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CERTECH

An overview of high temperature syngas purification

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Context

- Gasification is a good alternative for the valorisation of different types of carbonaceaous materials : biomass, coal, municipal solid waste, plastic waste …
- The main compounds of the syngas are
  - H_2 25-30 %v/v
  - CO 30-60 %v/v
  - CO_2 5-15 %v/v
  - H_2O 2-3 %v/v
  - Some low alcanes
  - impurities

Context

– Why do we need to remove the impurities from the syngas ?

Impurity types	Example	Apprehended effects
Sulphur compounds	H_2S,COS	Corrosion, emission to environment
Hydrogen Halides	HCl, HF	Corrosion, reaction with ammonia
Metal carbonyl	$Fe(CO)_5$, $Ni(CO)_4$	Deposit and accumulation downstream
Nitrogen compounds	NH_3, HCN, NO, N_2O	Emission to environment
Heavy metal	Hg, Cr, Mn, Zn, …	Deposition downstream et environment
Tars	Benzene, naphthalene,…	Coking, deposits downstream
Oxygen	O2	Oxidation of syngas
Particles	SiO_2, ash …	deposition downstream

Dry syngas purification processes for coal gasification systems, Makato Kobayashi, Elsevier

– Impurities have harmful effect during syngas utilisation

How to cleanup syngas ?

– Two ways can be used to remove impurities from the syngas :

1. **The Cold Gas Cleaning (CGC) process**
   + Well established wet syngas purification
   – But needs to work at low temperature (heat exhanger) and produces by-product which needs to be treated (water, solvent…)

2. **The Hot Gas Cleaning (HGC) process**
   + Works at high temperature, works with regenerable sorbent, less by-product to be treated, no heat exchanger needed.
   – Not well established syngas purification, still needs development.

How to cleanup syngas ?

- The Cold Gas Cleaning (CGC) steps :
  - cooling the gas at the right temperature (heat exchanger)
  - primary dust removal (filter or cyclone)
  - Unit of scrubbing (alkaly, HCl, HCN, fine particles, tar…)
  - H_2S absorption unit (amine, cold methanol, dimethyl ethers of polethylene glycol, …)
  - If necessary on COS hydrolysis process
  - Finally modify activated carbon for heavy metal recovery like Hg, could be also for dioxin

How to cleanup syngas ?

– Technique implemented for dry syngas purification (HGC)

Impurities	Technique could be used
Ash, solids particles	High temperature filtration (ceramic, metallic filter) (waste)
Sulphur compounds	Metal oxide (possible to regenerate)
Hydrogen Halides	Alkali metals, alkaline earth metals (salt: waste)
Metal carbonyl	Catalytic decomposition
Nitrogen compounds	DeNOx process
Heavy metal	Condensation (Activated carbon a low temperature, CuO for higher temperature)
Tars	Thermal cracking, catalytic cracking, condensation …

