2007' International Workshop on IGCC & Co-production and CO_2 Capture & Storage

Direct Hydrogen Production with Carbon Dioxide Capture

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Outline

- Direct Hydrogen Production from Coal and Hydrogen/Carbon Dioxide Separation
- Regeneration Cycle Characteristic of Hydrogen/Carbon Dioxide Separation Carrier
- Oxygen and Energy Supply During Separation Carrier Regeneration
- Carbon Dioxide Capture by Mineral

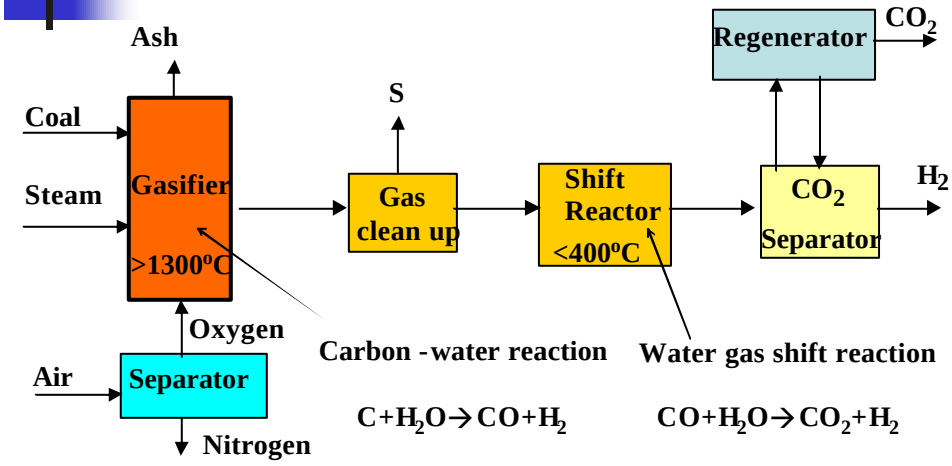
Carbon Storage Options

- **Geologic formations**
  - Enhanced oil recovery
  - Depleted oil and gas fields
  - Unminable coal beds
  - Deep saline aquifers
- **Deep ocean (Controversial)**
- **Mineral Carbonation**

Carbon Capture Options

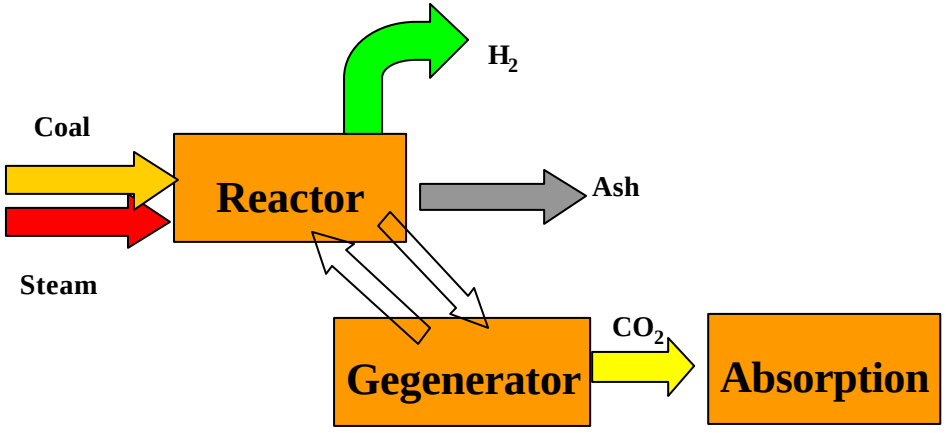
- **Post-Combustion**
- **Pre-Combustion**
  - Gasification
  - Hydrogen Production
- **Oxyfuel combustion**
- **Others (Chemical looping)**

Direct Hydrogen Production from Coal with Carbon Dioxide Capture



Conventional hydrogen production

Direct hydrogen production



1. Direct Hydrogen Production from Coal and Hydrogen/Carbon Dioxide Separation

Hydrogen production

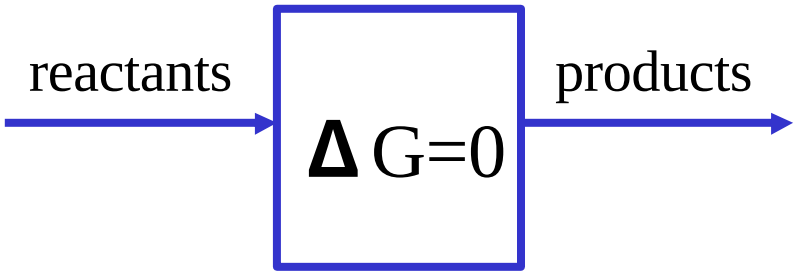
- Theory Analysis

- Autoclave experimental study

- Continuous flow experimental study

Research content simulation

- **Thermodynamic equilibrium model**

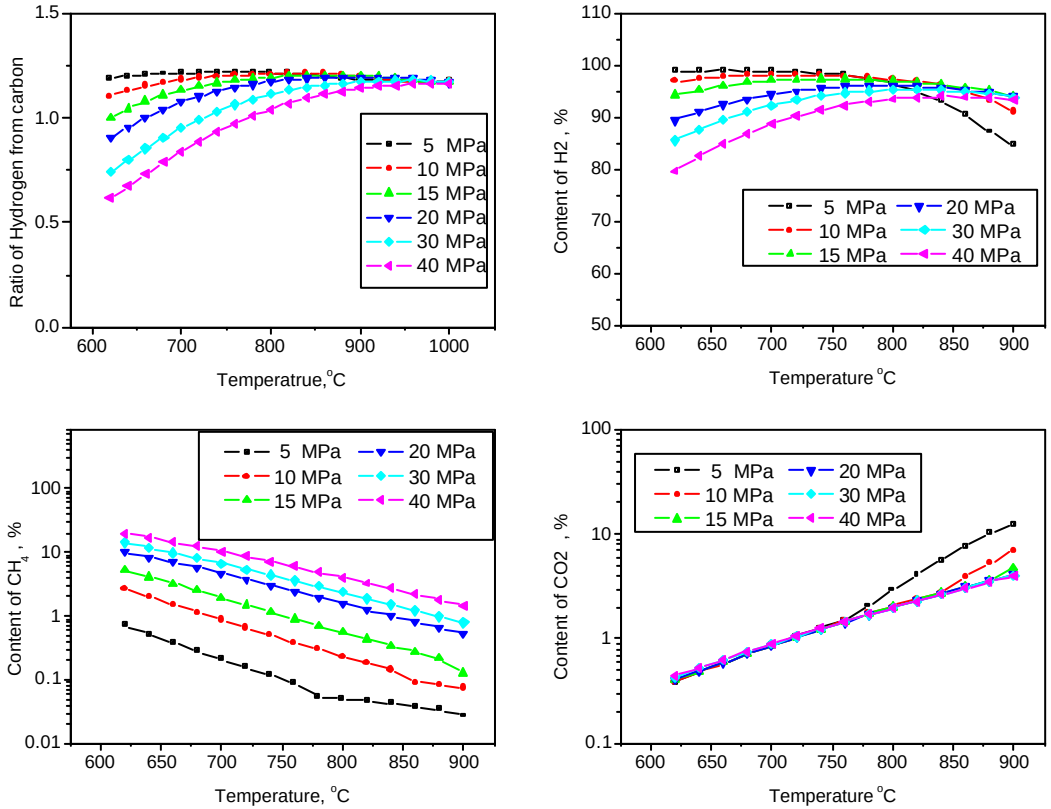


Gibbs reactor (T，P)

- **evaluation index**

Ratio of hydrogen from carbon $h = \frac{H_{hydrogen}}{4 \times C_{coal}}$

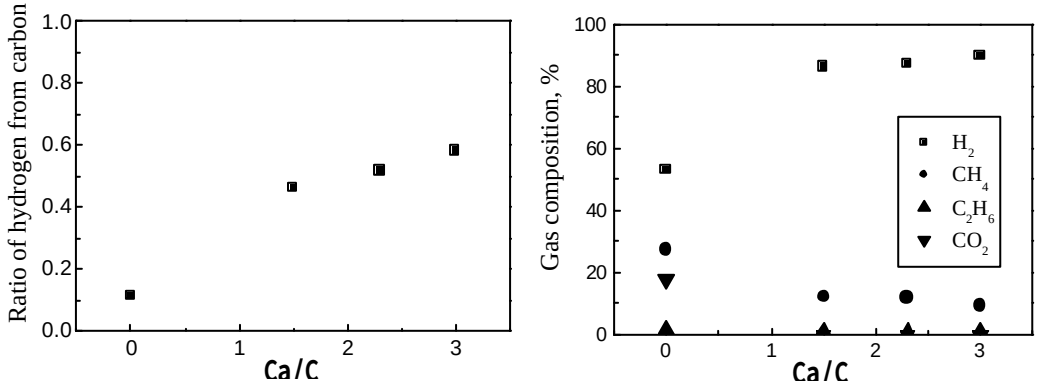
The results of analysis



The effect of temperature on hydrogen from coal ratio and the content of hydrogen, methane and carbon dioxide

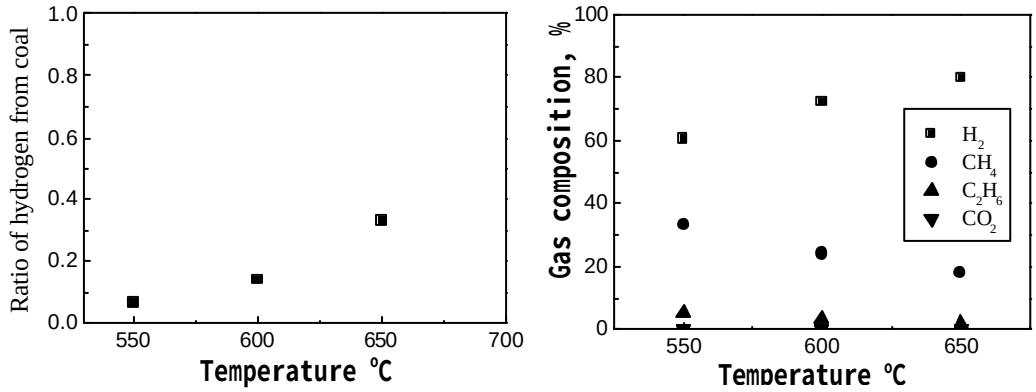
Experimental results autoclave

- **Absorbent is important**



The effect of Ca/C on hydrogen from carbon ratio and gas composition

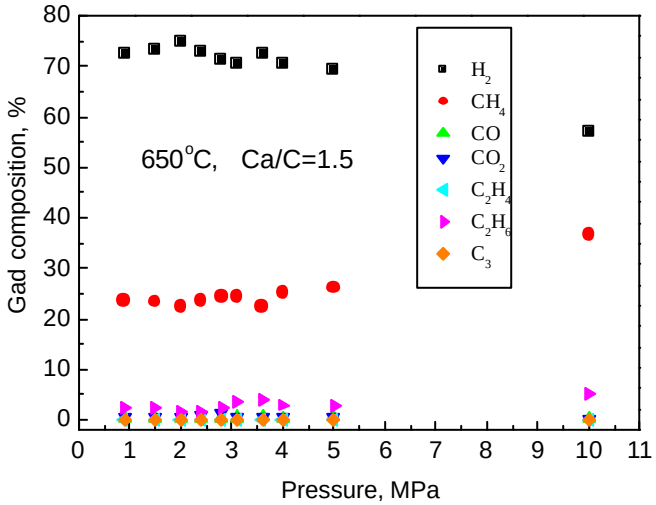
- **Temperature has a positive influence**



