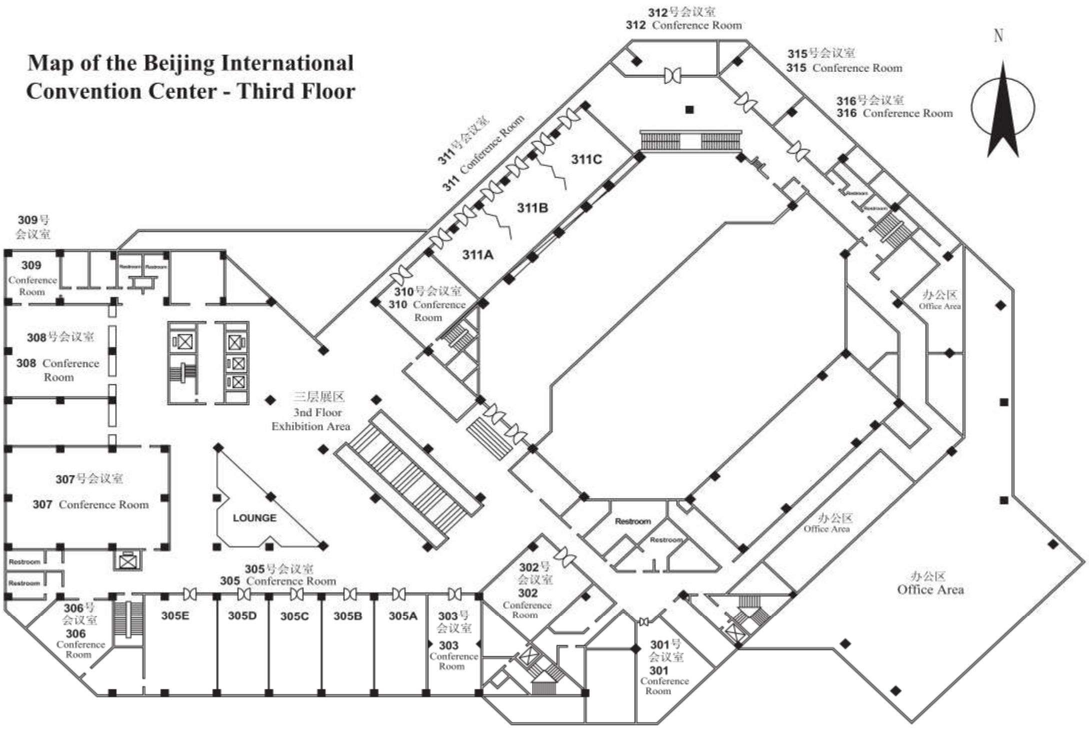
五、附　錄

(一) IPCC-30 舉辦場地-北京國際會議中心

(二) 發表之論文投影片

(一) IPCC-30 舉辦場地-北京國際會議中心

Beijing International Convention Center



SESSION MEETING ROOMS

Room 305 (A+B)
Sessions 1, 7, 13, 19, 25, 31, 37, 43, 49

Room 305 C
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Room 308
Sessions 5, 11, 17, 23, 29, 35, 41, 47, 53

Room 305 D
Sessions 6, 12, 18, 24, 30, 36, 42, 48, 54

Registration
Sunday - Second Floor Lobby
Monday - Wednesday - Room 310

Sunday Evening Reception
Banquet Hall on the Second Floor of the North Star Continental Grand Hotel

Opening Ceremony
Convention Hall No. 1
Second Floor of the Convention Center

Plenary Sessions
Convention Hall No. 1
Second Floor of the Convention Center

Conference Luncheons
Monday and Tuesday - Banquet Hall on the Second floor of the North Star Continental Grand Hotel
Wednesday - Convention Hall No. 1
Second Floor of the Convention Center

Poster Presentations
Third Floor Exhibition Area

Exhibits
Third Floor Exhibition Area

(二) 發表的論文投影片

30th Annual International Pittsburgh Coal Conference
Beijing, CHINA, September 15 – 18, 2013

