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N_2O Decomposition by CaO under Conditions of Carbonator of Calcium Looping Cycle

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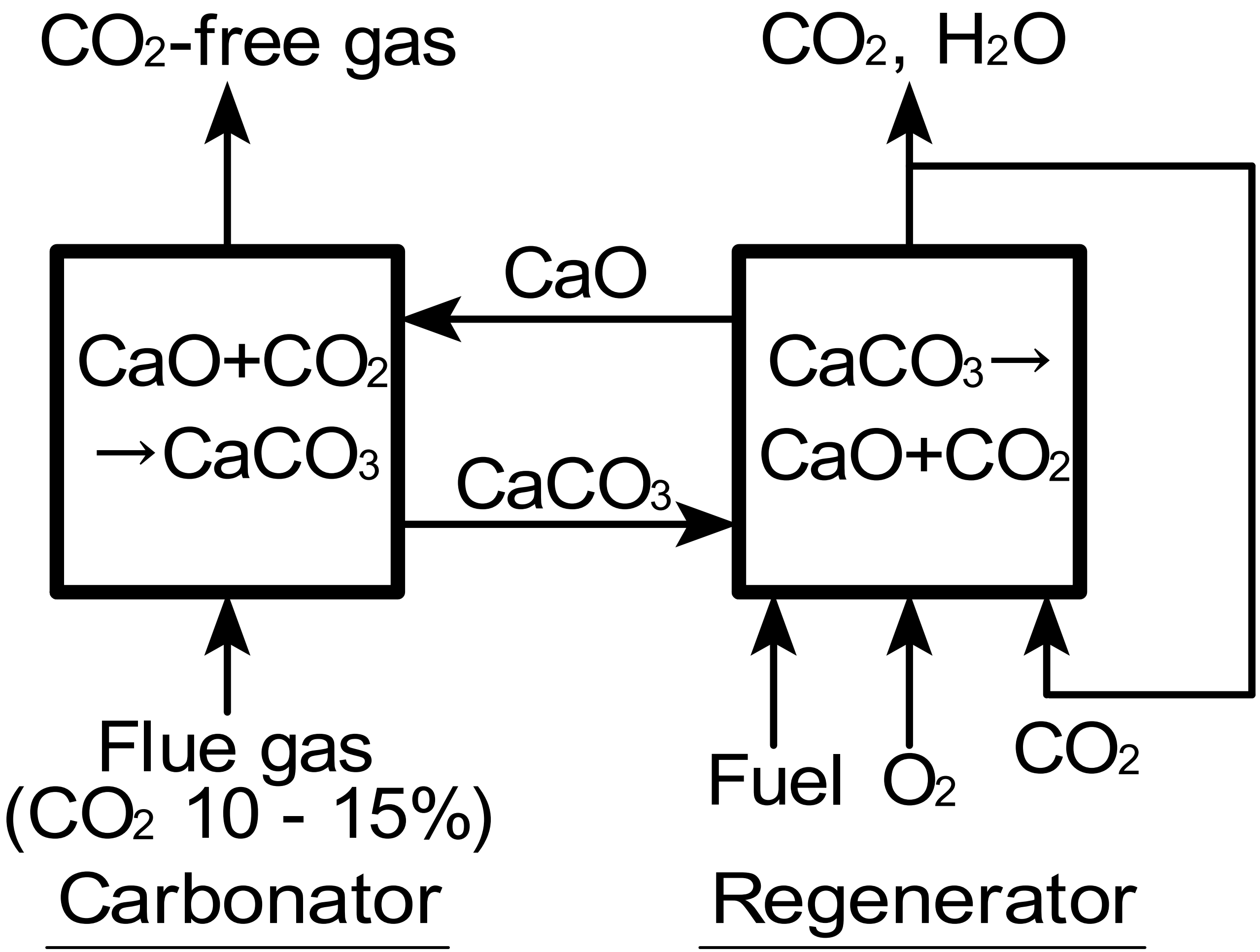
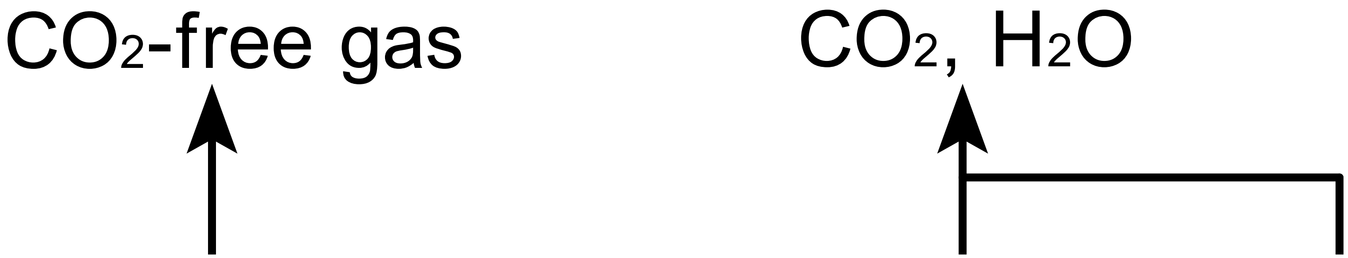
Principle of CaL process for CO_2 separation

CaL process consists of a carbonator and a regenerator. In the cabonator, flue gas from air-blown combustor is introduced. In the regenerator, fuel (coal) is burned to supply heat to decompose $CaCO_3$ to CaO.



Flue gas from air-blown FB combustor

CaL process consists of a carbonator (absorber) and a regenerator. In the regenerator, fuel (coal) is burned to supply heat to decompose $CaCO_3$ to CaO.