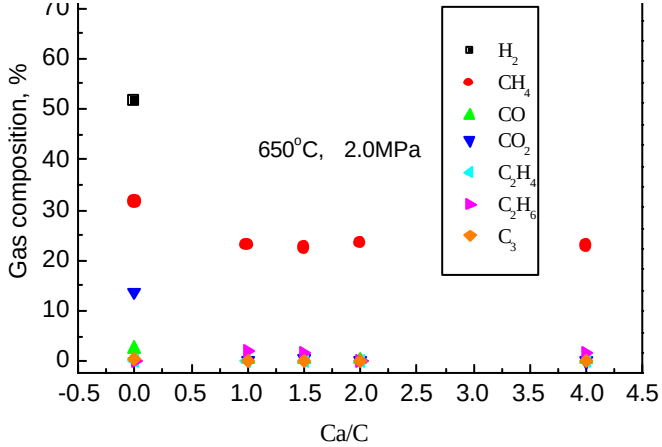
The effect of temperature on hydrogen from carbon ratio and gascomposition

Experimental results Autoclave

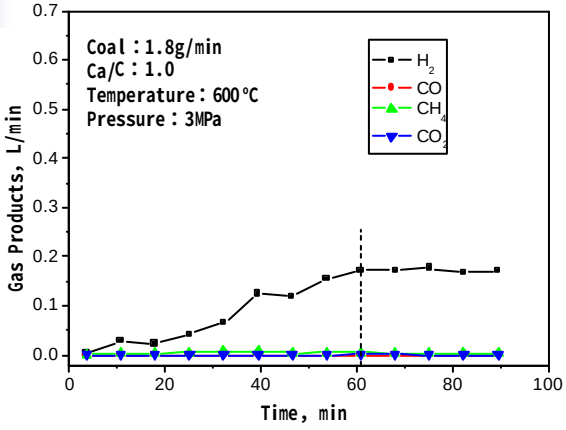
- The effect of pressure is not remarkable

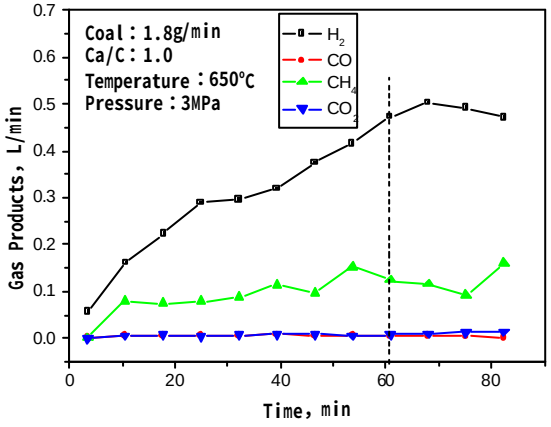


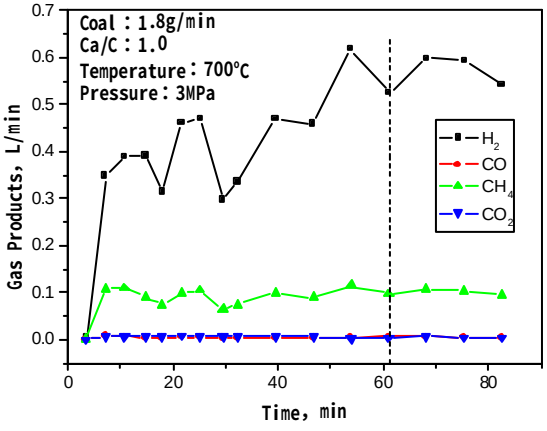
- Ca/C 1.0 is enough

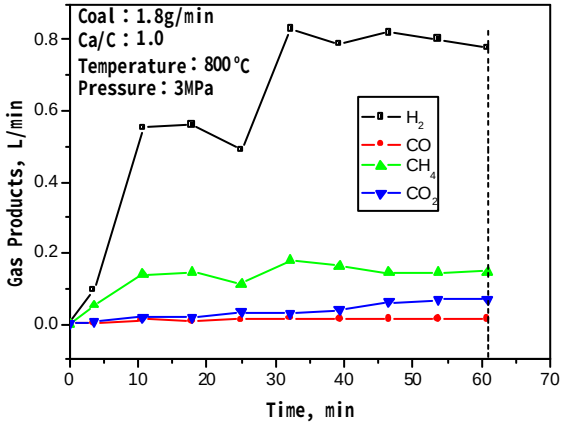


Experimental results continuous flow









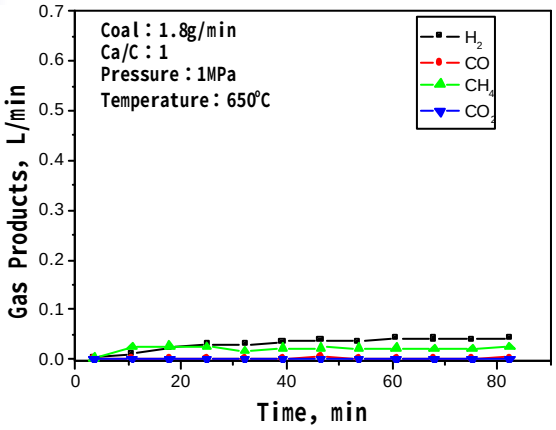
Effect of temperature

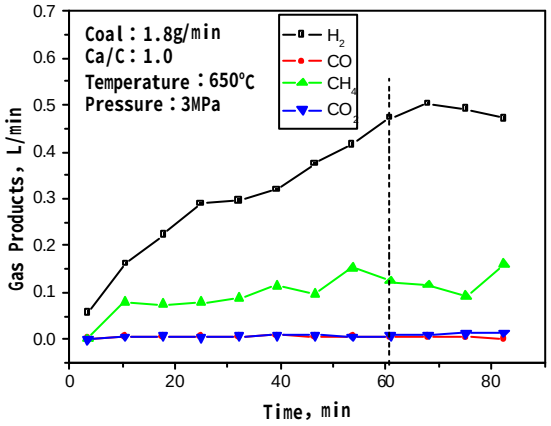
Experimental results continuous flow

Product gas concentrations at the dash line

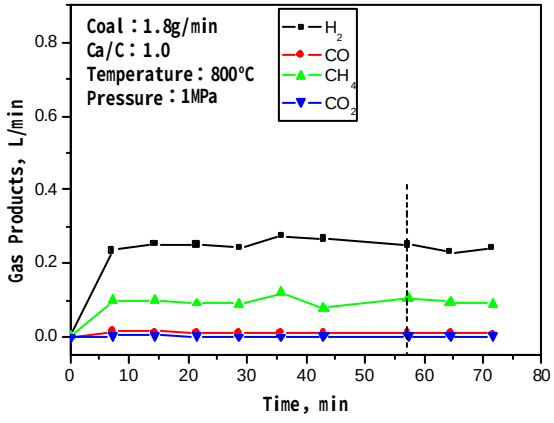
Temperature (°C)	Gas Products (%)						
	H_2	CH_4	CO	CO_2	C_2H_6	C_2H_4	H_2+CH_4
600	96.6	2.7	0.2	0.3	0.2	1.5	99.3
650	77.2	19.0	0.8	1.1	1.8	0.03	96.2
700	82.6	15.1	1.0	1.2	0.1	0.02	97.7
800	74.9	14.2	1.6	6.8	2.4	0.01	89.1