Sulfide Capturing Techniques for Advanced Fuel Conversion Process by Silica-Supported Sorbents

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2013/09/18

INER Institute of Nuclear Energy Research

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INER (Institute of Nuclear Energy Research)

- History: founded since 1968 and currently under the administration of Atomic Energy Council (AEC).
- Mission: the sole national research institute, dedicated to energy technologies R&D and promotion for peaceful applications of nuclear science in Taiwan.
- Location: in Longtan, Taoyuan County, ~30 miles SW away from Taipei (*about 1 hour drive*), in scenic and historic suburban surroundings close to the Shihmen Reservoir.

Institute of Nuclear Energy Research

Thirtieth Annual International Pittsburgh Coal Conference 2

Introduction

The Atmosphere CO_2 Concentration Change

- CO_2 concentration has increased rapidly from 280ppm to 400ppm since industrial revolution. (400.59ppm on June, 2013)
- Following this trend, it is estimated that CO_2 will exceed 450ppm within ten years.

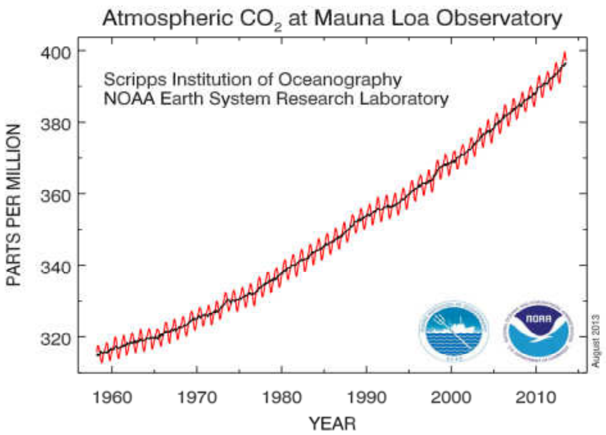


Fig.1. Atmosphere CO_2 concentration change with years

Source: NOAA http://www.esrl.noaa.gov/gmd/ccgg/trends/mlo.html#mlo *(2013.9)*

Scenario to Cut Down CO_2 Emission

- In order to maintain 2º increase of global temperature (2DS), before 2050 CO_2 emission has to be cut to half of the level in 2009.
- Improving electricity efficiency, developing renewable energy and CCS contribute to CO_2 abatement the most.

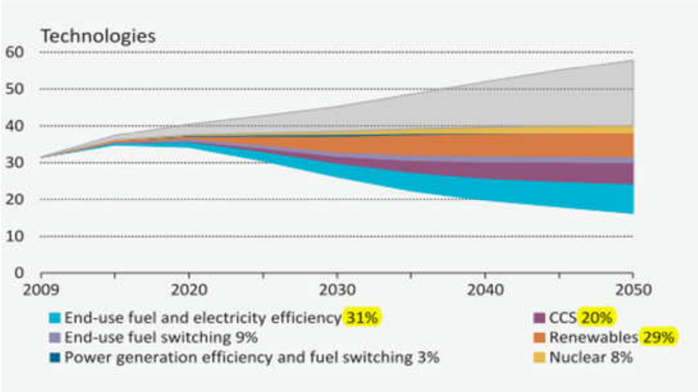


Fig.2. Key technologies for reducing CO_2 emission in blue map scenario (2DS)