Example of process flow diagram of dry syngas purification

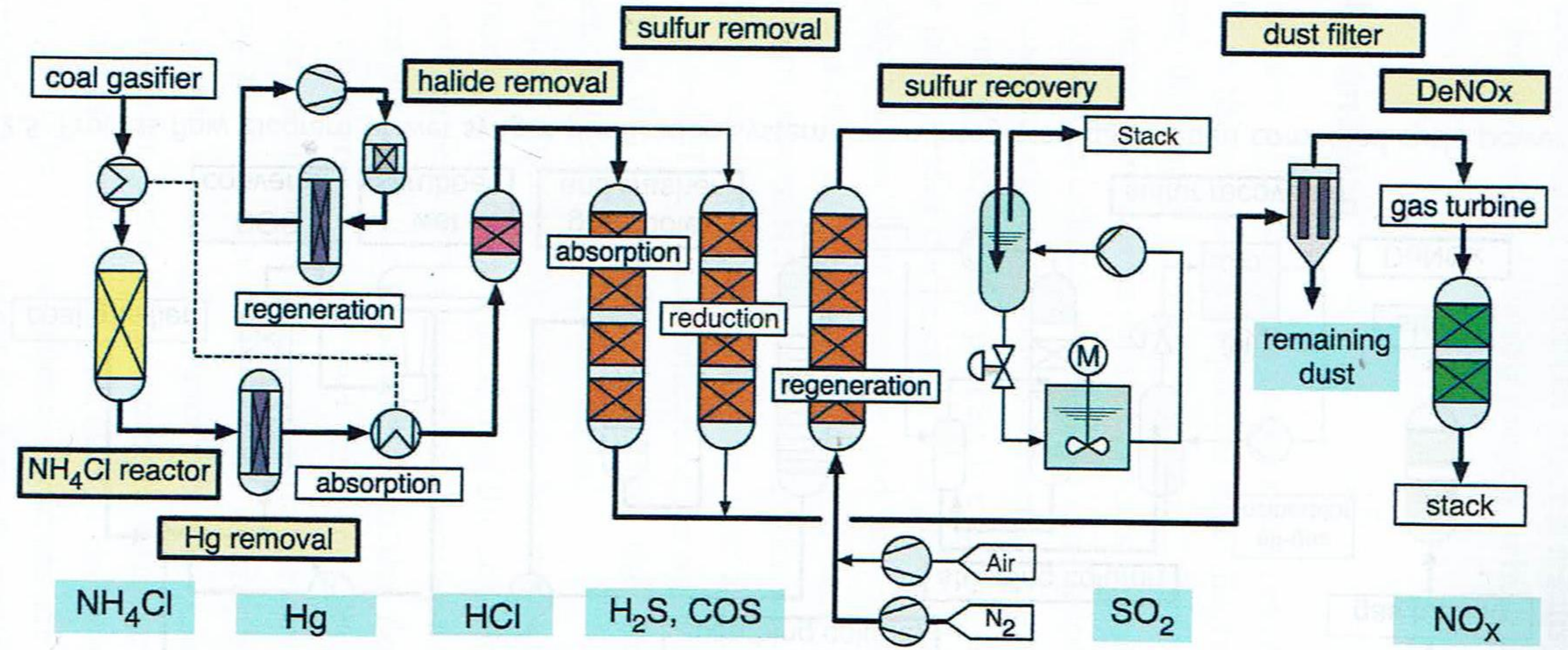

Figure 2.6 Process flow diagram of dry syngas purification system for an integrated gasification combined cycle power plant.

Dry syngas purification processes for coal gasification systems, Makato Kobayashi, Elsevier

Development of dry halides removal sorbent

Development of sodium aluminate base sorbent : $NaAlO_2$

$$NaAlO_2 + HCl \rightleftharpoons NaCl + 1/2\ Al_2O_3 + 1/2\ H_2O$$

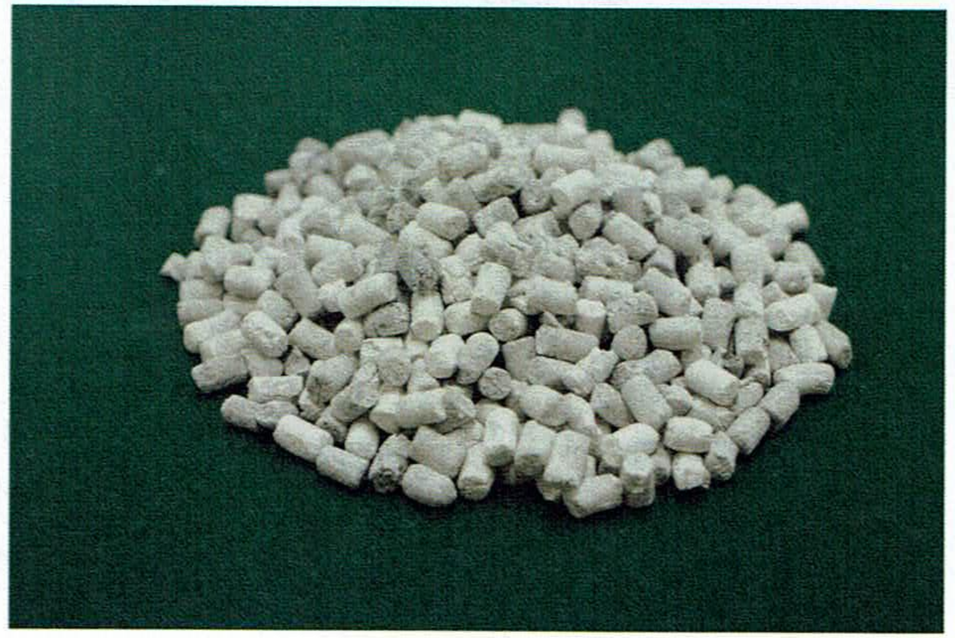

Fig. 4. Halide removal sorbent (SAS K) subjected to the syngas test.