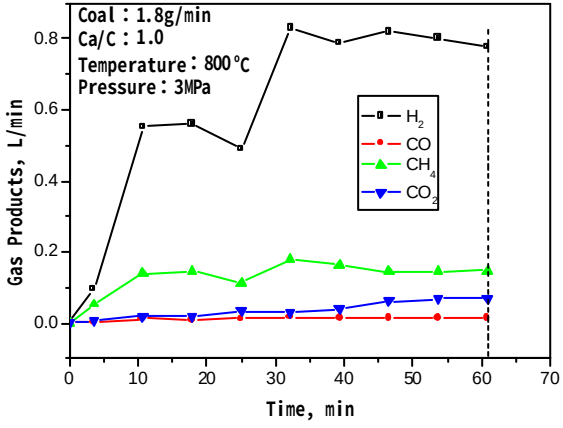
Experimental results continuous flow





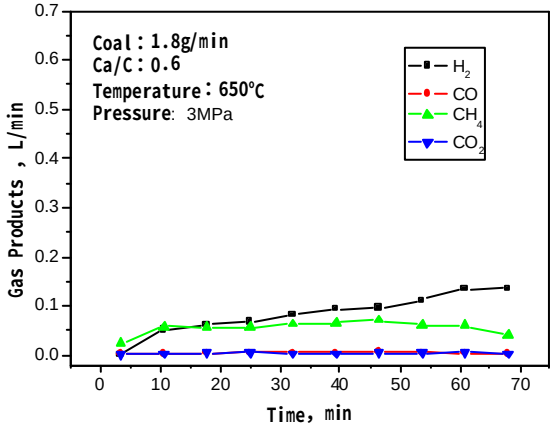
Effect of pressure, 650°C

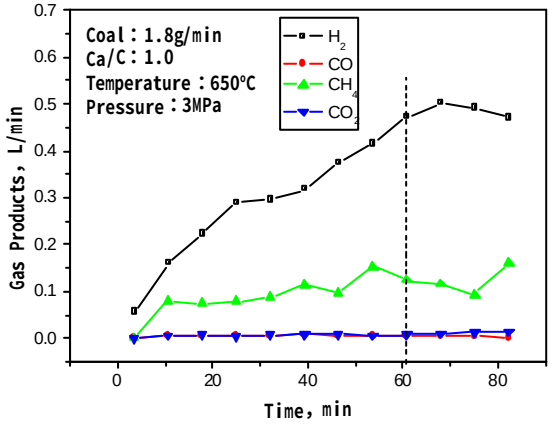


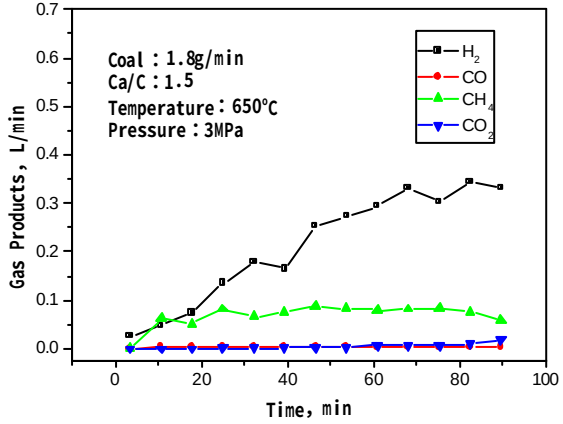


Effect of pressure, 800°C

Experimental results continuous flow

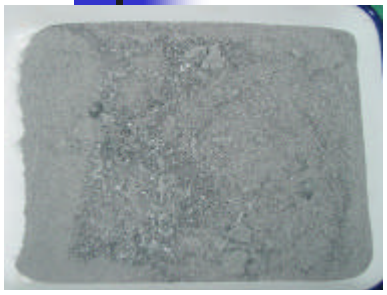






Effect of Ca/C，650°C，3MP

Experimental results continuous flow



600°C 3MPa

Ca/C:1.0

650°C 3MPa

Ca/C:1.0

700°C 3MPa

Ca/C:1.0

800°C 3MPa

Ca/C:1.0

650°C 3MPa

Ca/C:0.6

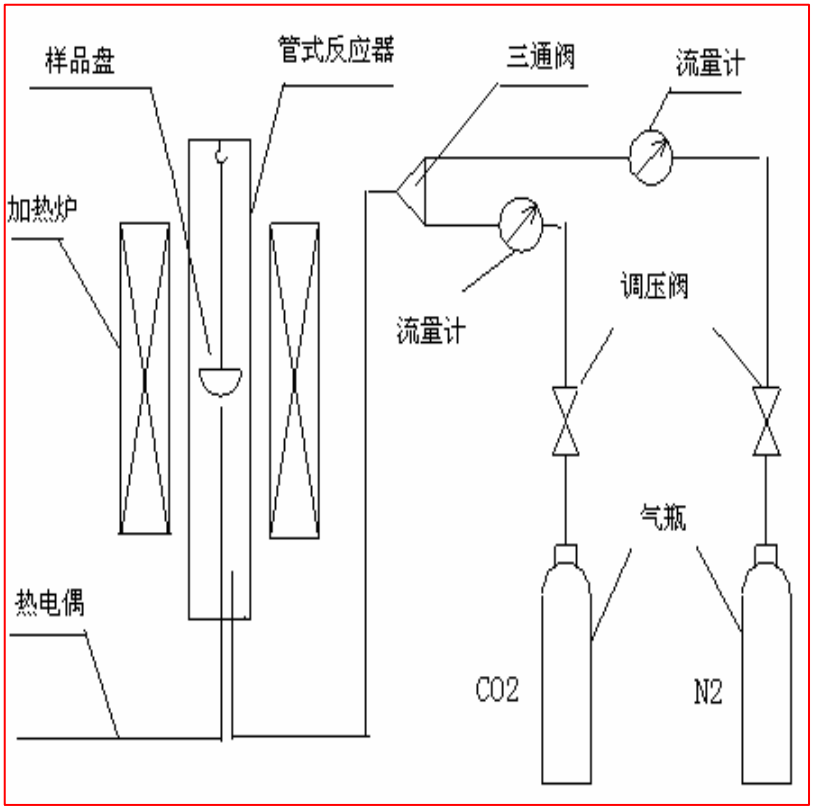
650°C 3MPa

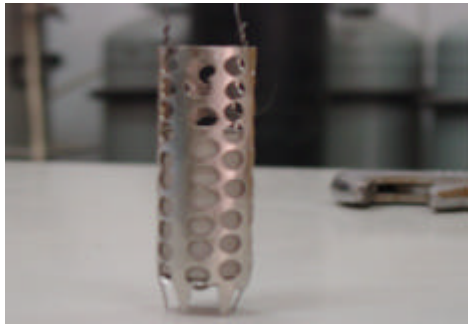
Ca/C:1.5

Photographs of residues

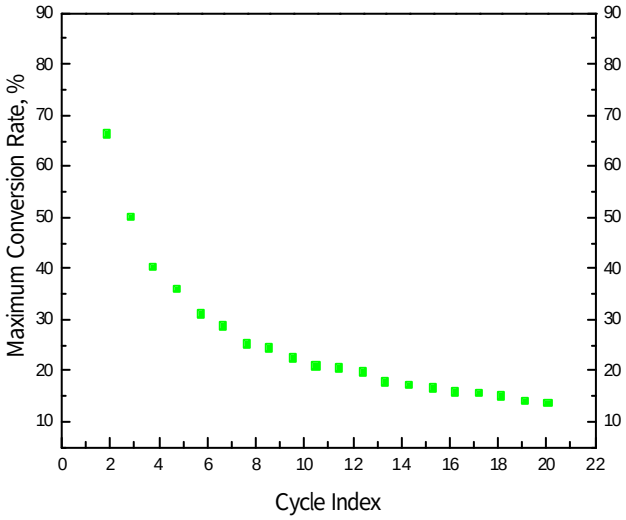
2. Regeneration Cycle Characteristic of Hydrogen/Carbon Dioxide Separation Carrier

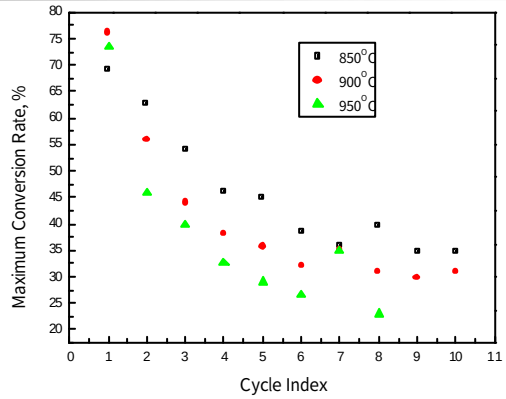
The flowsheet and experiment plant





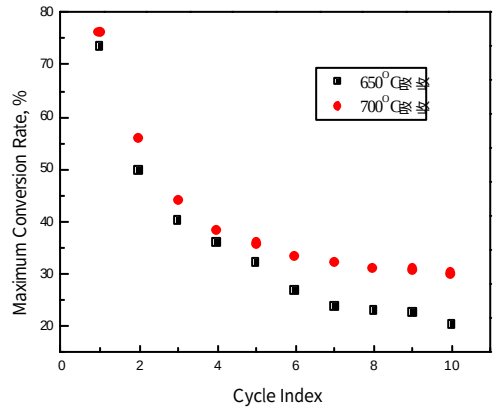
The capability of limestone-CaO in different calcine and regeneration conditions





The effect of temperature for the capability of CaO

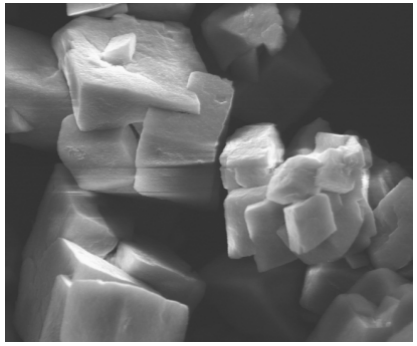
Regeneration condition：
1atm，100%N_2, 900 ℃ ,15min
Absorption condition：
1atm，30%CO_2/N_2, 650 ℃, 30min



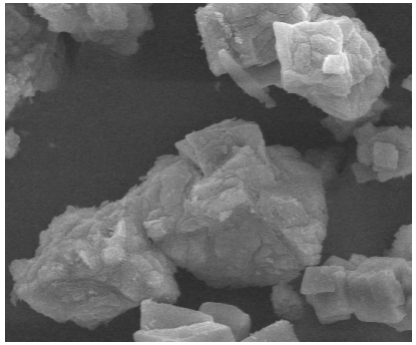
The effect of pressure for the capability of CaO

Cause of decline capability of absorption

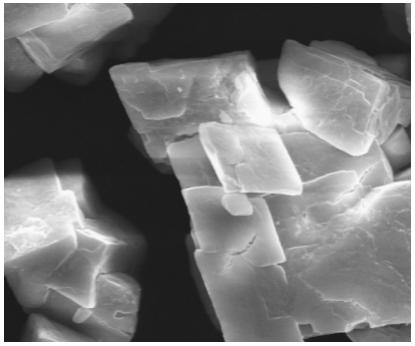
Original $CaCO_3$



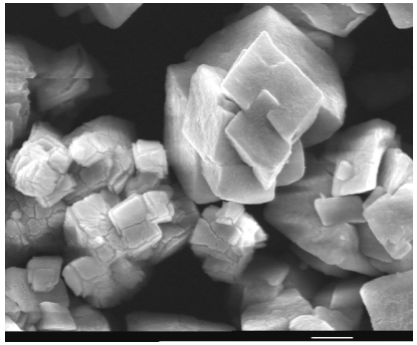
First absorption



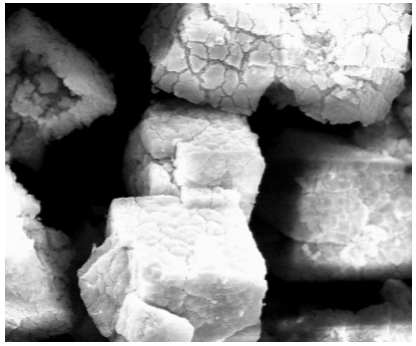
Tenth absorption



First regeneration



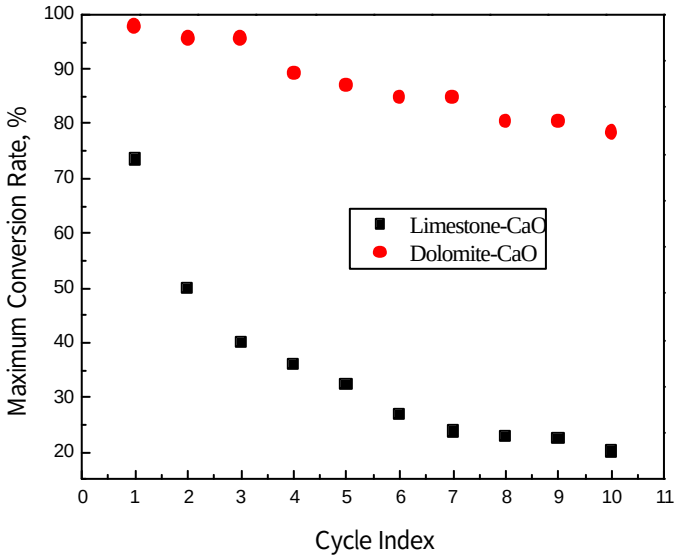
Tenth regeneration

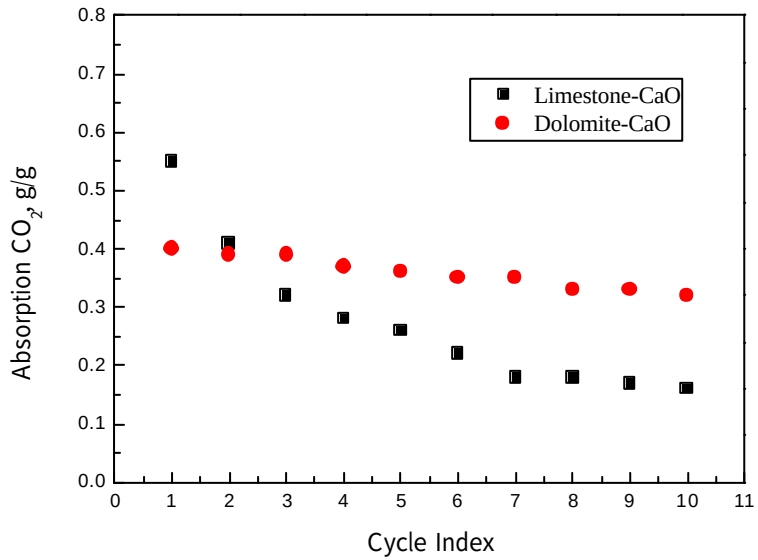


Fifteenth regeneration

Observation of surface shape in absorption carrier recycle process (1000X)