Low Carbon Technology-Advanced Fuel Conversion Process

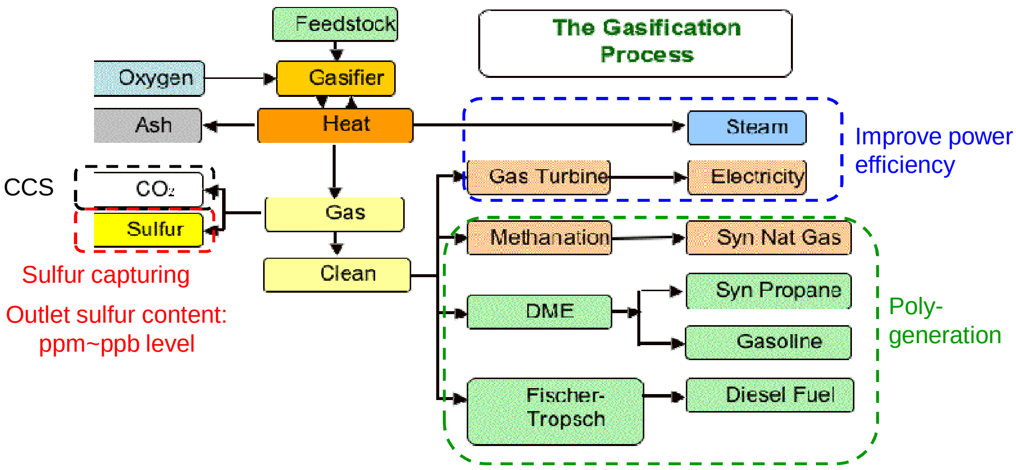


Fig.3. The advanced fuel conversion process with gasifier

Source: SynGas Technology, Inc. http://www.syngastechnology.com/gasification_2.html (2013.9)

Sulfur-Capturing Techniques

Table 1: Comparison of different sulfur-capturing techniques

process	absorption			adsorption
	Amine	*Rectisol*	*Selexol*	Warm-hot gas desulfurization
adsorbent/absorbent	MEA, MDEA	MeOH	DEPE	Metal oxide
pressure (Mpa)	<7	5.8	1.6-7.0	2-4
temperature (ºC)	25-60	-70~-30	-5~25	200-700
Sulfur concentration (ppm)	MEA<1 MDEA<0.1	<0.1	<5	<0.1
advantage	low cost, CO_2 coabsorption	CO_2 coabsorption	CO_2 coabsorption	high thermal efficiency (2-3%)
disadvantage	corrosion, solution degradation, foaming	high cost, tonxic, thermal-loss	high sulfur concentration, thermal-loss	attrition, stability

Source: Liu k. et al., 2010, Hydrogen and Syngas Production and PurificationTechnologies, AIChE, John Wiley & Sons, Inc., Hoboken, New Jersey.

Warm-Hot Gas Desulfurization

In-situ dsulfurization

- Limestone or dolomite.
  - Temperature: 950-1050 ºC
  - Pressures over 20 bar
  - CaS product
- Thermodynamic limitations
  - 90% sulfur removal
  - H_2S concentration of 300-500 ppmv
- Sorbents can only be used once
- CaS is not environmentally stable

Post-bed dsulfurization

Desulfurization: $MO_x + xH_2S \longleftrightarrow MS_x + xH_2O$

Regeneration: $MS_x + (3X/2)O_2 \longleftrightarrow MO_x + xSO_2$

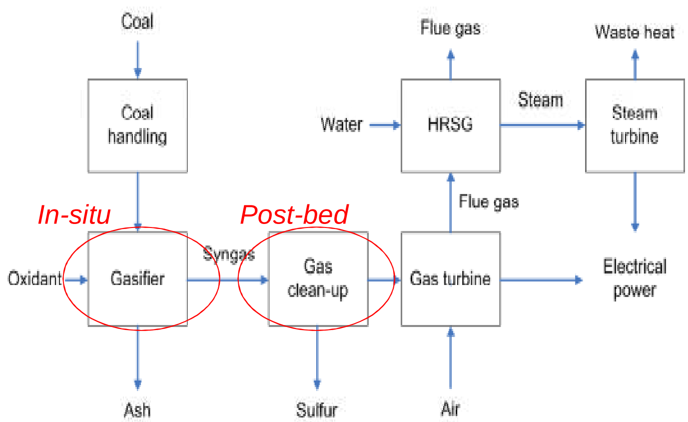


Fig.4. Integrated gasification combined cycle with gas clean-up unit

Source: A.T. Atimtay, Cleaner Energy Production with Integrated Gasification Combined Cycle Systems and Use of Metal Oxide Sorbents for H_2S Cleanup from Coal Gas, Clean Products and Processes, 2001. 2 (4): p.197-208.

