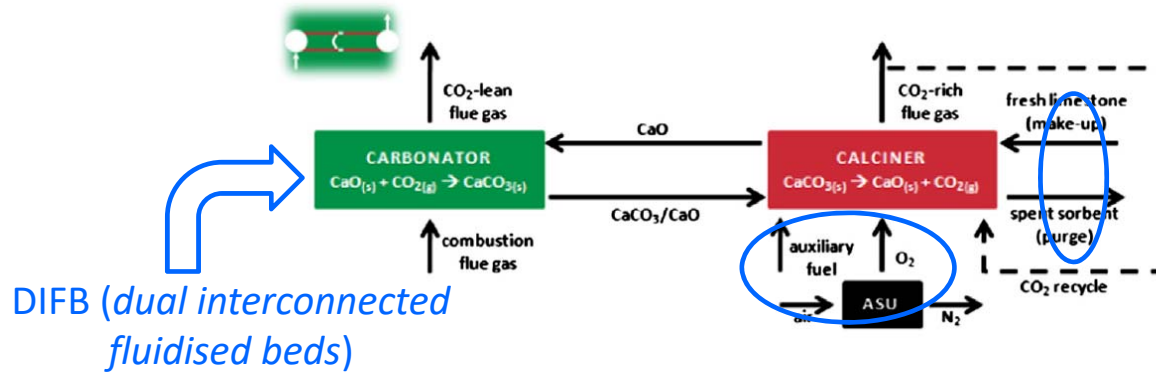
The impact fragmentation tendency of limestone particles in Calcium Looping cycles in the presence of steam and sulphur dioxide

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Essential facts

Among the different options envisaged by scientists and in political conferences to mitigate [global warming](#) related to CO_2 anthropogenic emissions → [post-combustion](#) CO_2 capture and further release in a concentrated stream, to be geologically stored or utilised in the chemical industry.

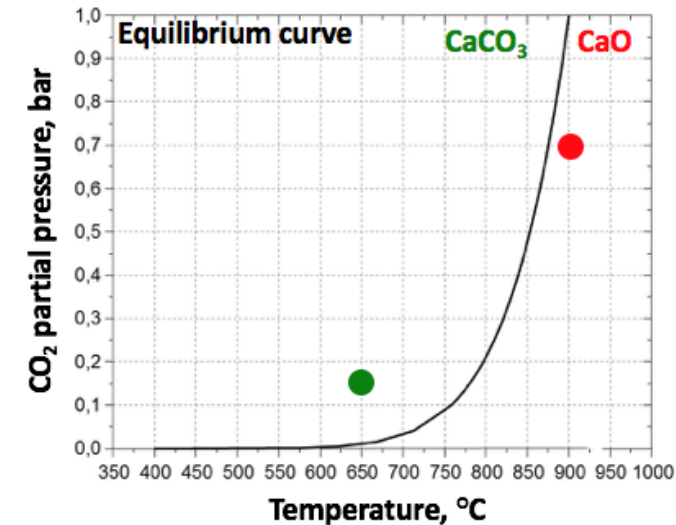
As alternative to the canonical process based on absorption with amine-solutions, [calcium looping](#) (CaL) relies on alternated CO_2 uptake and concentrated release by means of cheap calcium-based (limestone) sorbent.



Purge: sorbent deactivation by, e.g., [thermal sintering](#). Make-up also considers loss of material by [elutriation](#).

In the **carbonator**, CO_2 in the combustion flue gas is captured by CaO at around 600–700°C. The carbonator emits a **CO₂-lean** gas and a CaCO_3 -sorbent fed to the **calciner** for regeneration at around 900–950°C.

The endothermic calciner (operated as an oxy-fuel combustor) yields a **CO₂-rich** flue gas and regenerates the CaO -based sorbent (fed back again to the carbonator).



This research

SO_2 in the combustion flue gas can react irreversibly with the sorbent (**CaO sulphation**) thus subtracting available CaO and limiting CO_2 diffusion in the sorbent pores (CaSO_4 -based shell).

Steam in the combustion flue gas can improve the performance of the sorbent: increase in CO_2 diffusion through the sorbent pores and formation of surface OH groups (“catalytic” effect).

The aspects concerning the effect of SO_2 and H_2O have important consequences on the design of the CaL system.

Aim of this study is to scrutinise the effect of steam in presence of SO_2 , and their mutual interaction in CaL tests carried out in a novel lab-scale twin fluidised bed reactor and using an *ex situ* impact test device. **Results** are expressed in terms of CO_2 capture capacity and fragmentation tendency.