The capability of dolomite(白云石)-CaO in different regeneration and absorption conditions

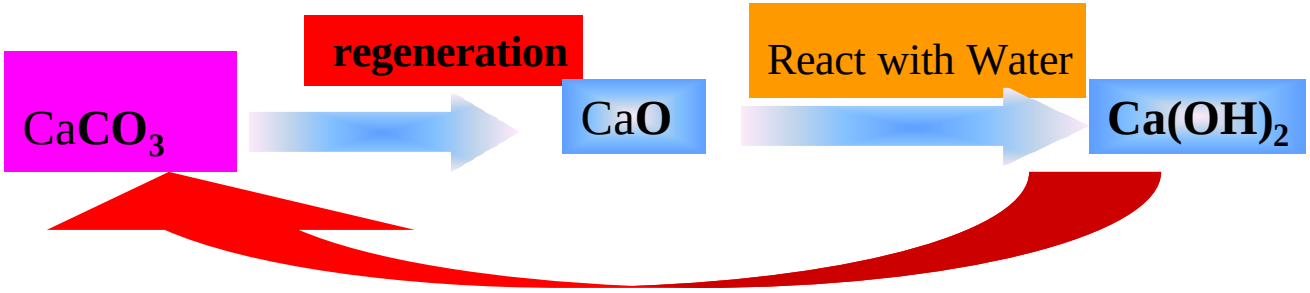




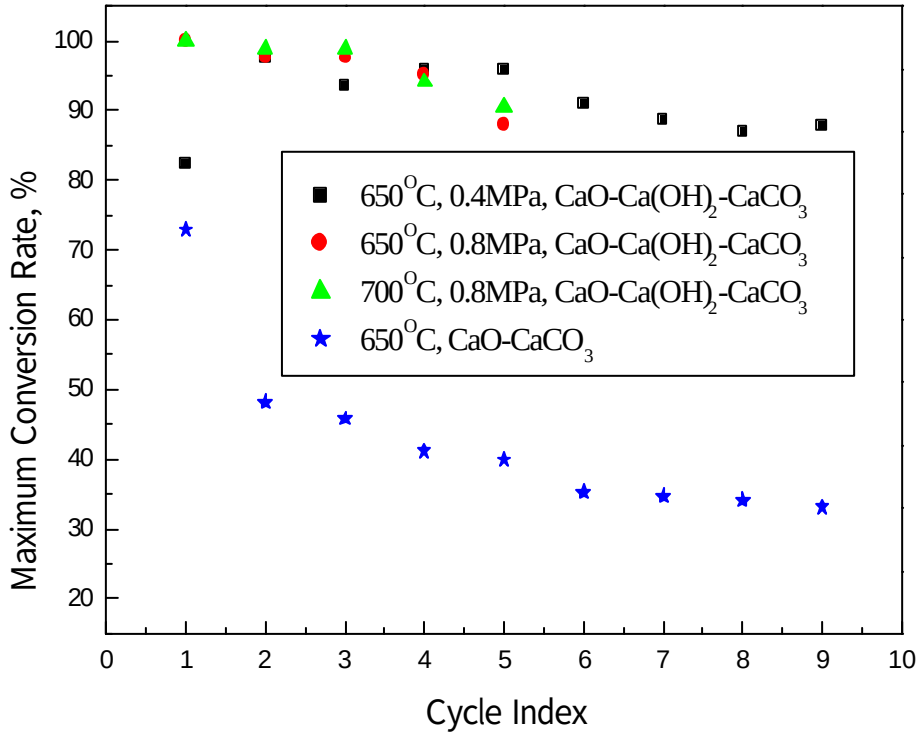
Regeneration condition：1atm，100%N_2, 900 ℃ ,15min
Absorption condition：1atm，30%CO_2/N_2, 650 ℃, 30min

The study on improving the capability of absorption after recycling

- Design the appropriate process
- Do some treatment on surface of Separation carriers



Recycle activity improvement of absorption carrier — React with steam

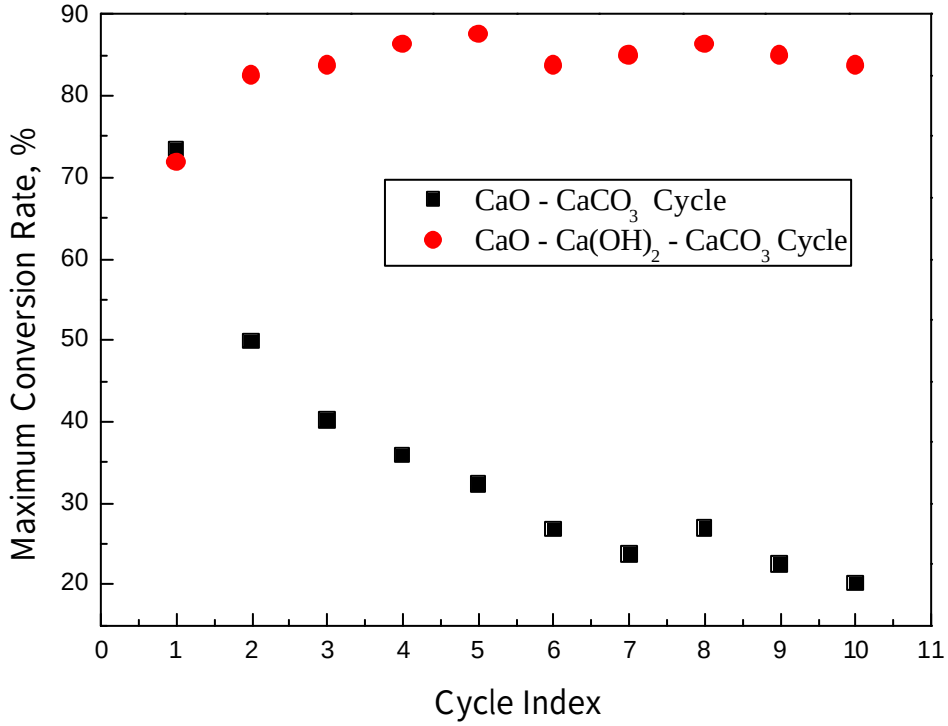


Regeneration condition：1atm，100%N_2, 900 ℃ ,15min

Absorption condition：1atm，30%CO_2/N_2, 30min

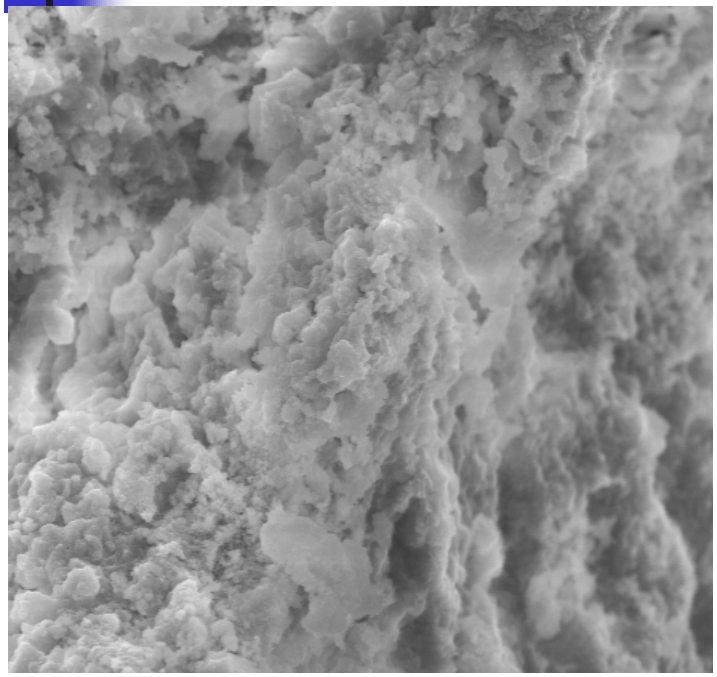
Recycle activity improvement of absorption carrier —

React with water

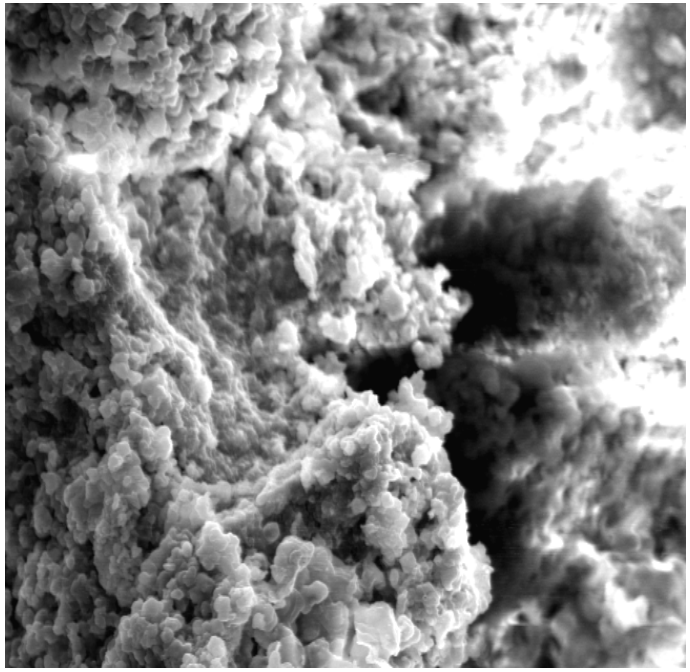


Regeneration condition：1atm，100%N2, 900 ℃ ,15min
Absorption condition：1atm，30%CO2/N2, 650 ℃, 30min

Surface Characteristic after hydration



after regeneration,11 times cycle with hydration treatment



after absorbtion,11 times cycle with hydration treatment

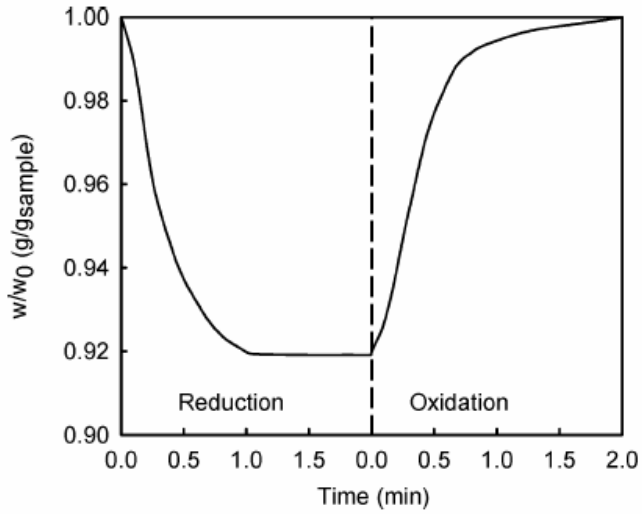
Nice pore space connectivity, uniform pore size distribution, uniformly distributed pore on the surface