Objective

- Prepare silica-supported sorbents.
- Investigate physical properties of sorbents before and after adsorption reaction.
- Compare performance of different kind of sorbents
- Conduct multi-cycle tests and examine activity behavior of sorbents.

Experimental

Silica-Supported Sorbents

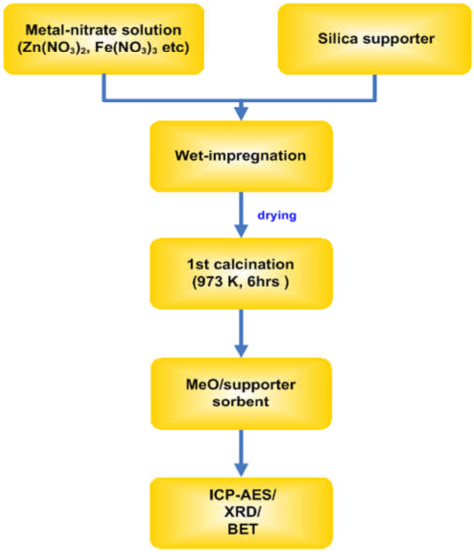


Fig.5. Flow chart of sorbents preparation

A: 20%-Mn/SiO_2 (MnSi)
B: 20%-Zn/SiO_2 (ZnSi)
C: 20%-Cu/SiO_2 (CuSi)
D: 20%-Fe/SiO_2 (FeSi)

Experimental Facilities

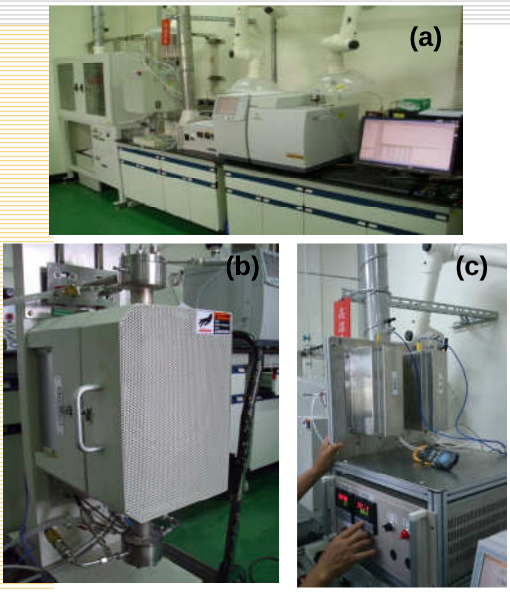
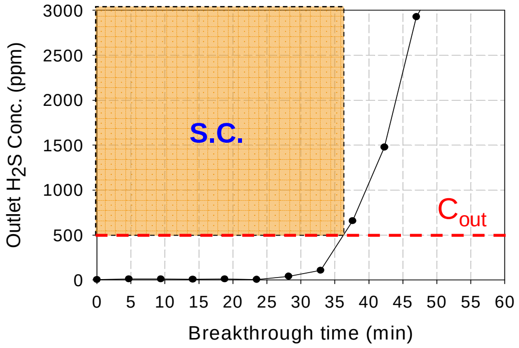


Fig.6.Experimental facilities: (a) sulfide-capturing process, (b) Inconel tube, (c) steam generator

- Sulfide capturing process
  - *Syngas simulator:*
    For tuning syngas composition
  - *Fixed-bed reactor:*
    1. Quartz tube (1 bar)
    2. Inconel tube (1~20 bar)
  - *GC:*
    For analyzing outlet sulfide concentration
  - *Steam generator:*
    For generating overheated steam at 200-400ºC

Sulfur Capacity Calculation

$$S.C.(g-S/100\ gsorbent)=WHSV\times\frac{M}{24.5}\times\int_0^t(Cin-Cout)dt$$



- WHSV: weight hourly space velocity (mL/g.hr)
- M: molecular weight of H_2S (g/mole)
- 24.5: the molar volume of H_2S at 1atm and 298K (L/mole)
- C_{in} and C_{out}: inlet and outlet H_2S concentration (%), respectively
- t: breakthrough time (min).