Main operating conditions

Reference sorbent: German limestone (“EnBW”), CaCO₃-rich, initial amount 20 g, 0.4–0.6 mm.

Fluidisation material: 0.9–1 mm silica sand, inert to reaction and attrition.

CaL test: ten complete cycles of calcination/carbonation (plus eleventh calcination).

	Calcination	Carbonation					
Temperature, °C	940	650					
Test duration, min	20	15					
Fluidisation velocity, m/s	0.5	0.5					
Gas composition (balance air)		DRY	STECAR	DSP	DSR	SCSP	SCSR
CO ₂ , %vol	70	15					
H ₂ O, %vol	0	0	10	0	0	10	10
SO ₂ , ppm	0	0	0	75	1500	75	1500

To simulate oxy-firing

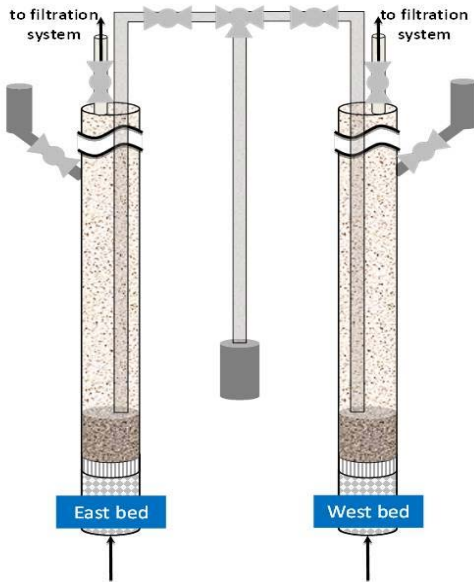
To simulate combustion flue gas

To simulate a pre-desulphurised combustion flue gas

To simulate an un-desulphurised combustion flue gas

Sorbent	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	TiO ₂	LOI
EnBW	0.30	0.13	0.08	56.01	0.26	n.d.	0.02	n.d.	0.01	43.50

Twin bed system and analyses



Lab-scale (ID=40 mm) electrically-heated apparatus, purposely designed.

Two identical bubbling fluidised beds, both operate in batch mode.

Connected by a duct (ID=10 mm), partially immersed in both beds, for fast pneumatic conveying of the sorbent from one reactor to the other.

The system is able to recreate a realistic particle thermal and mechanical history, while keeping the experimental complexity lower than for a fully continuous looping system.

Cylinders of CO₂ and SO₂, and steam generation system.

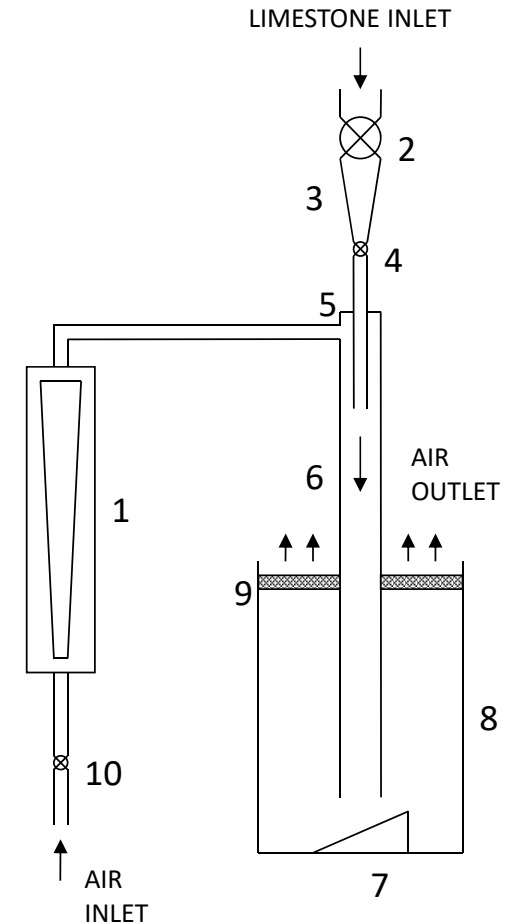
NDIR gas analysis at the outlet: CO₂ capture capacity ξ , g of CO₂ captured in each carbonation stage per g of sorbent.