Good absorption stability

3. Oxygen and Energy Supply During Separation Carrier Regeneration

Chemical Looping Combustion (CLC)

- **MeO/Me denote recirculated oxygen carrier solid material.**
- **Key issue in the system: Oxygen Carriers (OC)**
- **Ni, Fe, Cu have been tested as promising OC.**



- **Fuel reactor**

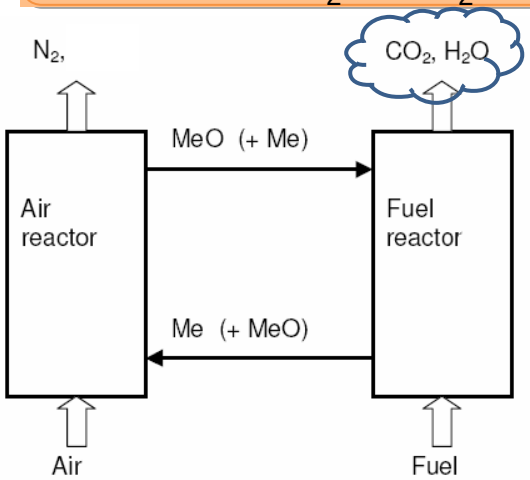
  $MeO + CH \rightarrow Me + CO_2 + H_2O$

- **Air reactor**

  $Me + O_2 \rightarrow MeO$

Total reaction:

$CH + O_2 \rightarrow CO_2 + H_2O$



What we need - High ability for transporting oxygen

- **High reaction rates in the oxidation/reduction**
- **High oxygen transport capacity**
- **Low cost**
- **Sufficient durability**

	R_0
NiO/Ni	0.21
CuO/Cu	0.2
Fe_2O_3/Fe_3O_4	0.03
Mn_3O_4/MnO	0.07

Oxygen Radio: $$R_0 = \frac{(m_{ox} - m_{red})}{m_{ox}}$$

Conversion of OC: $$X = \frac{\Delta m}{(m_{ox} - m_{red})} \times 100\%$$

Mass-bassed conversion: $$w = \frac{\Delta m}{m_{ox}} = R_0 X$$

Different OC can transfer different amounts of oxygen per mass unit.

$CaSO_4$: New OC under developing

- **Very cheap:**
  - Widespread natural sulfates
  - Main byproduct of phosphoric acid plants
  - Flue gas desulfurization units
- **R_0 is perticular larger: 47%**

- **Stable:**
  - $CaSO_4$:stable in oxidation conditions under 1150℃
  - CaS: stable in reduction conditions

$$CaSO_4 + C \leftrightarrow CaS + CO_2$$

$$CaSO_4 + 4H_2 \leftrightarrow CaS + 4H_2O$$

$$CaSO_4 + 4CO \leftrightarrow CaS + 4CO_2$$

$$CaS + 2O_2 \leftrightarrow CaSO_4$$

Use $CaSO_4$ as OC

- **Air reactor:**

$CaS + 2O_2 \leftrightarrow CaSO_4$ ΔH_c^0 =-957.44 kJ/mol

$3CaSO_4 + CaS \leftrightarrow 4CaO + 4SO_2$ >1000dc

- **Fuel reactor:** ΔH_c^0

$CaSO_4 + CH_4 \leftrightarrow CaS + CO_2 + 2H_2O$ 67.46 kJ/mol

$CaSO_4 + 4H_2 \leftrightarrow CaS + 4H_2O$ -185.56 kJ/mol

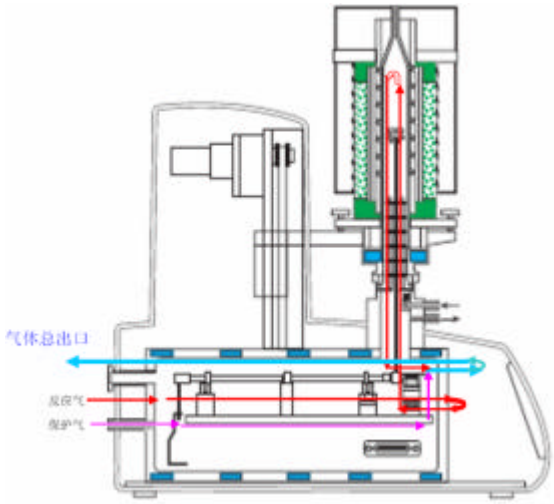
$CaSO_4 + 4CO \leftrightarrow CaS + 4CO_2$ -174.16 kJ/mol

$CaSO_4 + CO \leftrightarrow CaO + CO_2 + SO_2$

850dc, CO=10%, FTIR results show that SO_2 is blow 0.5%.

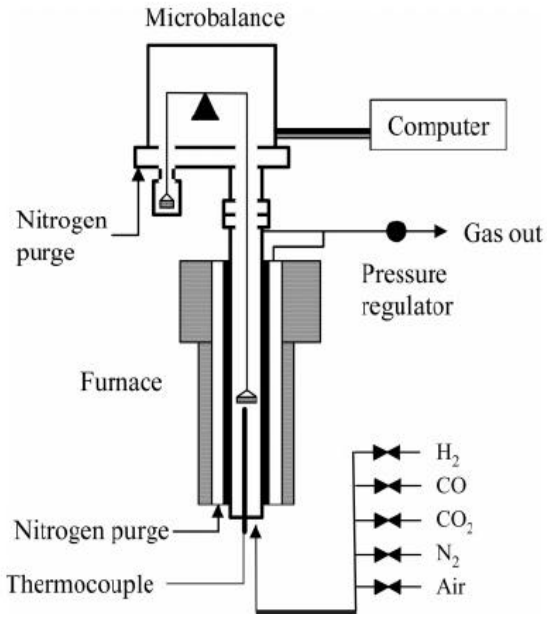
Simultaneous sequestration with CO_2

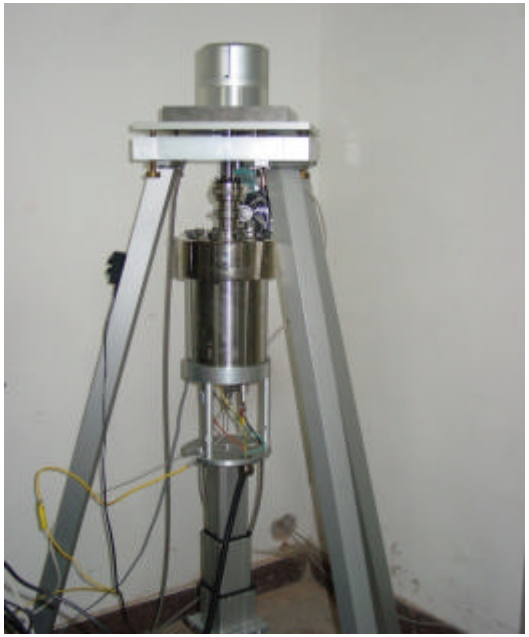
Experimental Setup



The experiments with CH_4 as reducing agent were performed in a atmospheric Linseis STA-pt1600 TG-DSC analyzor

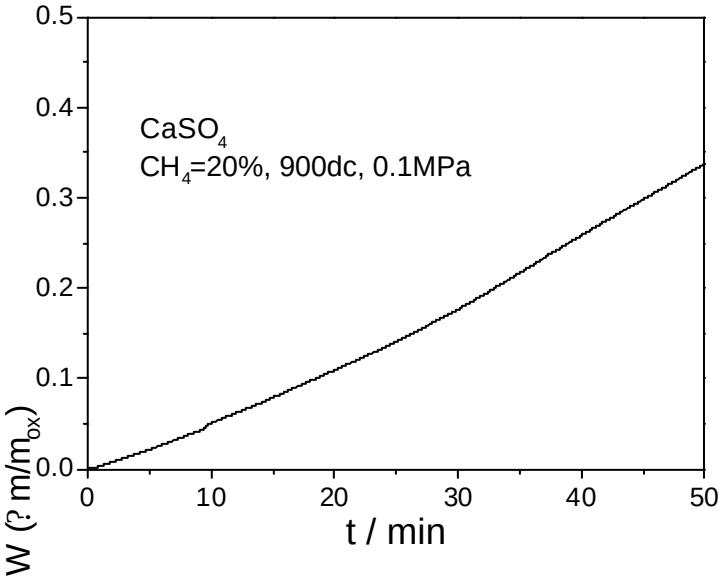
Experimental Setup

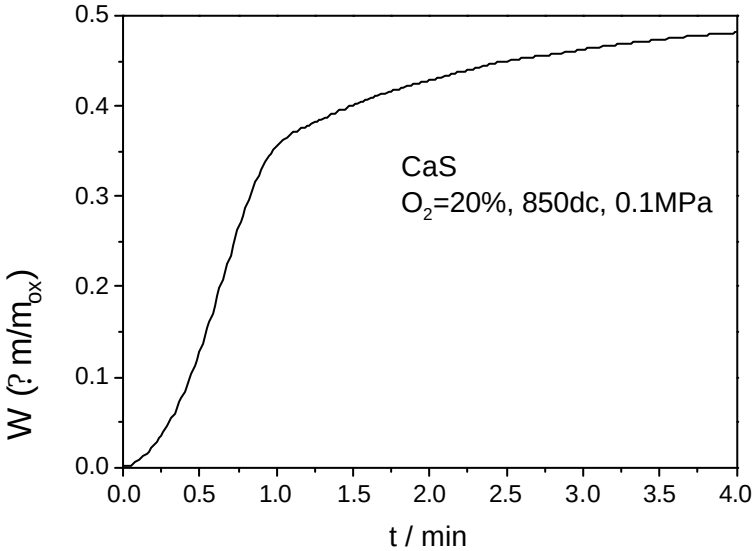




The experiments at higher pressures and with H_2 and CO as reducing agent were carried out in a pressurized thermogravimetric analyzer (PTGA), Cahn TherMax 500