Flue gas fr

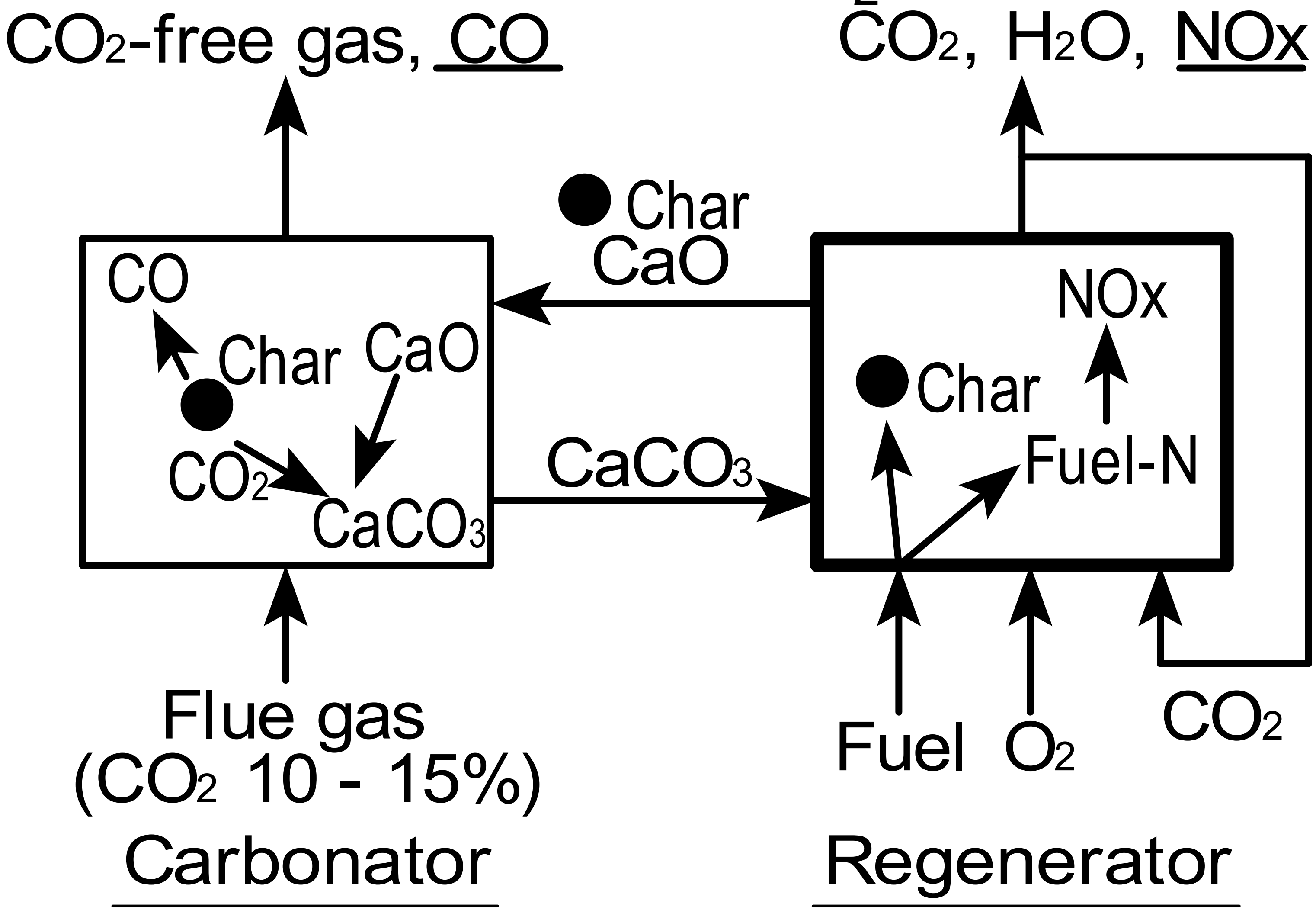
contain N

Char transportation from regenerator to carbonator

Coal combustion in regenerator.