Impact test apparatus

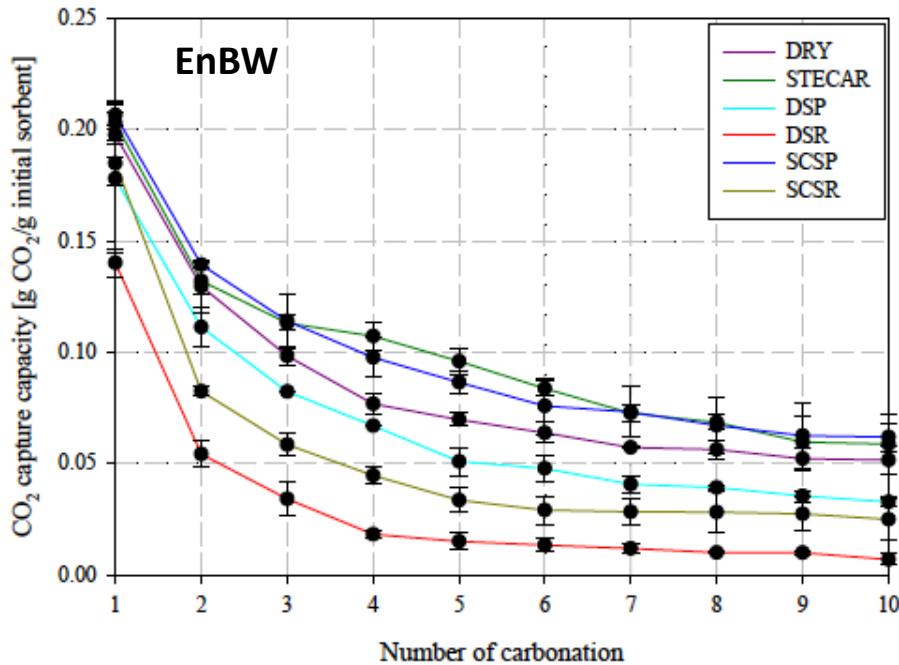
- Sorbent size = 400-600 μm
- Impact velocity up to 42 m s^{-1}

After eleventh calcination:

- Sorbent particles subject to impact tests, to obtain the [particle size distribution](#) and to assess particle fragmentation. Mean Sauter diameter d_s and value of the quantity f , the fraction of sorbent fragments i.e. the particles finer than 0.4 mm.



CO₂/SO₂ capture



All cases: ξ decreases due to sintering. Ex.: base-case **DRY**, -75% after 10 cycles.

STECAR: addition of steam improves carbonation. After 10 cycles, +15% vs. **DRY**.