Tests of $CaSO_4$ as OC

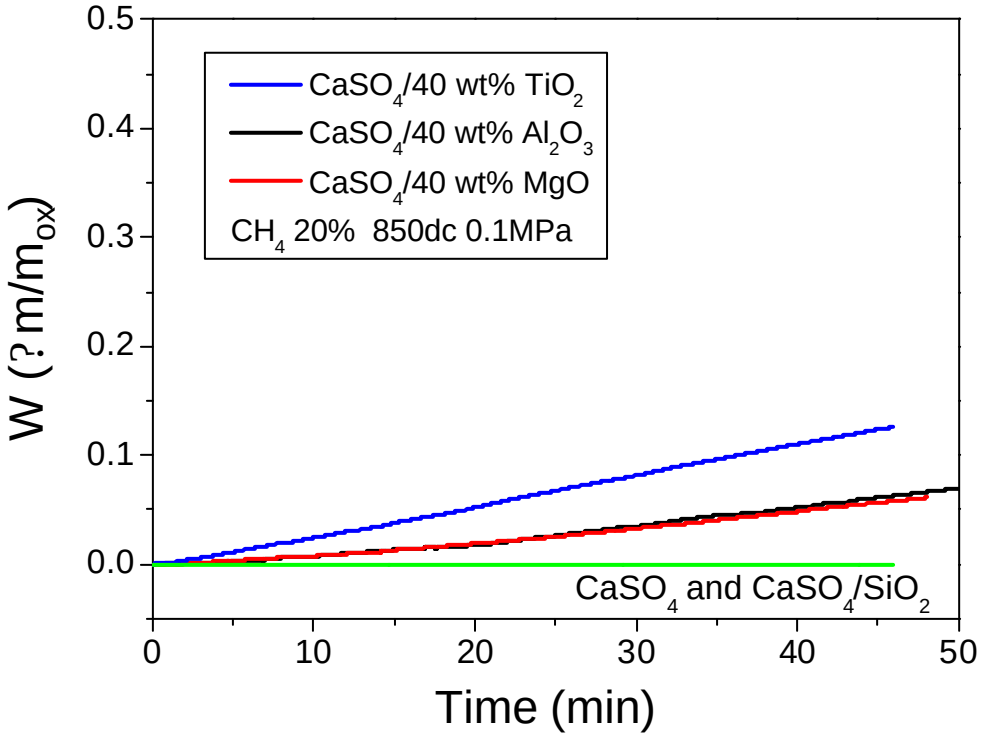




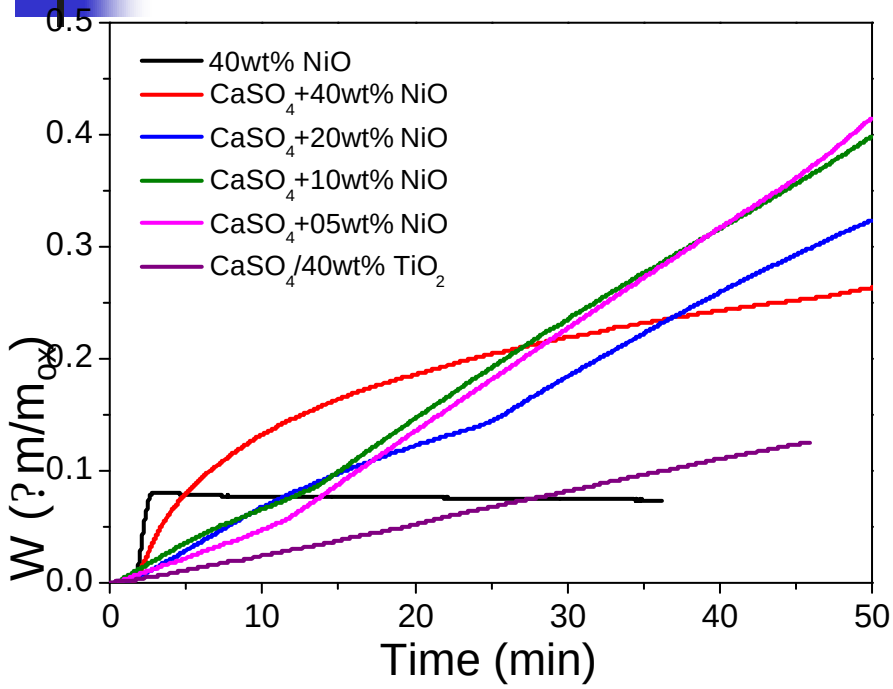
Reduction rates is too low even at 900dc.

Oxidation rates is quick

Enhancement by supported on inerts



Effect of active aids additions

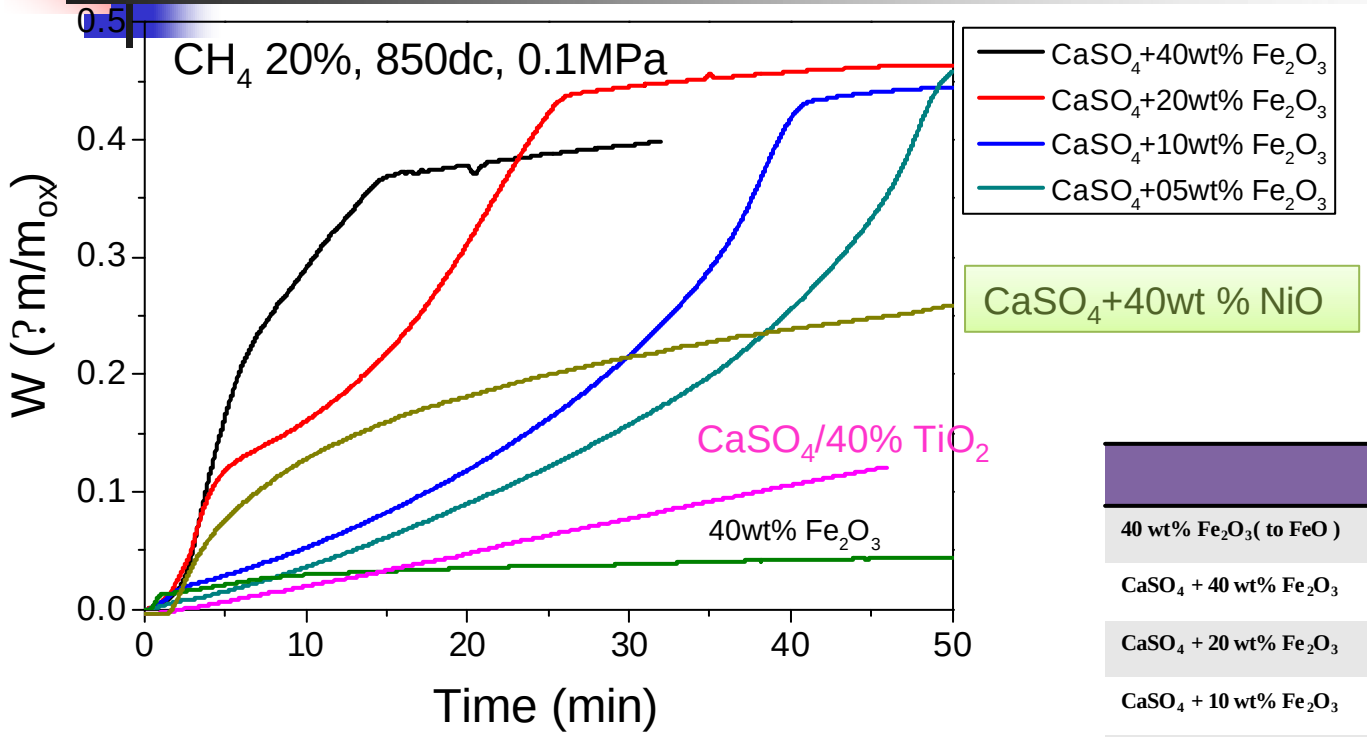


CH_4 20%, 850dc, 0.1MPa

	R_0
40 wt% NiO	0.082
$CaSO_4$ + 40 wt% NiO	0.366
$CaSO_4$ + 20 wt% NiO	0.416
$CaSO_4$ + 10 wt% NiO	0.443
$CaSO_4$ + 05 wt% NiO	0.4565
$CaSO_4$ + 40wt% TiO_2	0.282

Active aid, NiO, is added by impregnation method

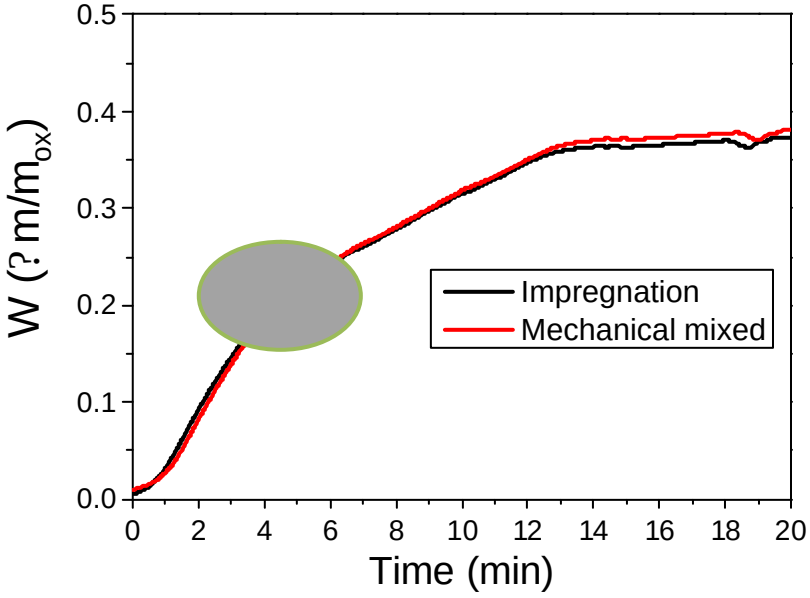
Effect of active aids additions

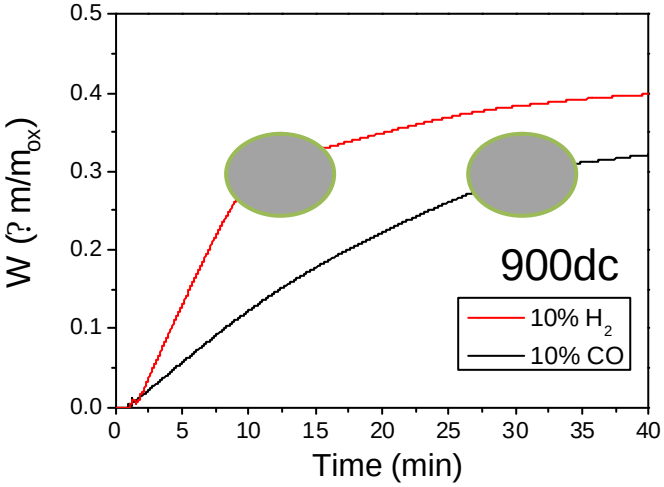


	R_0
40 wt% Fe_2O_3(to FeO)	0.04
$CaSO_4$ + 40 wt% Fe_2O_3	0.366
$CaSO_4$ + 20 wt% Fe_2O_3	0.416
$CaSO_4$ + 10 wt% Fe_2O_3	0.443
$CaSO_4$ + 05 wt% Fe_2O_3	0.4565