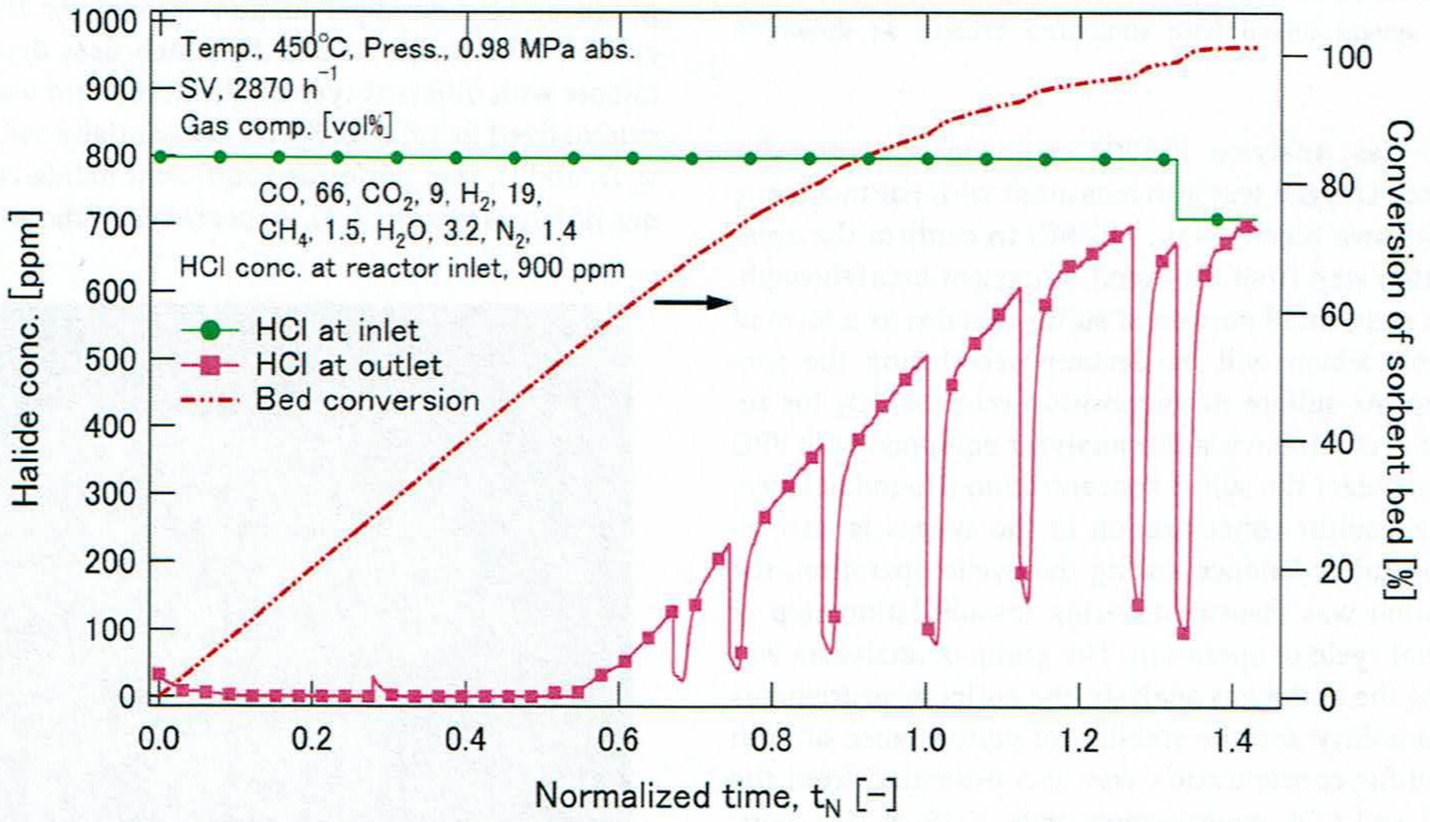

Fig. 6. Halide removal test result for SAS K at oxy-fuel test condition at laboratory.

Halides removal is necessary to prevent halogenation of the substrate used for the suflur removal

M Kabayashi et al, Fuel 250 (2019) 144-153

Development of dry sulfur removal sorbent

– Metal oxides are good candidate

$$MeO + H_2S \longrightarrow MeS + H_2O$$

$$MeS + 3/2\ O_2 \longrightarrow MeO + SO_2$$

Zn, Cu, Ni and Ce : H2S < 10 ppm

Ca, Fe and Mn : H2S ≅ 100 ppm

Development of dry sulfur removal sorbent

Kobayashi et al presented a sulfur removal process with mixed oxide : $ZnFe_2O_4$

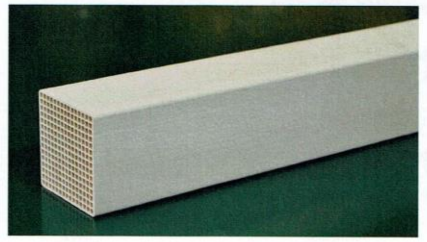

Fig. 5. Honeycomb desulfurization sorbent subjected to the syngas test.