→ Formation of char and transportation of char with CaO

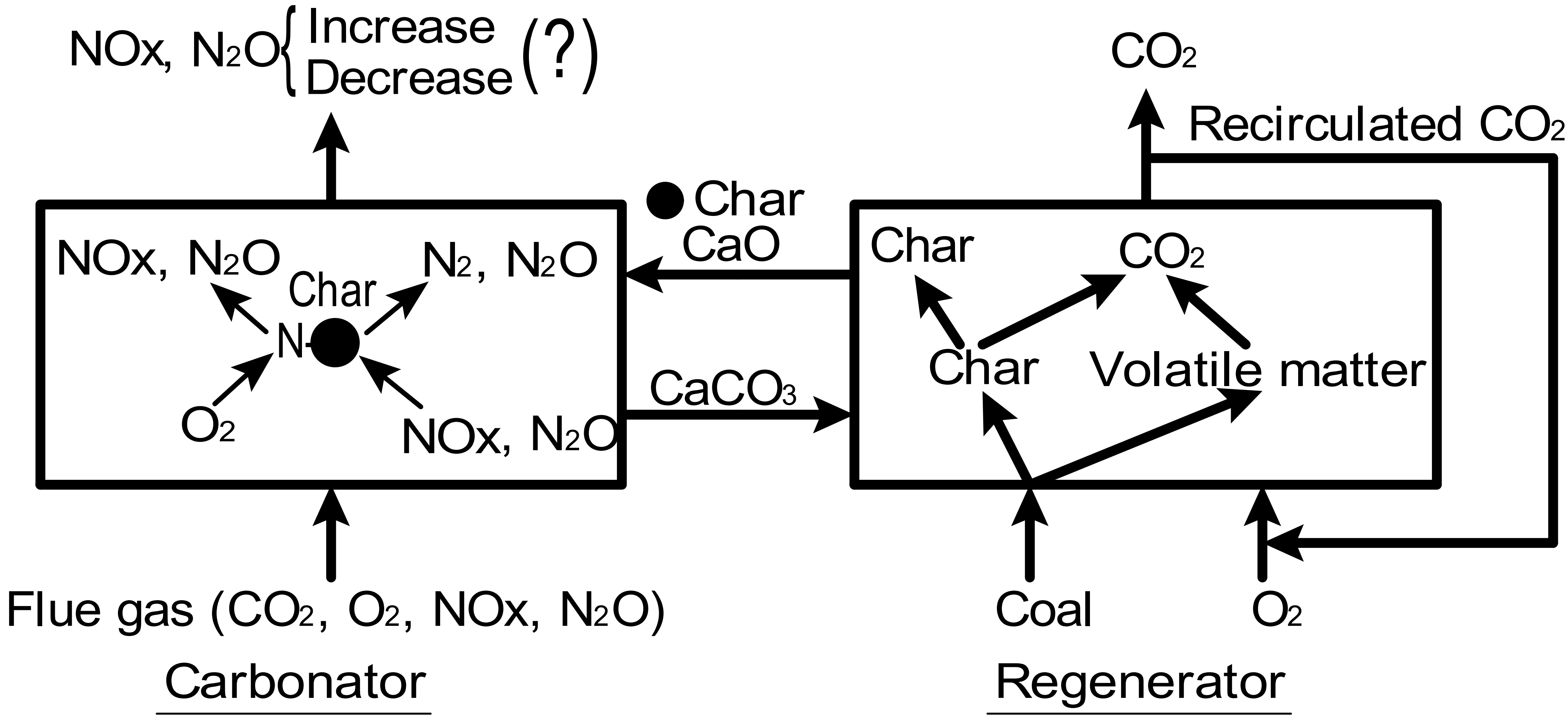
→ Formation of CO and/or CO_2



Possible roles of char in carbonator

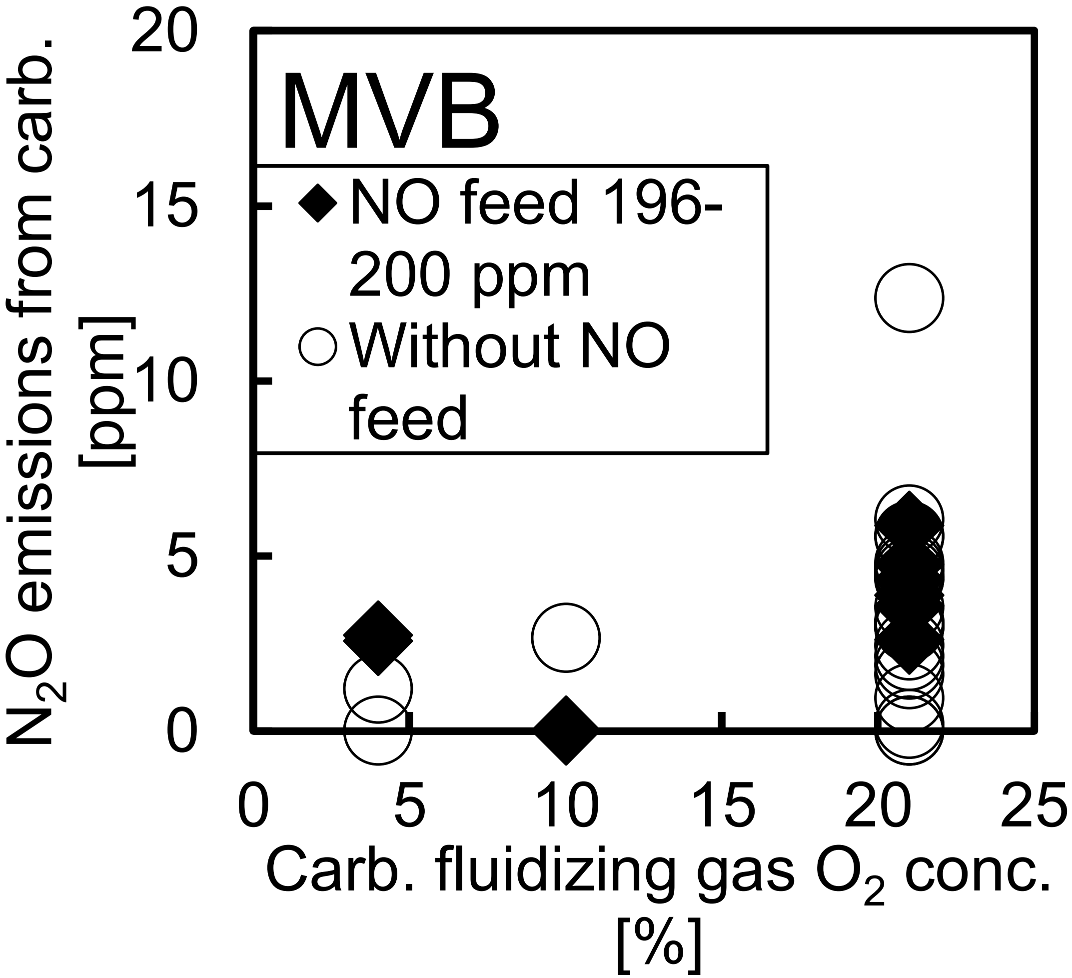
Char is expected to have different roles in carbonator:

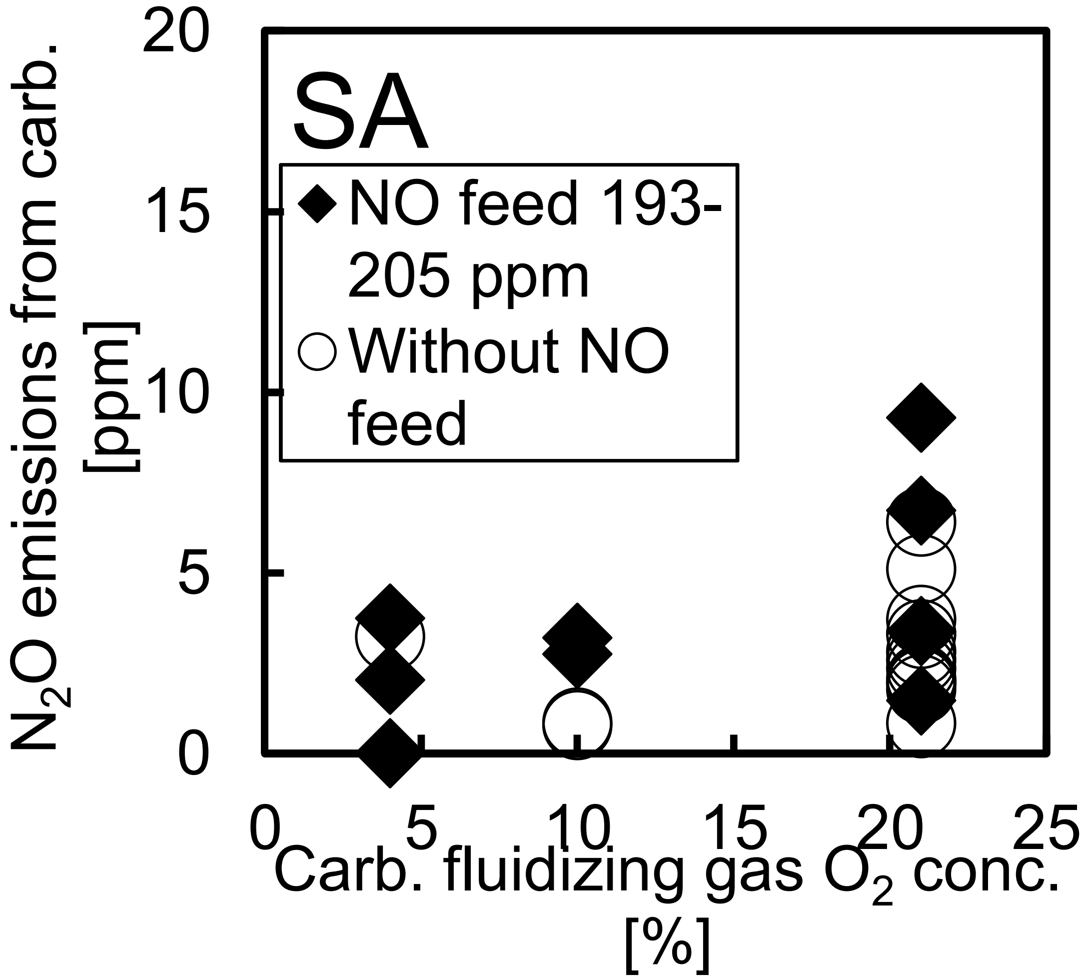
- Oxidation of char-N : formation of N_2O
- $C+N_2O \rightarrow N_2$: N_2O reduction



N_2O formation from char oxidation/NO reduction

N_2O emissions from char combustion / NO reduction by char were only slight (<10 ppm = 0.3% CO_2-equivalent).