Fe_2O_3, with impregnation method

Effect of active aids additions



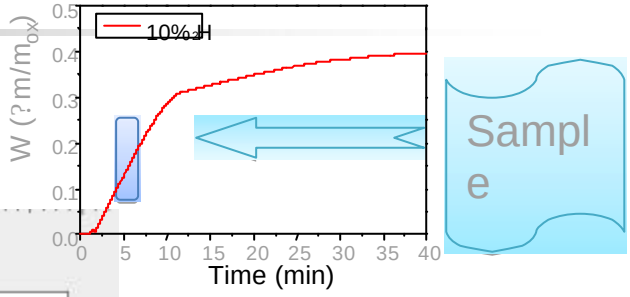


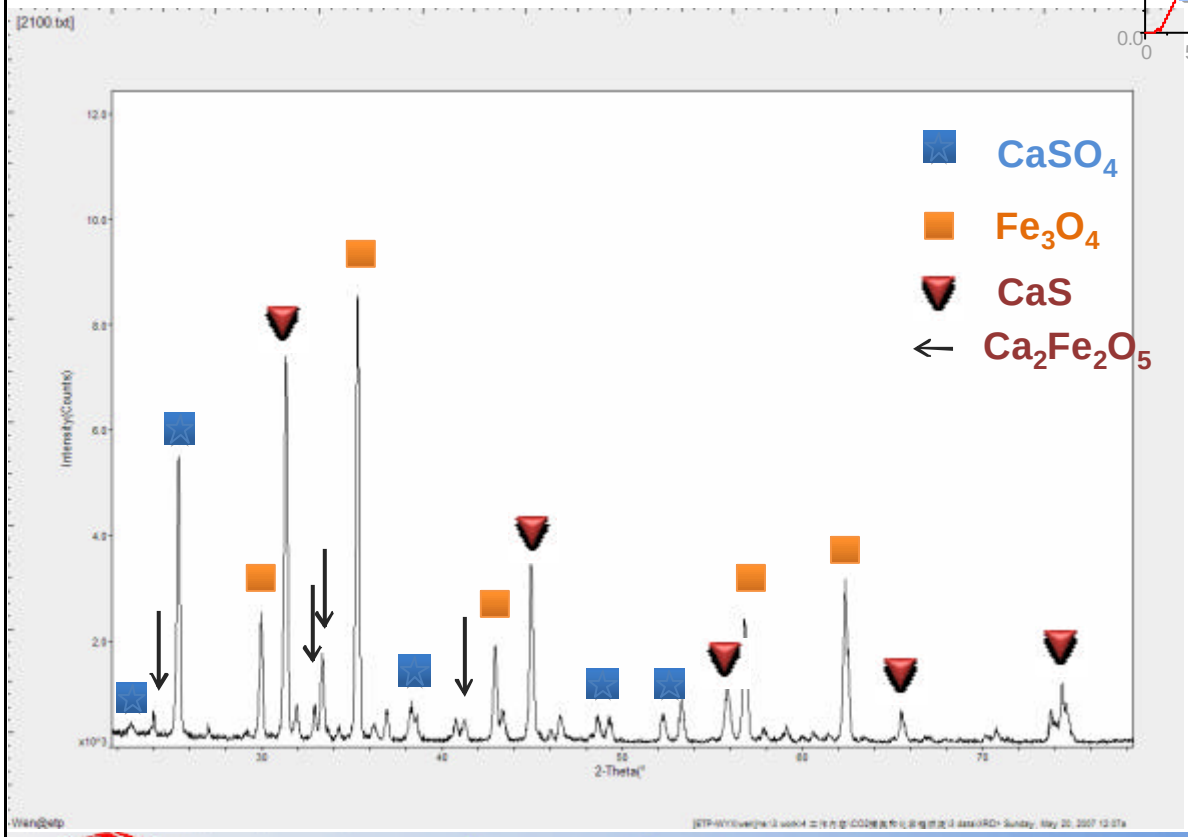
CH_4 20%, 850dc, 0.1MPa

10% H_2 or CO, 900dc, 0.1MPa

$CaSO_4$+40 wt% Fe_2O_3 is effective, even with mechanical mixed

XRD Analys

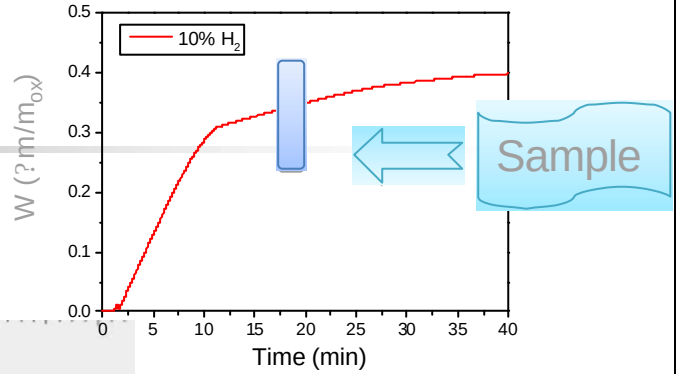


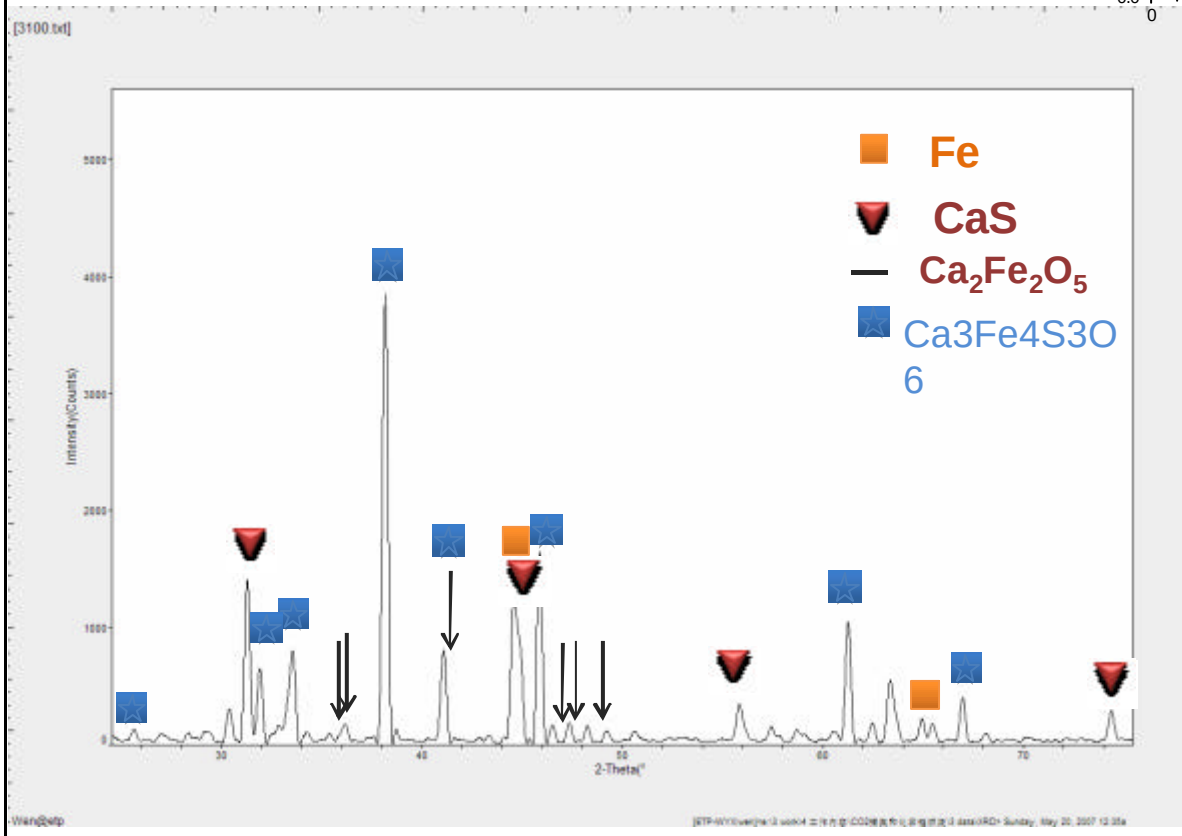


All Fe_2O_3=>Fe_3O_4
Contribute to
convertion <1%

Quick:
$CaSO_4$=>CaS
80% Convertion
in 10min !!

XRD Analys

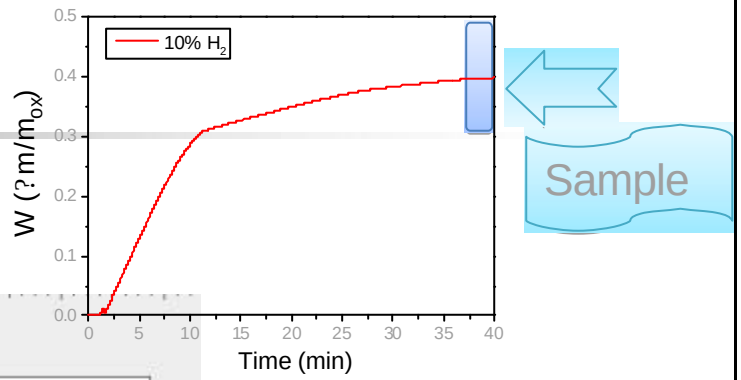


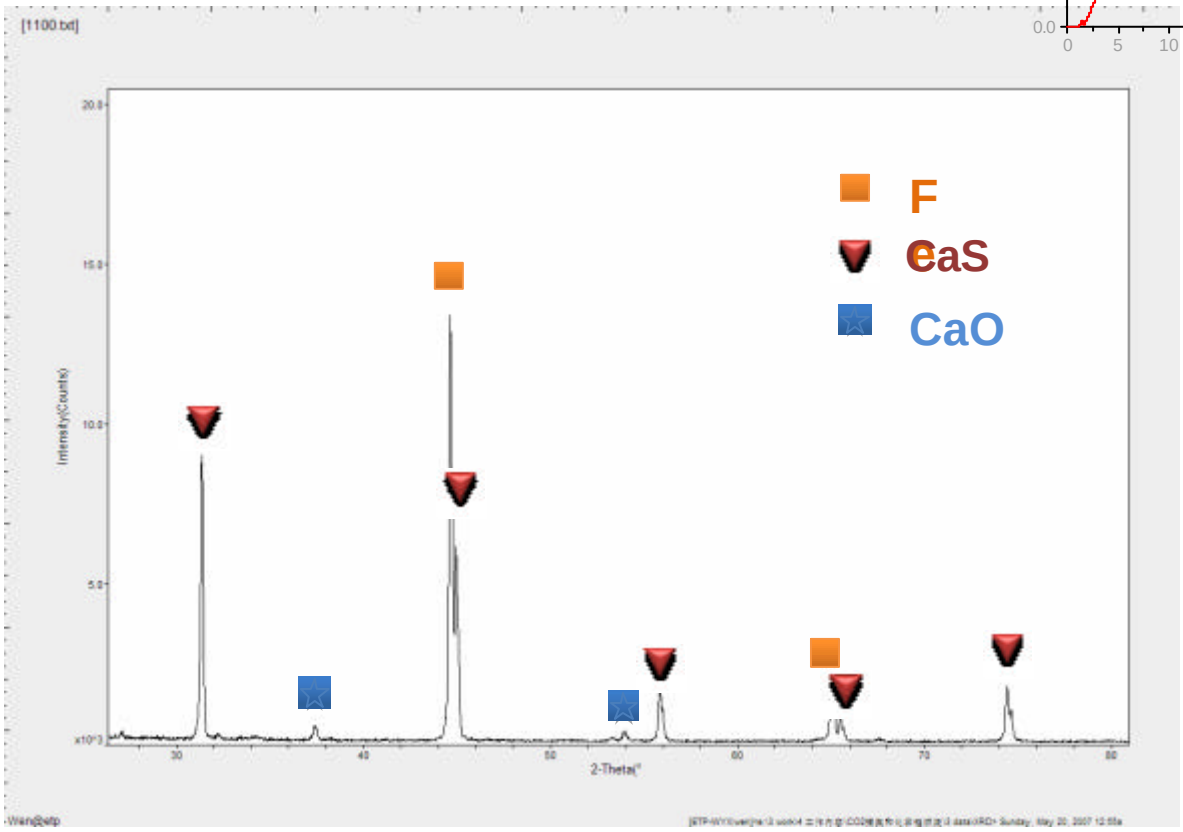


NO $CaSO_4$,
but Fe is shown.