Fig.7. Breakthrough curve and geometry of sulfur capacity

Source: Tseng T.K., Chang H.C., Chu H., Chen H.T., Hydrogen Sulfide Removal from Coal Gas by the Metal-Ferrite Sorbents Made from the Heavy Metal Wastewater Sludge. J. Hazard. Mater., Vol.160, p.485, 2008.

Result & Discussion

Physical Properties of Sorbents

Table 2: ICP results for silica-supported sorbents

Solid sorbent	Metal-oxide loading
20%-FeSi	17.98%
20%-MnSi	18.83%
20%-ZnSi	18.21%

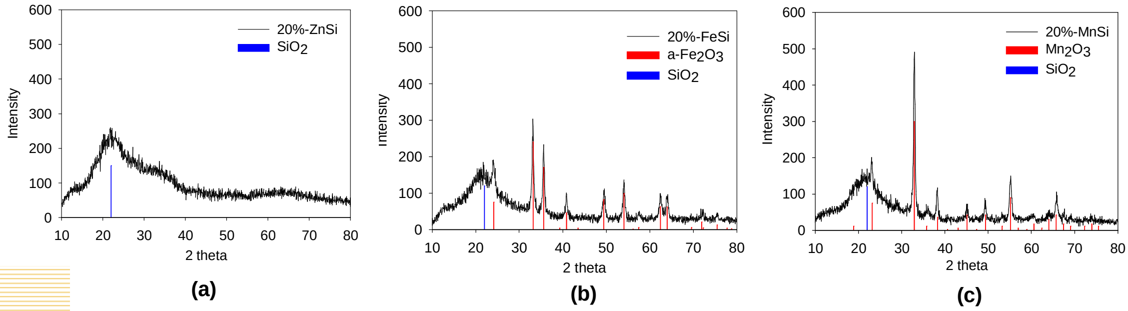


Fig.8. XRD patterns of silica-supported sorbents: (a) 20%-ZnSi, (b) 20%-FeSi, (c) 20%-MnSi

Comparison of Desulfurization Performance (1)

- Temperature: 700 ºC
- WHSV: 8000 mL/g.hr
- Syngas composition:
  - 30% CO
  - 10% H_2
  - 1% H_2S
  - N_2 balance

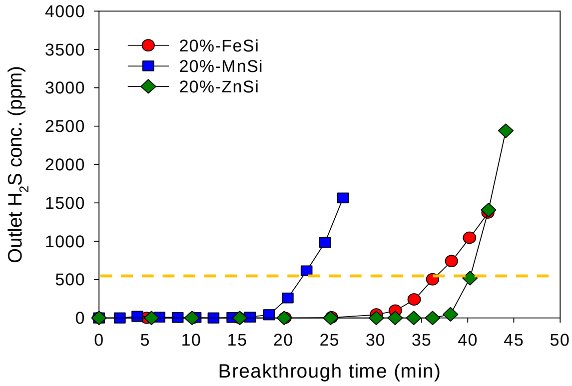


Fig.9. Breakthrough curves of silica-supported sorbents (30% CO, 10% H_2, 1% H_2S, N_2 for balance, WHSV= 8000 mL/g.hr, T=700˚C)

Comparison of Desulfurization Performance (2)

- Desulfurization performance of 20%-ZnSi is similar to that of 20%-FeSi, and both are superior to 20%-MnSi.
- Because 20%-ZnSi showed better sulfur-capturing ability, it will be used for advanced study later.