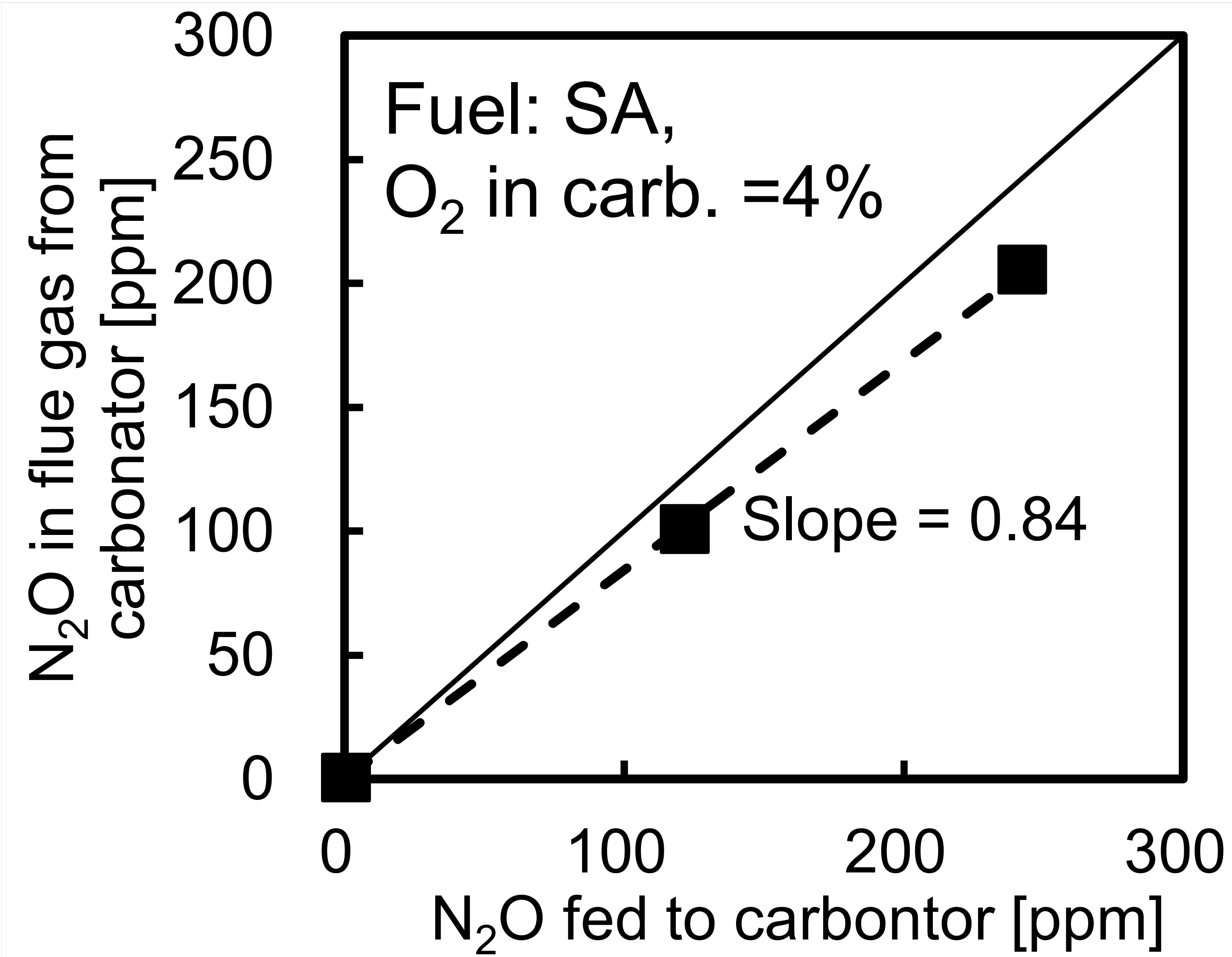




(Shimizu et al., J. Jpn. Inst. Energy, 94, 841-850, 2015)

Reduction of fed N_2O in carbonator

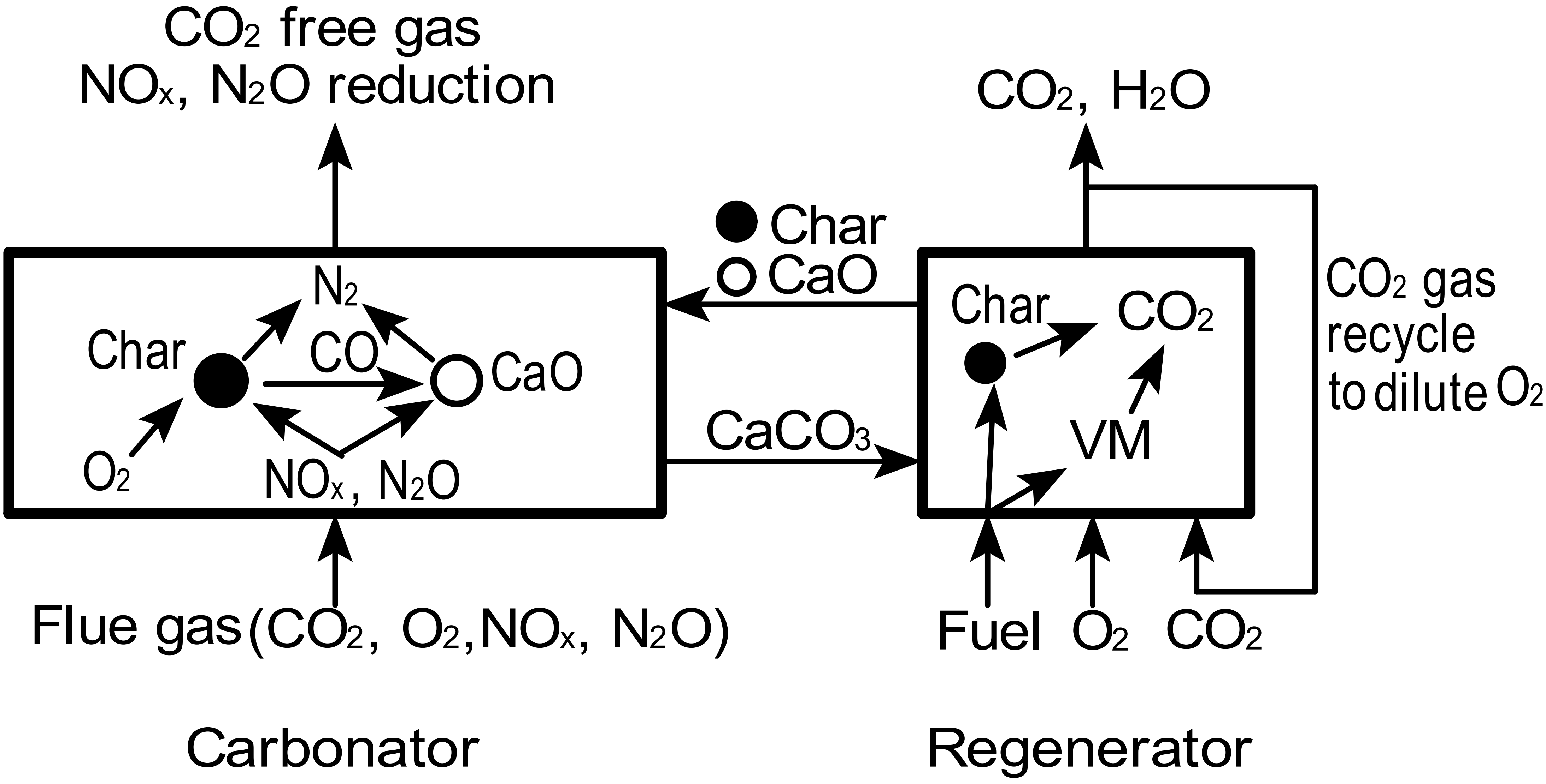
For semi-anthracite, about 16% of N_2O in fluidizing gas was reduced in carbonator.