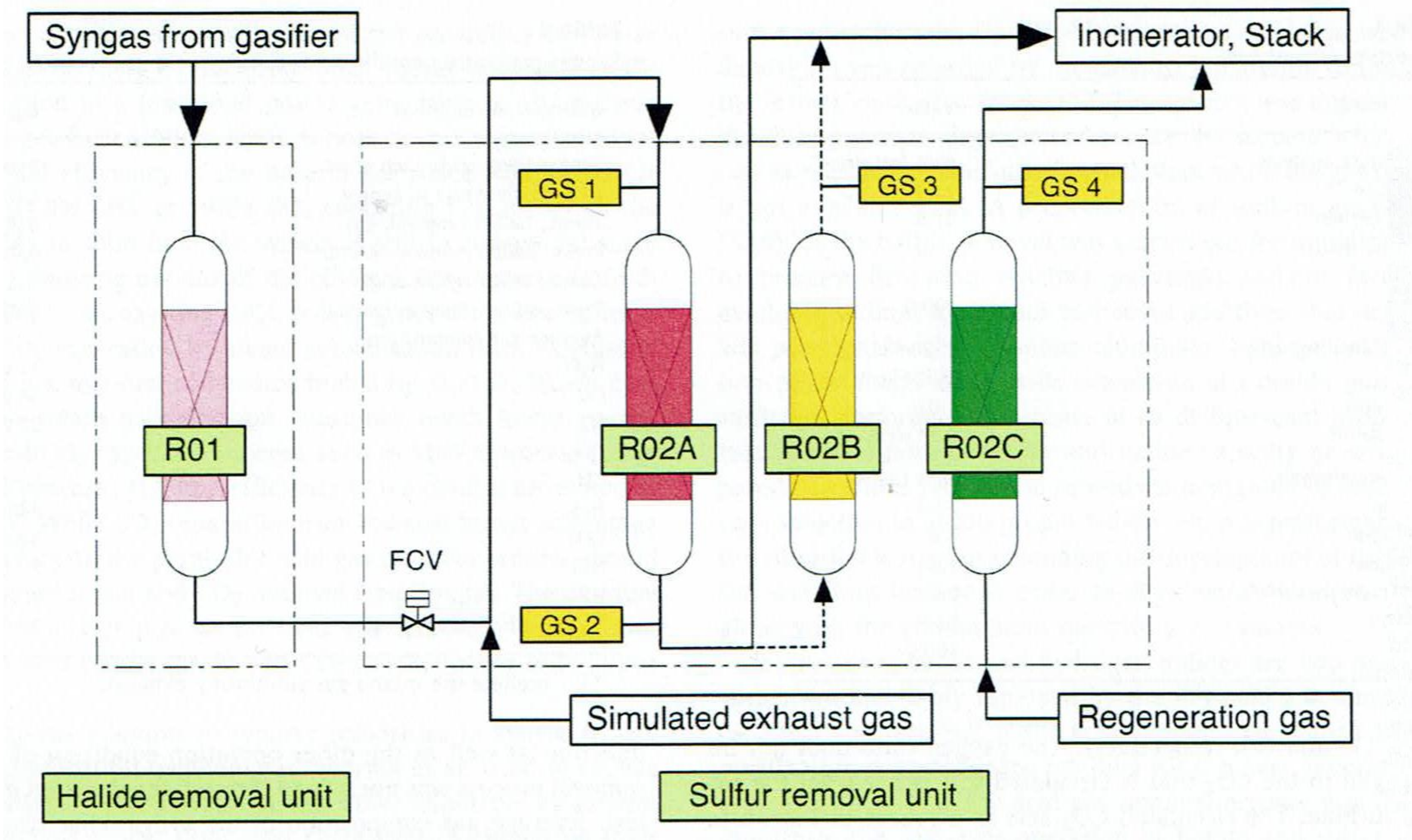

Fig. 2. Dry acid gas removal test facility installed at the O_2/CO_2-blown gasifier test plant.

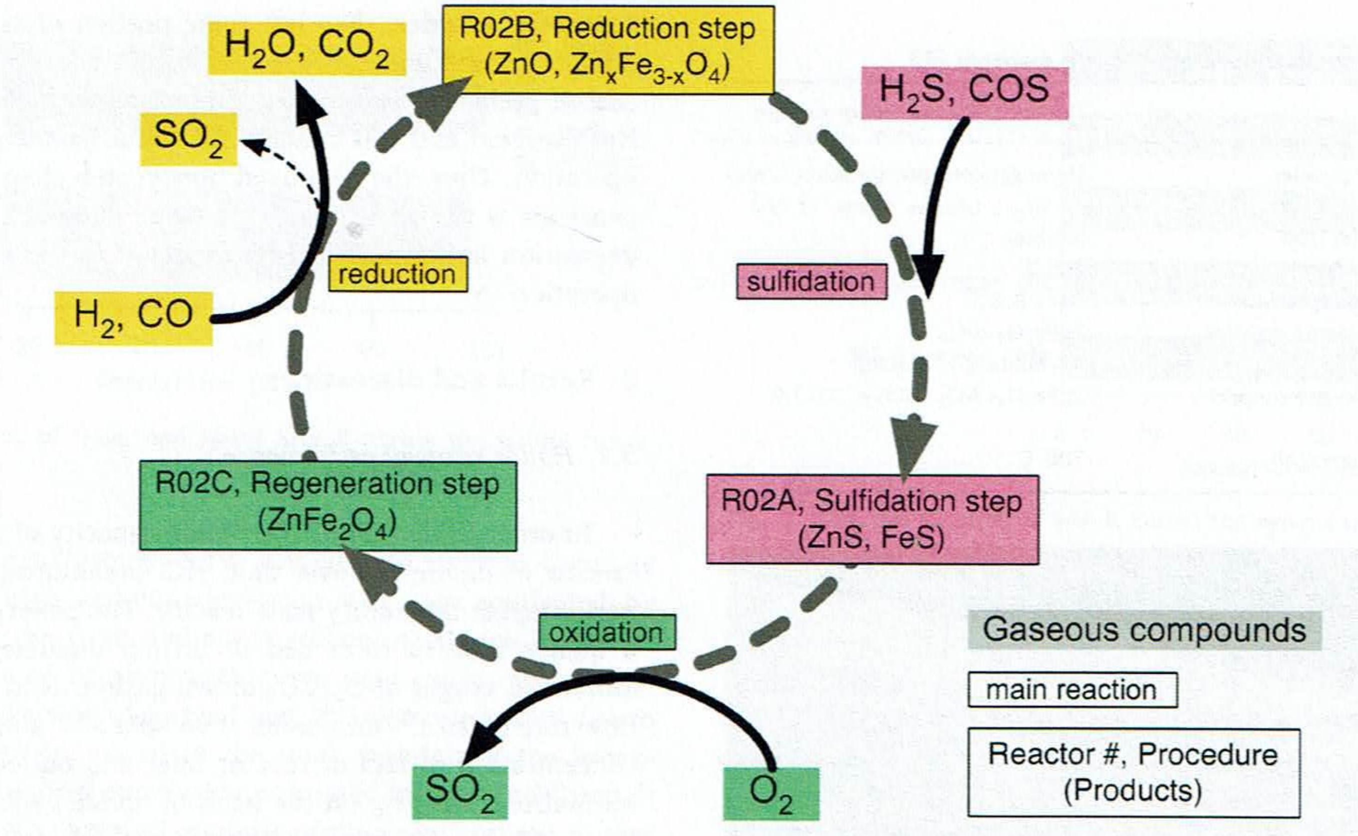

Fig. 3. Schematic diagram of the cyclic operation of the sulfur removal unit.