Table 3: The desulfurization performance of different type of sorbents

Sorbents	Breakthrough time (min)	Sulfur capacity (g-S/100g sorbent)
20%-ZnSi	39	6.86
20%-FeSi	37	6.50
20%-MnSi	21	3.69

Desulfurization Performance at different WHSV (1)

- Temperature: 700 °C
- WHSV: 8000-20000 mL/g.hr
- Syngas composition:
  - 30% CO
  - 10% H_2
  - 1% H_2S
  - N_2 balance

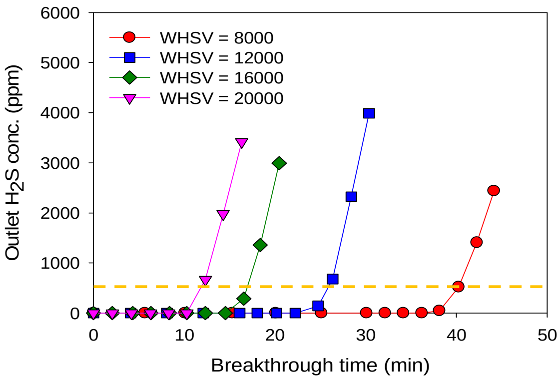


Fig.10. Breakthrough curves of 20%-ZnSi sorbents at different WHSV range (30% CO, 10% H_2 , 1% H_2S, N_2 for balance, T=700˚C)

Desulfurization Performance at different WHSV (2)

- S.C. almost didn't change between 8000-12000 mL/g.hr, and continued to decrease while WHSV > 16000 mL/g.hr.
- Choosing 12000 mL/g.hr as operational parameter is beneficial to shorten reaction time and maintain desulfurization performance.

Table 4: The desulfurization performance of 20%-ZnSi with WHSV

WHSV (mL/g.hr)	Breakthrough time (min)	Sulfur capacity (g-S/100g sorbent)
8000	39	6.86
12000	25	6.59
16000	17	5.98
20000	11	4.83

Multi-Cycle Reaction

- **Desulfurization:**
  - Temperature: 700 ºC
  - WHSV: 12000 mL/g.hr
  - Syngas composition:
    - 30% CO
    - 10% H_2
    - 1% H_2S
    - N_2 balance
- **Regeneration:**
  - Temperature: 700 ºC
  - WHSV: 13960 mL/g.hr
  - Gas composition:
    - Air (21% O_2, N_2 balance)

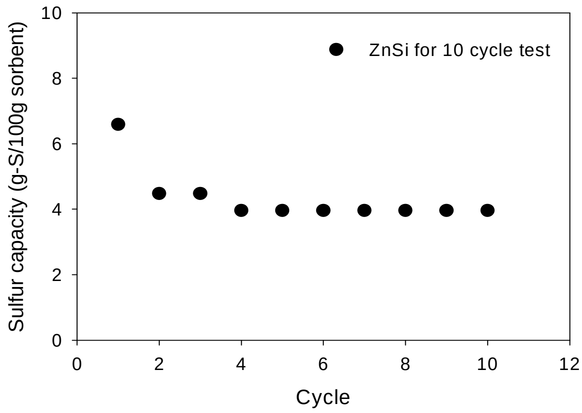


Fig.11. The sulfur capacity change of 20%-ZnSi sorbents for 10 multi-cycle tests (30% CO, 10% H_2, 1% H_2S, N_2 for balance, WHSV=12000 mL/g.hr, T=700˚C)

Desulfurization Performance of Sorbents with Cycles

- S.C. dropped rapidly from 6.59 to 4.48 g-S/100g sorbent at 2nd-3th cycle, and finally maintained at 3.96 g-S/100g sorbent until 10th cycle.
- S.C. finally became 60% of initial value after 10th cycle.