(Shimizu et al., 6th HTSLC Meeting (Milan, Italy, 2015)

Expected N_2O reduction by CaO in carbonator

CaO is expected to catalyze N_2O decomposition and reduction by CO which is formed by char oxidation.

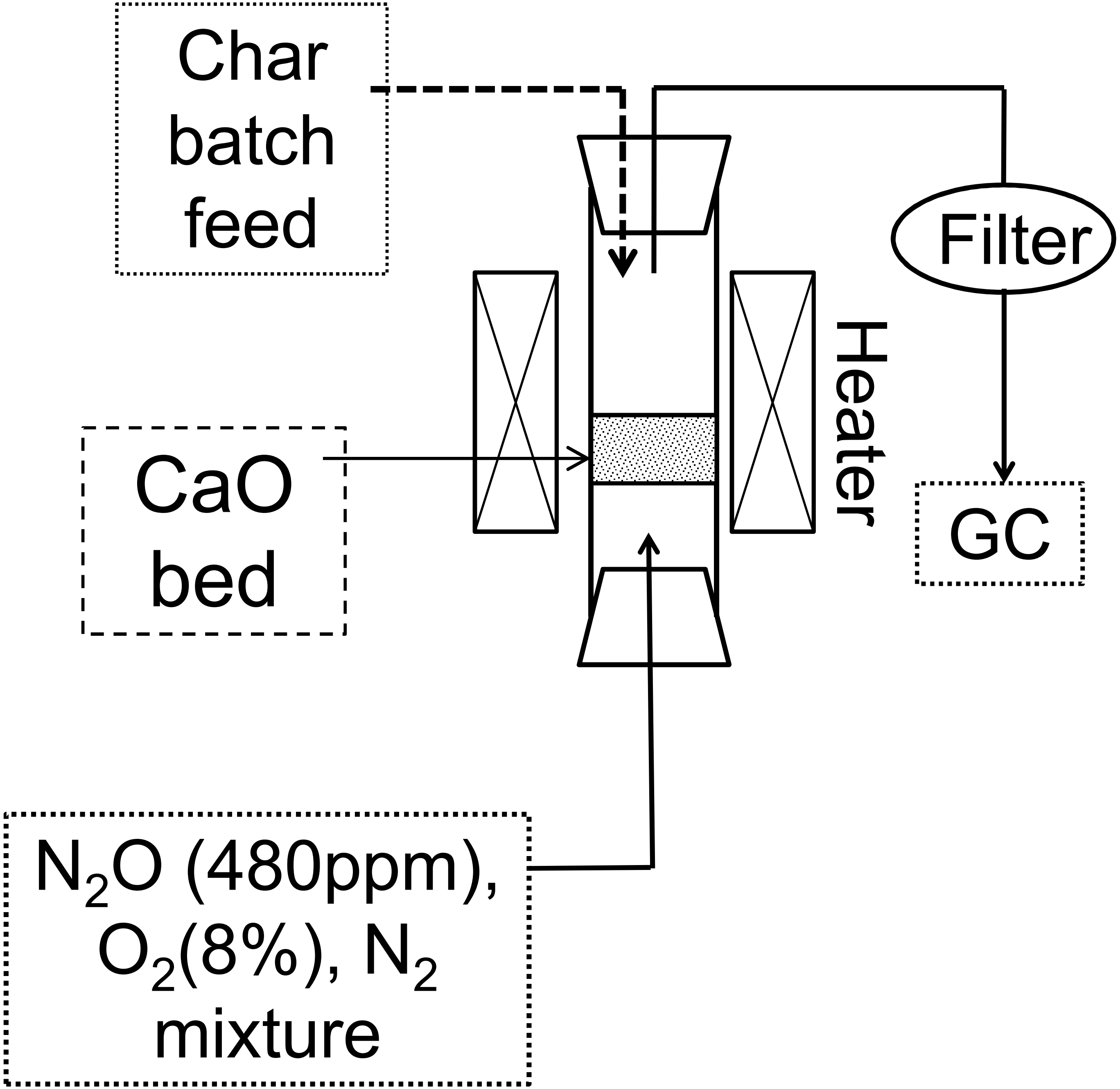


This work

Basic study on N_2O decomposition by CaO using quartz FB reactor

N_2O-containing gas was fed to a bubbling fluidized bed of CaO at 600 ^oC to evaluate N_2O decomposition. Also batch feed of char to the CaO bed was conducted.

Experimental apparatus



<u>Quartz FB</u>

ID 26mm

Limestone (0.35-0.42 mm) calcined at 900 °C

Static bed height H_s=7 cm

Temp. 600 °C

U_{gas}= 17cm/s

(H_s/U_{gas}=0.4 s)

Char batch feed

Char was prepared by heating at 900 ^oC in N_2.
Batch feed was conducted.