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Development of dry sulfur removal sorbent

$ZnFe_2O_4$ honeycomb: sulfidation, regeneration and reduction cycles

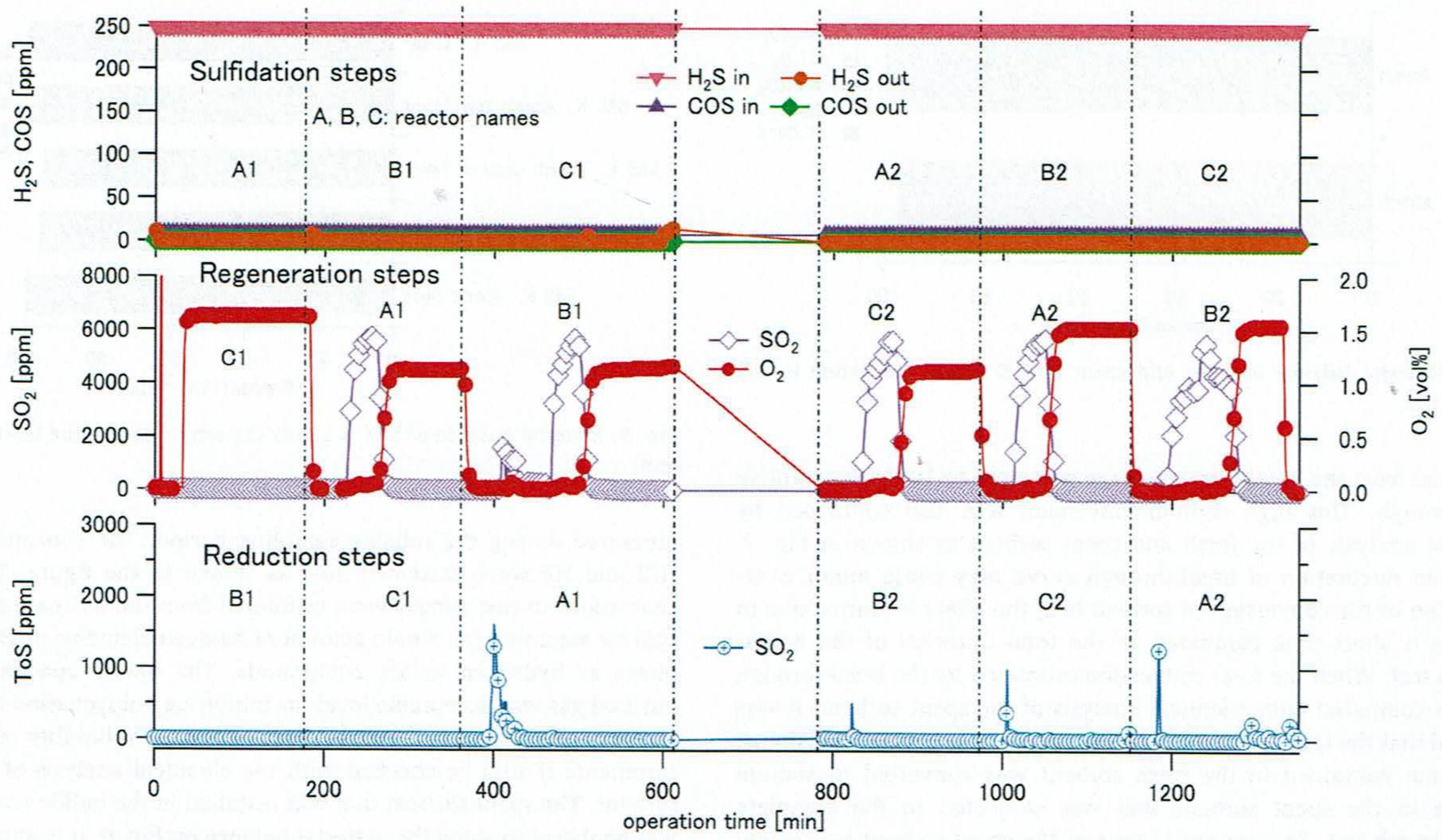

Fig. 10. Comprehensive performance test results obtained for the sulfur removal unit during 1st and 2nd cyclic operation of three reactors at the syngas test.