Table 5: The desulfurization performance of 20%-ZnSi with reaction cycles

Cycle	Breakthrough time (min)	Sulfur capacity (g-S/100g sorbent)
S1	25	6.59
S2	17	4.48
S3	17	4.48
S4	15	3.96
S10	15	3.96

Structure Change with Cycles (1)

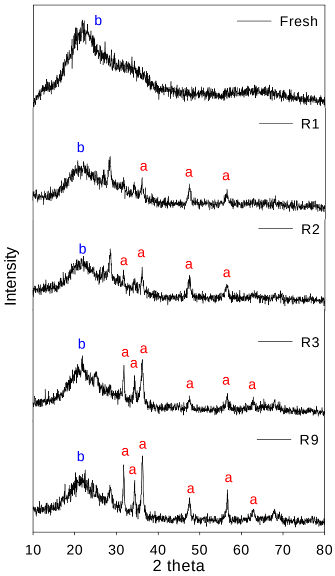


Fig.12. XRD pattern of 20%-ZnSi sorbents with reaction cycles (a: ZnO, b: SiO_2)

The crystalline phase after regeneration with cycles

- There is no ZnO phase being observed on fresh state, but ZnO peak appeared and grows up with cycles.
- After regeneration, there is no sulfate observed on XRD pattern.

※ Sulfate formation: $ZnS+2O_2 \rightarrow ZnSO_4$

Structure Change with Cycles (2)

- By continuous operation at high temperature (700ºC), grain size grows up with reaction cycles, and this also induces pore shrunk and BET area declined.

Table.6: The physical properties of 20%-ZnSi with reaction cycles

Cycle	*d (101)*	BET (m^2/g)
Fresh	N.A.	153
R1	0.07 nm	118
R2	0.12 nm	100
R3	0.15 nm	83
R9	0.28 nm	77

※Scherrer formula:

$$d = \frac{B\lambda}{\beta \cos\theta} \text{, (B = 0.9, } \lambda = 0.15406 \text{ nm)}$$

Desulfurization Performance vs. Structure

- S.C. is negatively related to grain size, but positively related to BET area with cycles.
- It is due to BET area declined by sintering that desulfurization performance decreases with cycles.

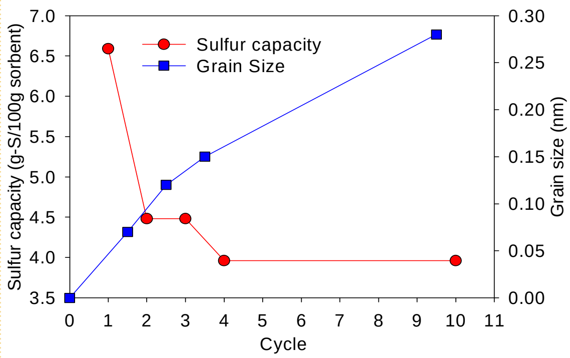


Fig.13. Sulfur capacity vs. grain size with reaction cycles

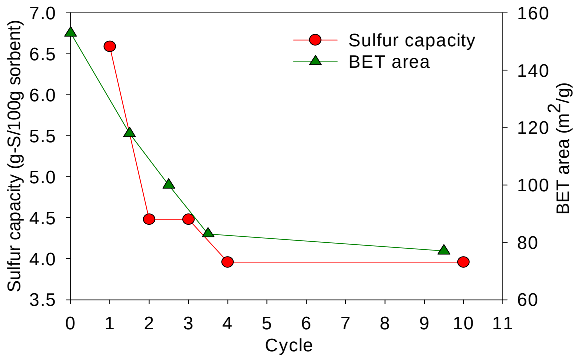


Fig.14. Sulfur capacity vs. BET area with reaction cycles

Summary

- Desulfurization performance: 20%-ZnSi ~ 20%-FeSi > 20% MnSi.
- Desulfurization performance maintains almost constant between 8000-12000 mL/g.hr.
- The sulfur capacity of sorbents dropped to 60% of initial value after 10 reaction cycles, and this is because BET surface area declined by sintering.

Acknowledgements

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