Analyses of char

Ash (dry)	Moist. (sample)	C (daf)	H(daf)	N(daf)
23.3	2.0 - 3.5	95.8	0.6	1.2

VM content: 2 - 3% of combustible part. (TGA weight loss in N_2 between 200 – 600 ^oC)

Results and Discussion

- N_2O decomposition by CaO without char
- Char batch feed to CaO/inert bed

N_2O decomposition **without char feed**

Silica sand bed: nearly 0% conversion

(no thermal decomposition at 600 ^{o}C)

CaO bed: nearly 100% decomposition

(480ppm at inlet → <1 ppm at outlet)

$k\tau$ = ln(In/Out) > 6.2*

k: first-order rate constant :[1/s]

τ: contact time [s]

(*: This value includes bubble-emulsion mass transfer resistance)

Rate of N_2O reduction by CaO

In dry gas, rate expression is:

$k_{N2O}(0) = 2.8x10^7 exp(-1.057x10^4/T)=154$ [1/s].

(Shimizu et al., Energy Fuels 2000, 14, 104-111)

Gas-solid contact time: $\tau = 0.2$ s

→ $k_{N2O}\tau = 30$

→ Contribution to N_2O reduction.

N_2O decomposition by CaO in the presence of H_2O

In the presence of water, rate expression is:

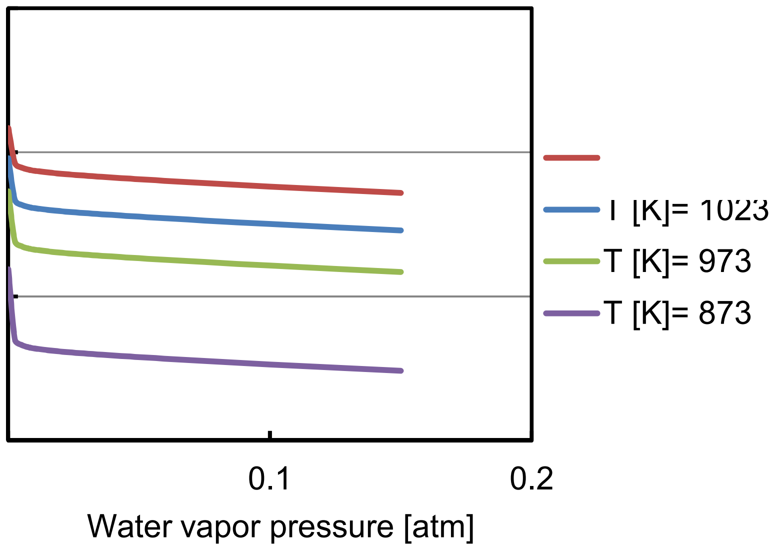
$$k_{N2O} = \frac{k_1}{1+K_1P_{H2O}} + \frac{k_2}{1+K_2P_{H2O}}$$

(Shimizu et al., Energy Fuels 2000, 14, 104-111)

$k_{N2O}(0)=k_1+k_2$, $k_2/k_{N2O}(0)$ = 0.0011T - 0.685

$k_{N2O}(0)$ =

K_1= 43exp



At 600 °C and

and P_{H2O}=0.1

k_{N2O}=34 s^{-1}

→ Contribution to N_2O reduction is expected.

Char batch feed to CaO bed

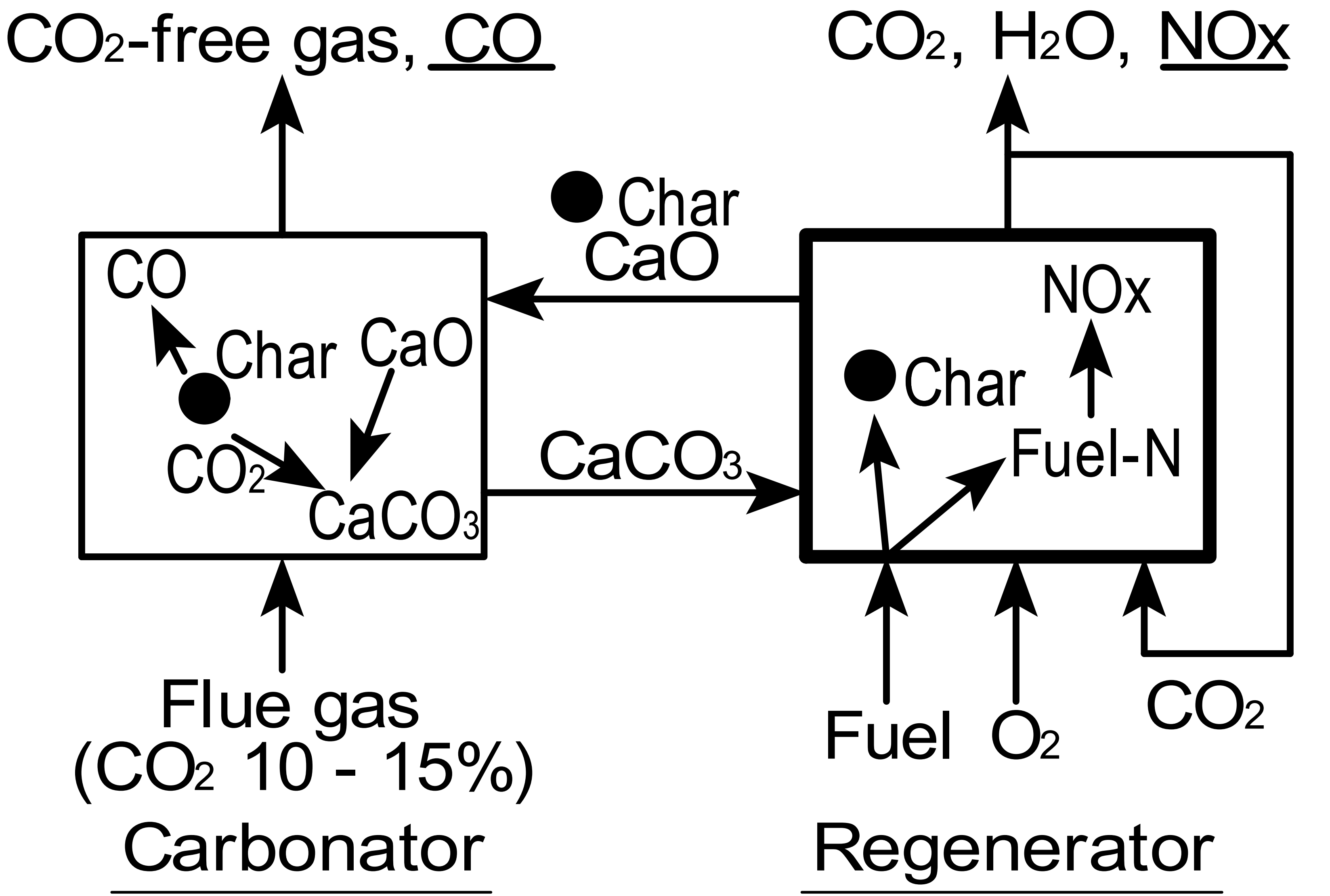
During the experiments, char batch feed (40 – 50 mg) was conducted. Formation of CO, CO_2 and change in N_2O were observed.