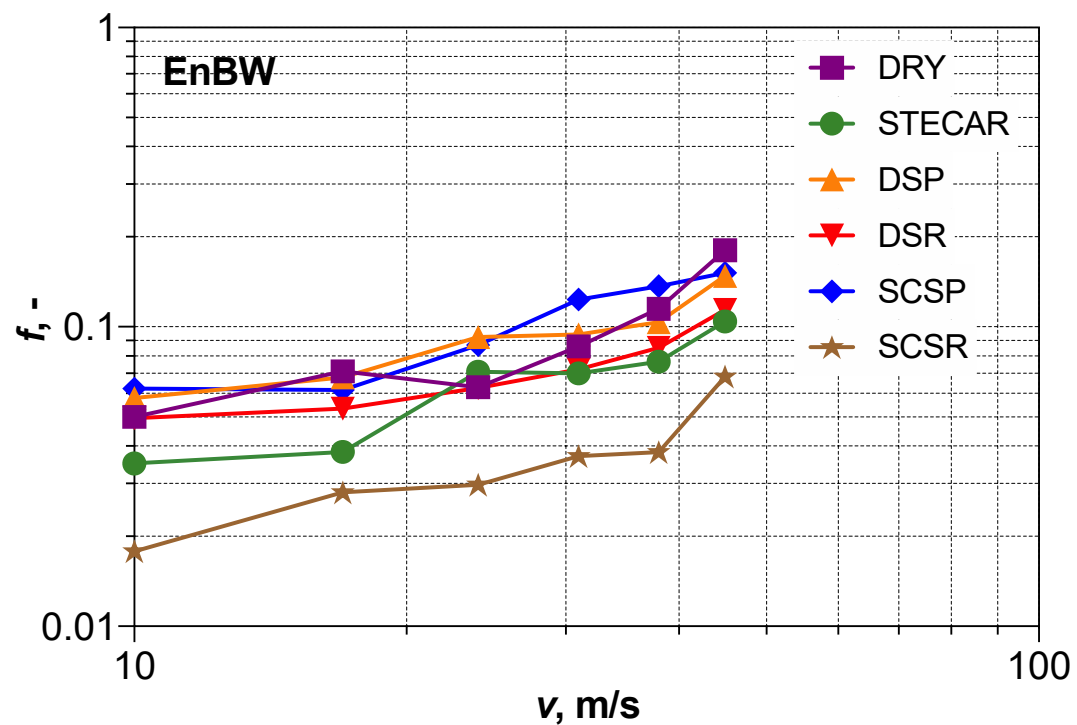
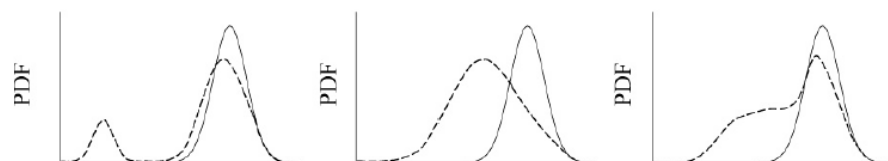
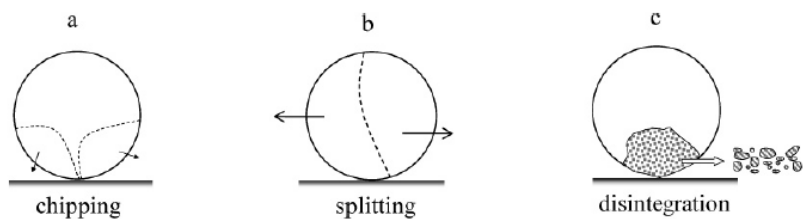
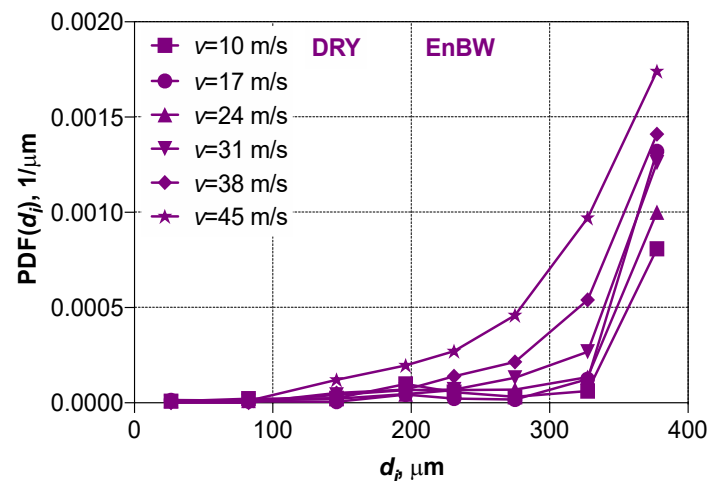
The presence of SO₂ during carbonation (**DSP**, **DSR**) produced a decline in ξ .

DSP, [SO₂]=75 ppm: overall loss -82%, and after 10 cycles -36% vs. **DRY**.

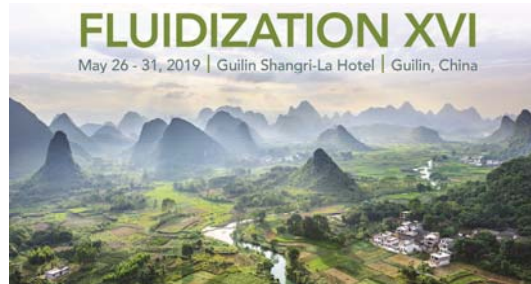
DSR, [SO₂]=1500 ppm: overall loss -95%, and after 10 cycles -86% vs. **DRY**.

The negative effect of SO₂ was counterbalanced by addition of steam: **SCSP**>**DSP**, **SCSR**>**DSR**. **SCSP** is even better than **DRY**.

Sorbent fragmentation



f = fraction of sorbent fragments (particles finer than 0.4 mm)



The present study sheds light on the influence of H_2O and SO_2 in flue gases on CO_2 uptake by limestone under realistic calcium looping conditions.

Steam exerts a beneficial effect on CO_2 uptake, that can be large to the point of compensating the detrimental effect of SO_2 when the concentration of the latter is small. This may be the case of flue gases that are desulphurised prior to Ca looping.

All cycled sorbents are resistant to impact fragmentation. For all the samples, the PDF curves suggest a prevailing chipping fragmentation mode. When SO_2 is present, the formation of an extensive hard CaSO_4 shell makes the sorbent particles even more resistant to fragmentation.