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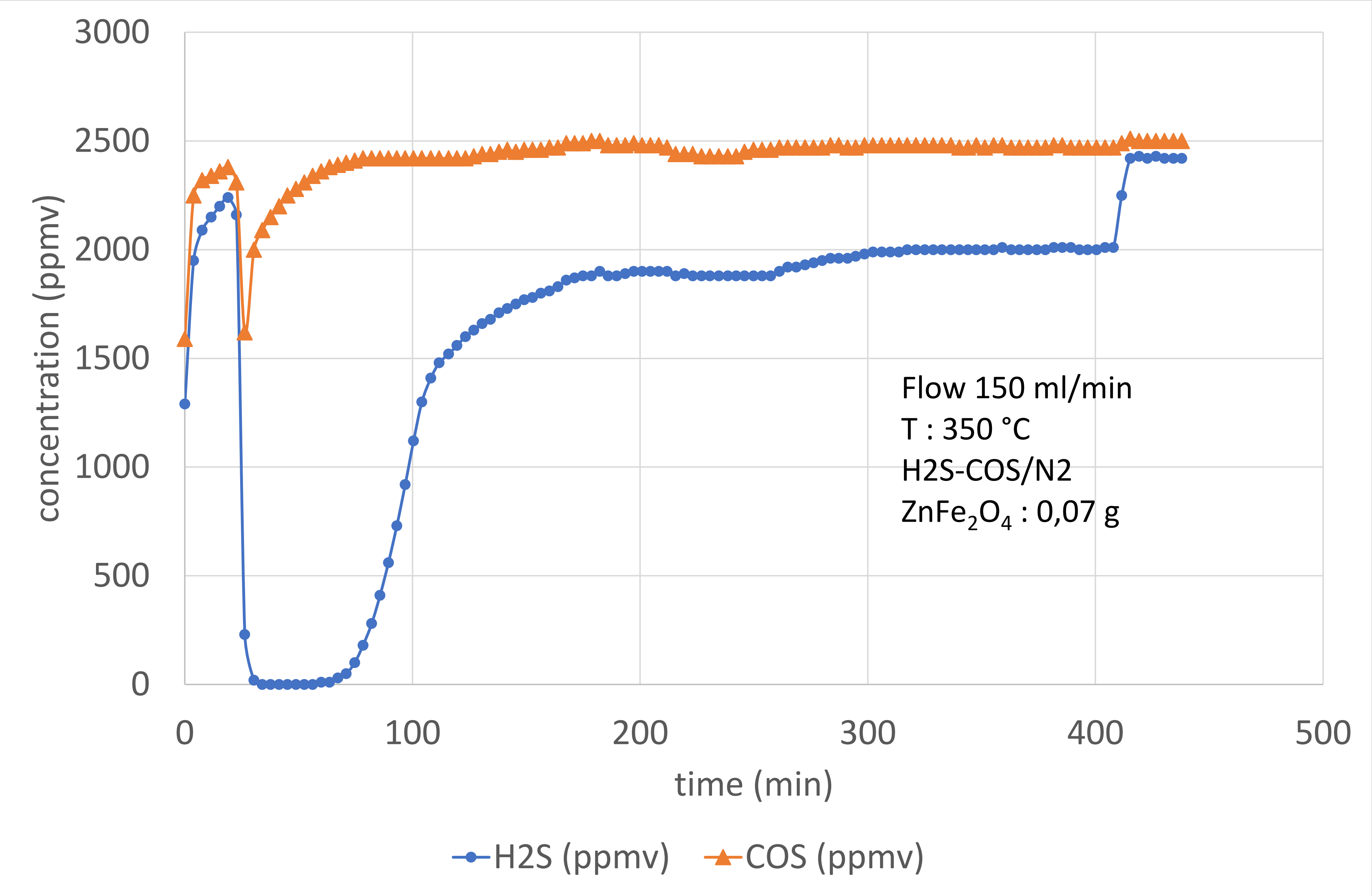
Development of dry sulfur removal sorbent

$ZnFe_2O_4$ synthetized by Certech, example of breakthrough curve



Flow 150 ml/min
T : 350 °C
H_2S-COS/N_2
$ZnFe_2O_4$: 0,07 g

molar ratio of S/(ZnFe) = 0,52 at breakthrough
molar ratio of S/(Zn+Fe) = 1,95 at the end of the test

Development of dry mercury removal sorbent

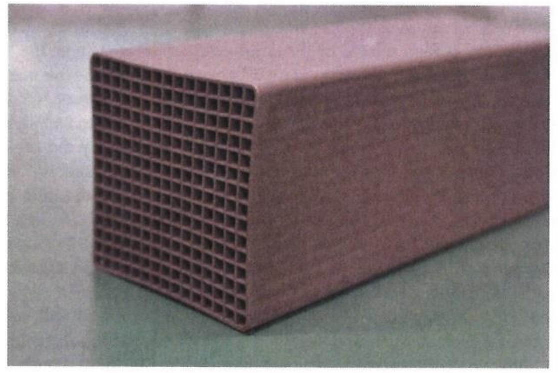


Fig. 2. Appearance of an A-CBS honeycomb.

Development of a CuO base sorbent

Pre –sulfidation treatment (120 °C)

$$xCuO + y\,H_2S \longrightarrow Cu_xS_y + xH_2O + (y-x)H_2$$

Mercury removal (140 °C)

$$Cu_xS_y + z\,Hg° \longrightarrow zHgS + Cu_xS_{y-z}$$

Hg recovery (250 °C)

$$zHgS + zO_2 \longrightarrow zHg° + zSO_2$$

H. Akio and M. Kabayashi , Fuel 253 (2019) 1385-1391

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Development of dry mercury removal sorbent

Example of Hg removal test :

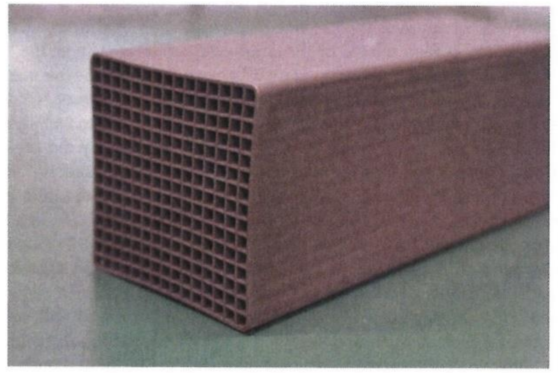

Fig. 2. Appearance of an A-CBS honeycomb.