Under the present condition, however, the effect of char feed on N_2O decomposition was not clear because sufficiently high N_2O decomposition was observed without char feed.

Anticipated problem with char transportation

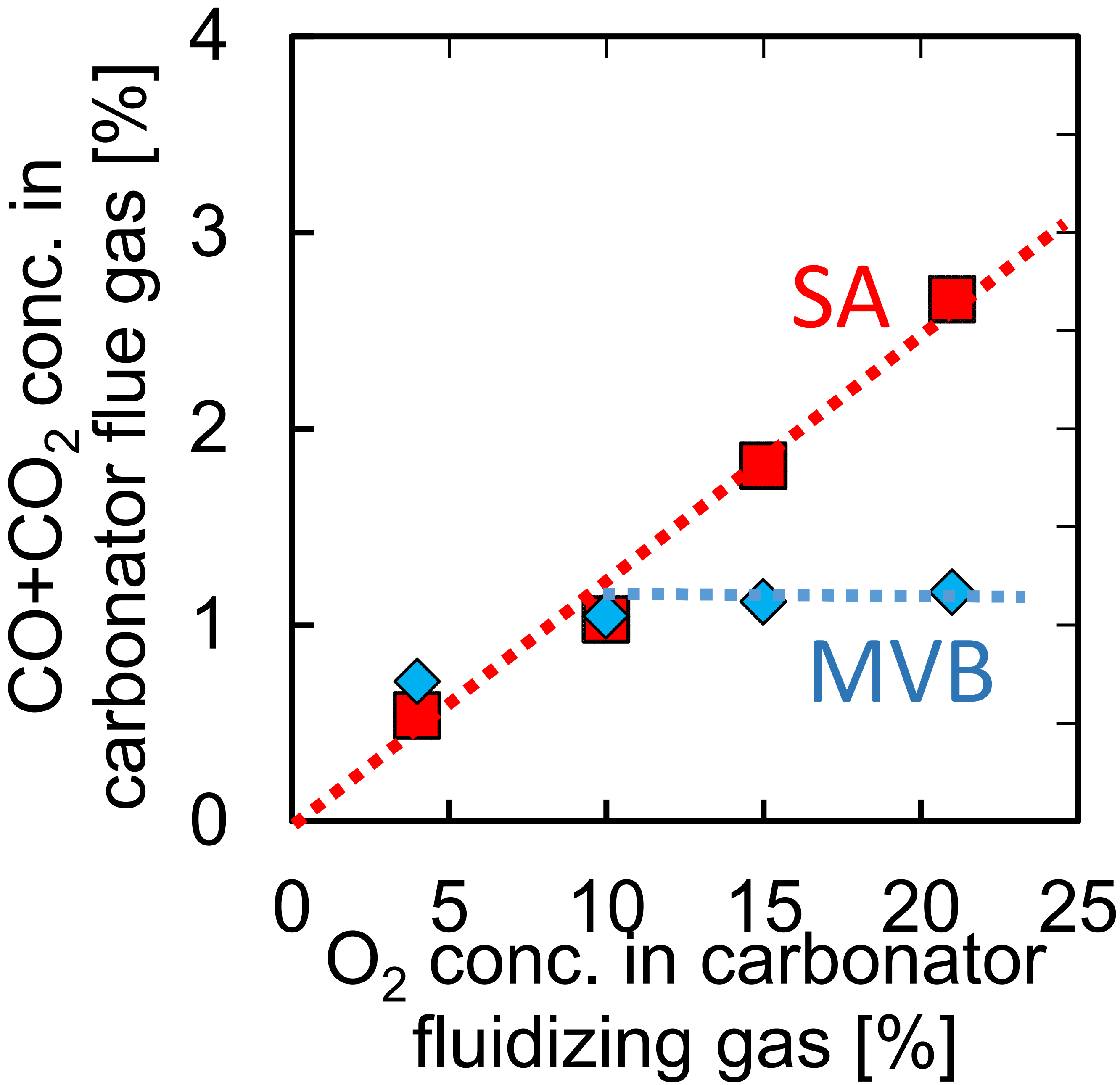
Transportation of char to carbonator

→ Low temperature oxidation of char → Formation of CO



Formation of CO and CO_2 in carbonator (dual-FB)

Char transportation to carbonator →CO & CO_2 formation when sand was employed as bed material for dual-FB experiments.