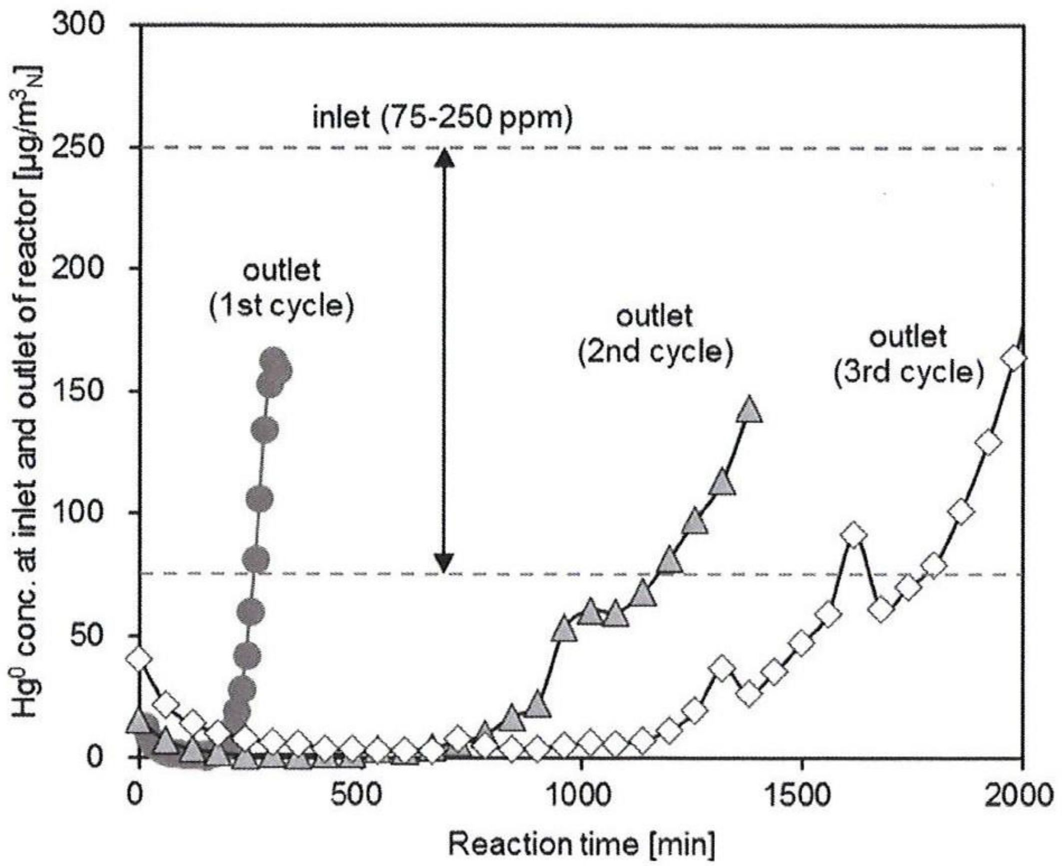

Fig. 5. Mercury breakthrough curves of the pre-sulfidized A-CBS honeycomb in three cyclic tests.

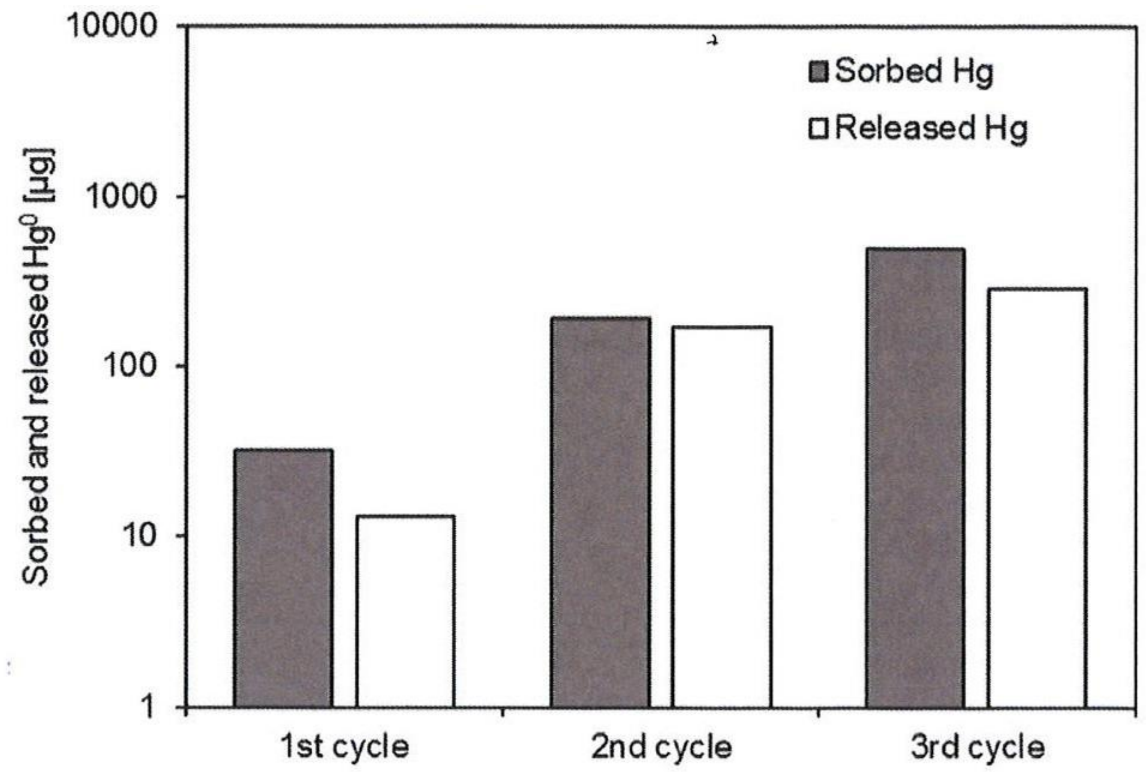

Fig. 7. Mercury balance obtained by gas analysis during the sequential operation using an A-CBS honeycomb.

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Development of dry mercury removal sorbent

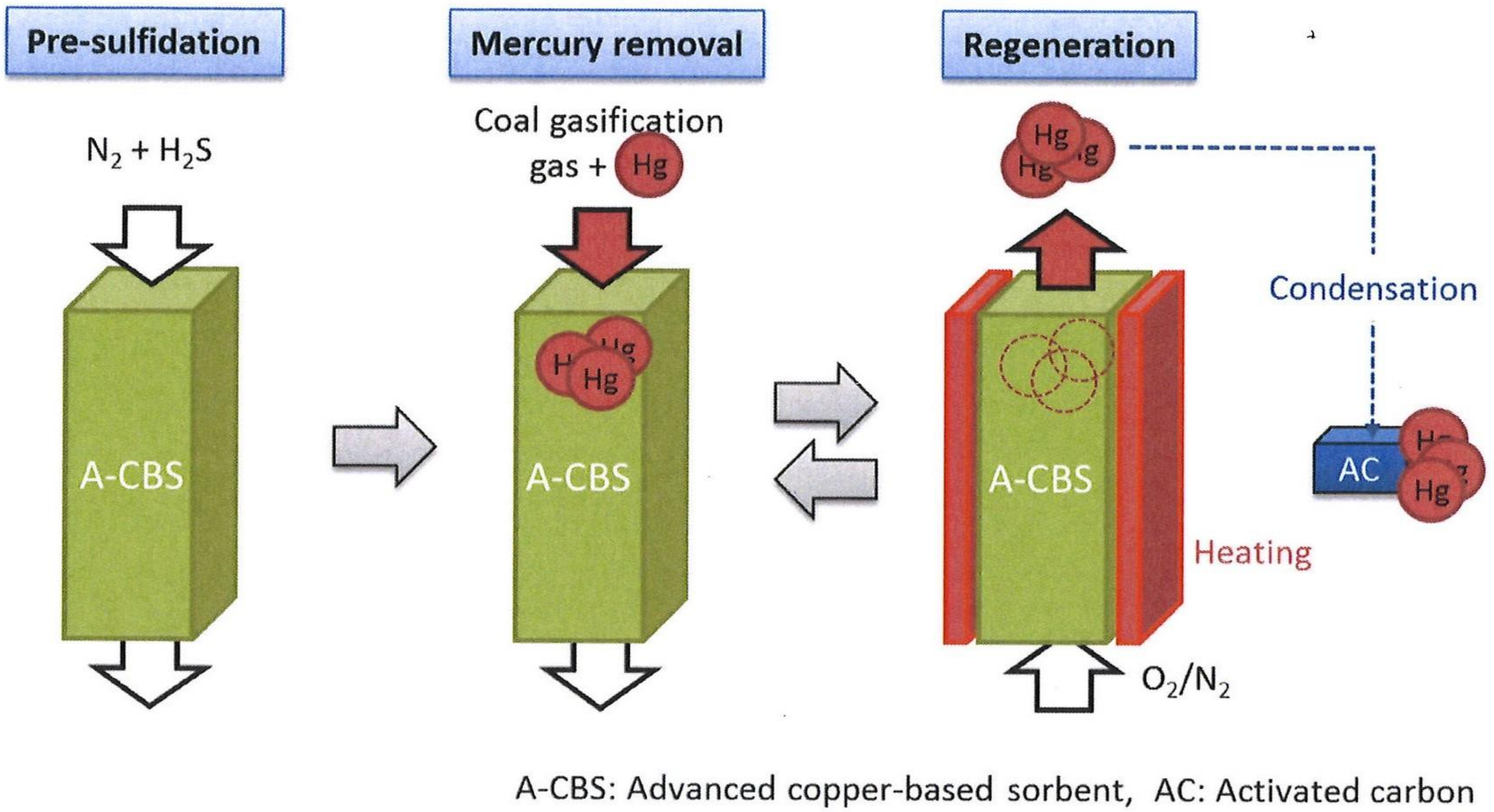

Fig. 10. Image of the mercury removal process using the A-CBS honeycomb.

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Conclusion

- Some researches are ongoing to develop dry sorbent for syngas purification :
  - Sodium aluminate base sorbent for halides removal (production of waste
  - Regeneratable zinc ferrite base sorbent for H_2S and COS removal
  - Regeneratable copper oxide base sorbent for Hg removal.

- Some work is still needed to upgrade the pilot test for industrial use.

Conclusion

- Advantage of dry cleaning processes :

  - No needs to cooldown the syngas at low temperature
  - Elimination of wastewater treatment
  - Removal of halides impurities a higher temperature
  - regenerable of sulfur and mercury removal sorbent

Acknowledgements

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