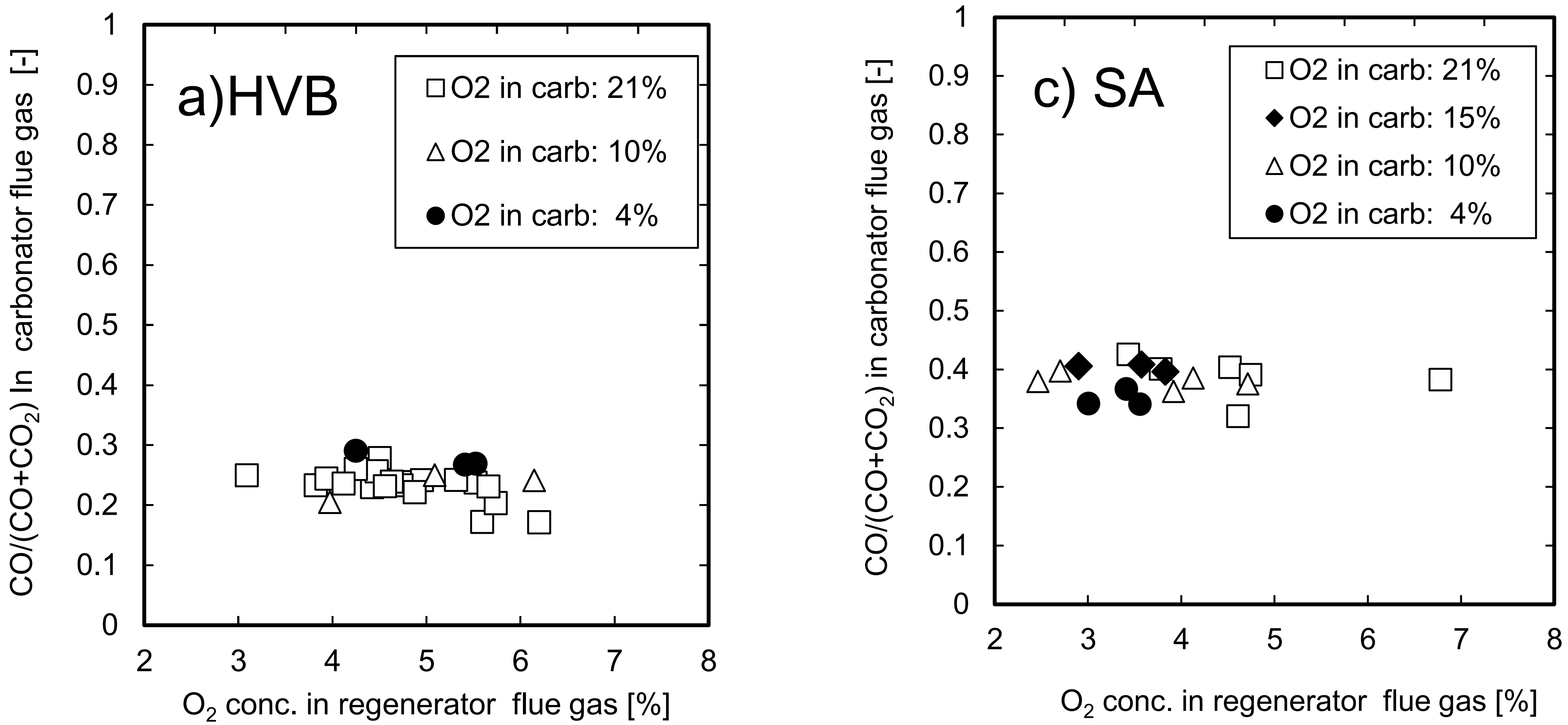


(Shimizu et al., J. Jpn. Inst. Energy, 94, 841-850, 2015)

Previous results of CO emissions from carbonator

When sand was employed as bed material, 20 – 40% of carbon oxidized in the carbonator was converted to CO.

→CO in gas = 1000 – 2000 ppm



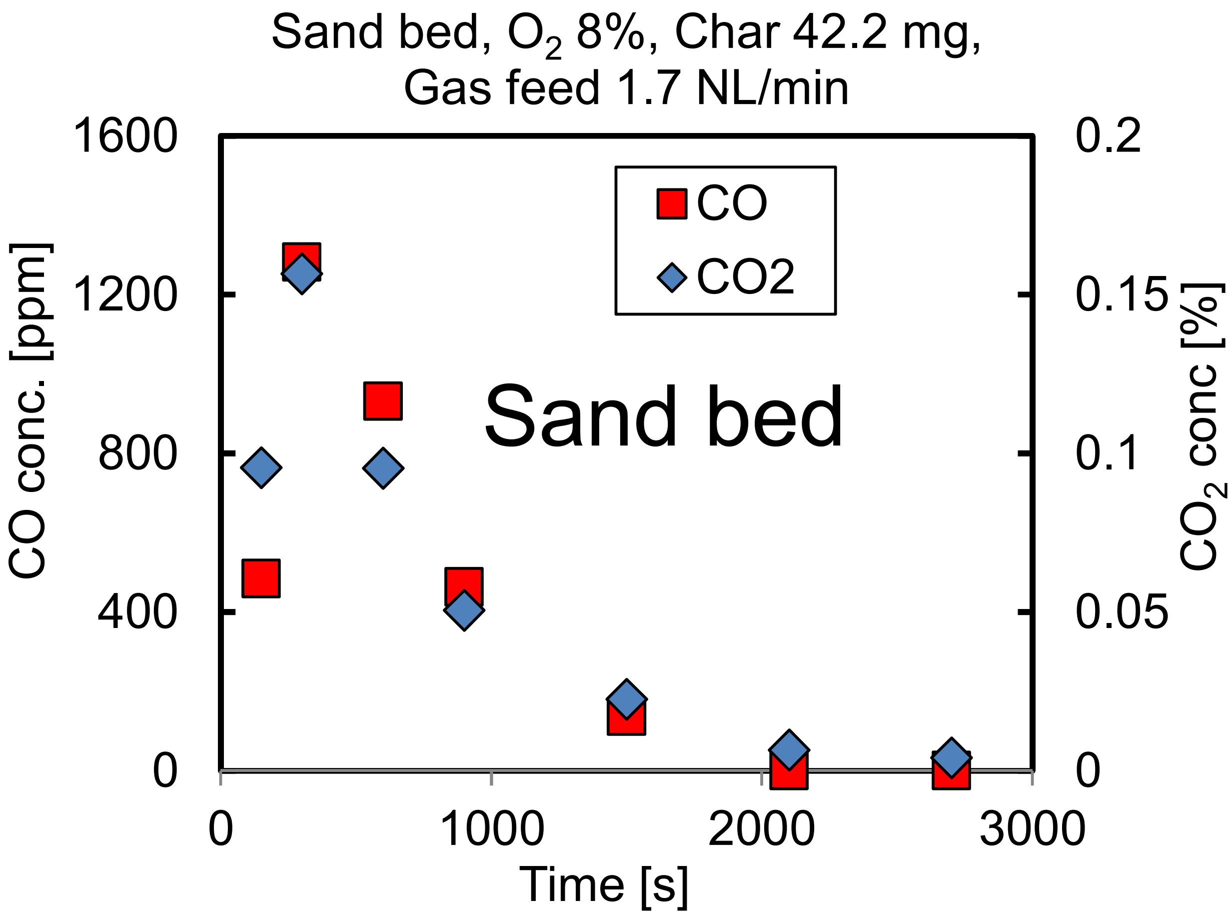
(Shimizu et al., J. Jpn. Inst. Energy, 94, 841-850, 2015)

Present results of CO formation from char

Selectivity to CO was reduced from 0.45 for sand bed (similar to dual-FB results) to zero (<detection limit) for CaO bed. CaO bed can suppress CO emissions even when char is transported to carbonator.

Selectivity to CO

Sand bed	CaO bed
0.45	0



Conclusions

It is expected that carbonator of CaL process can work as N_2O abatement reactor because CaO can work as N_2O decomposition catalyst.

Char particles are known to be transported from regenerator to carbonator and form CO there. The presence of CaO is expected to reduce CO emissions from carbonator.

Acknowledgements

The authors express their thanks to the financial supports from The Iwatani Naoji Foundation.