High contents of CaFeSO are formed which **results in the low reaction rate!!**

XRD Analys

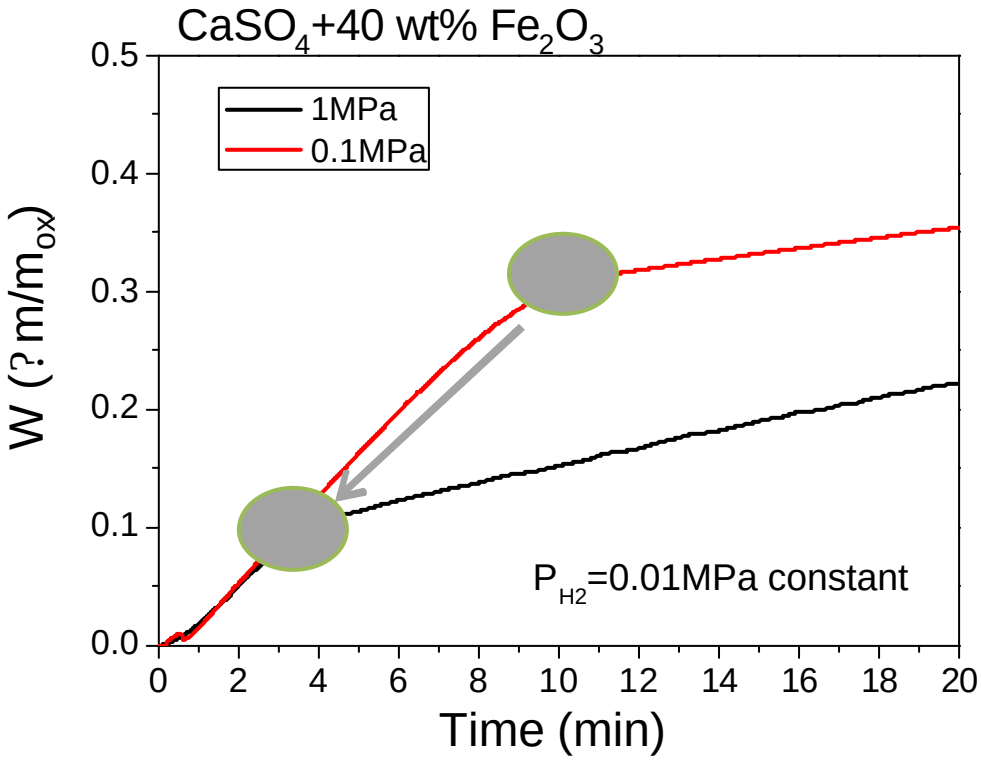




Totally reduced;

A little CaO is formed

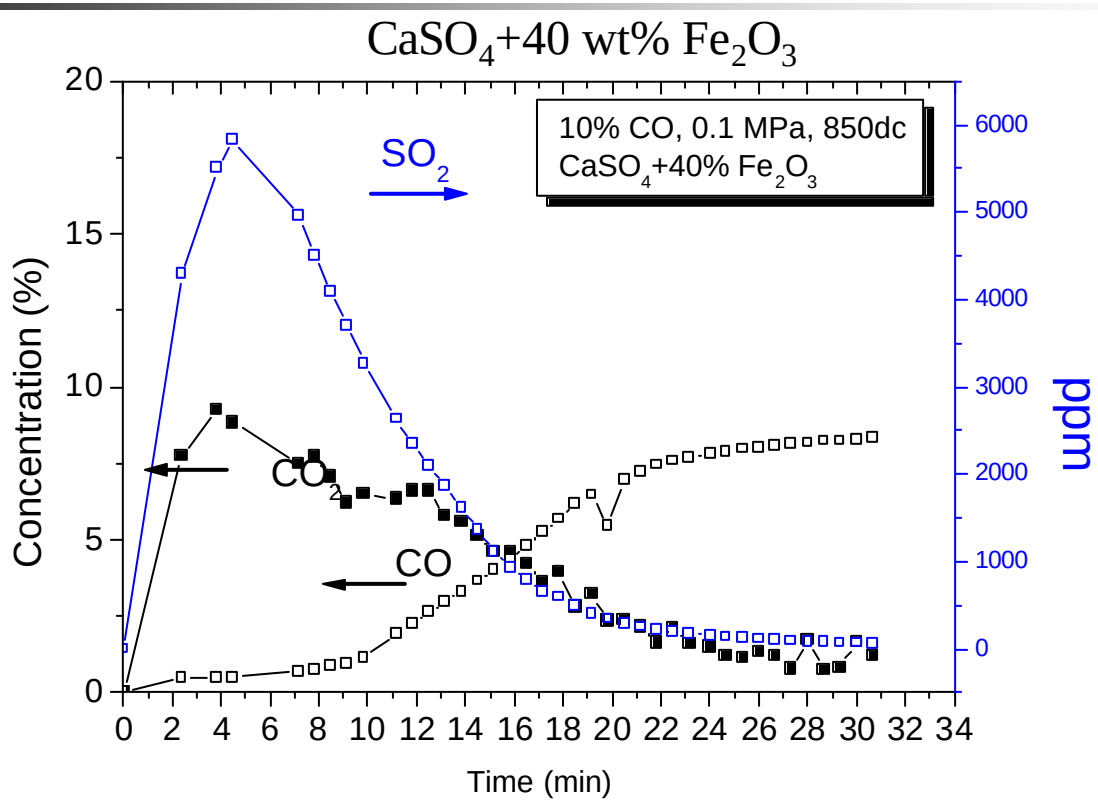
Effect of Reaction Pressure



High Pressure isn't a favorable factor. Because it accelerates the transformation of CaFeSO compounds.

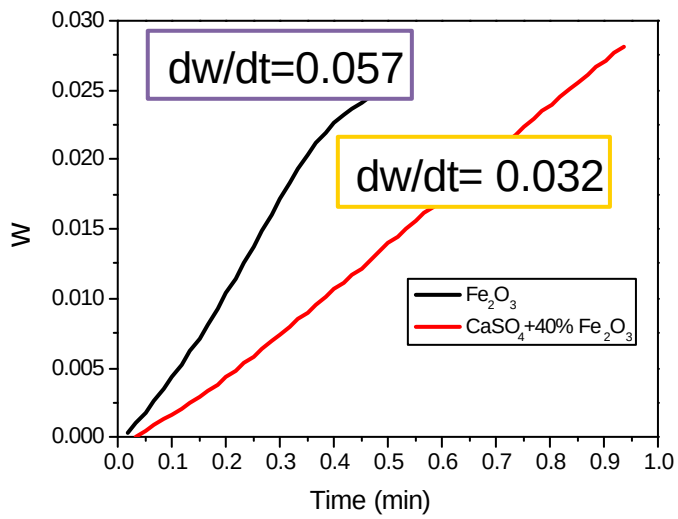
H_2 10%, 900dc, 0.1 and 1MPa. The partial pressure of H_2 was constant as 0.01MPa

Gas Composition



Along with full convertion of CO to CO_2, SO_2 was detected.

Data evaluation for reactor design



Mass-based conversion: $w = \frac{\Delta m}{m_{ox}} = R_o X$

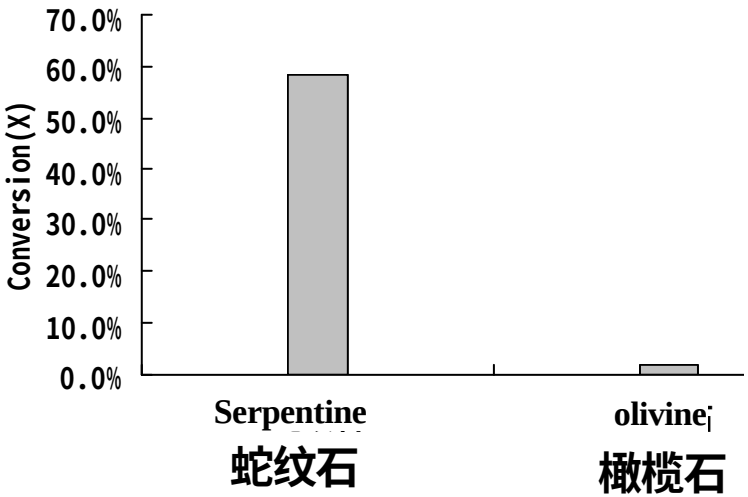
- OC reciuculation rate between air and fuel reactor is equal, if w is keep constant.
- The mass of bed needed in the fuel reactor is inversely proportioinal to dw/dt.

So, if w is 0.01kgO/kgOC, use CH_4 as reductant,
$M_{bed}(Fe_2O_3)$= 400kg/MW → M_{bed}(Ca40Fe)= 1.8 $M_{bed}(Fe_2O_3)$= 20kg/MW

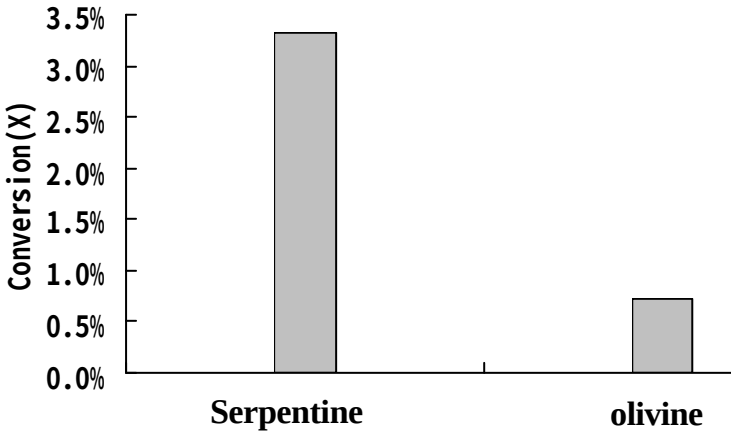
4. Carbon Dioxide Capture by Mineral

Experimental research: **Carbon Capture**

Performance Comparison with CO_2 capture by different minerals



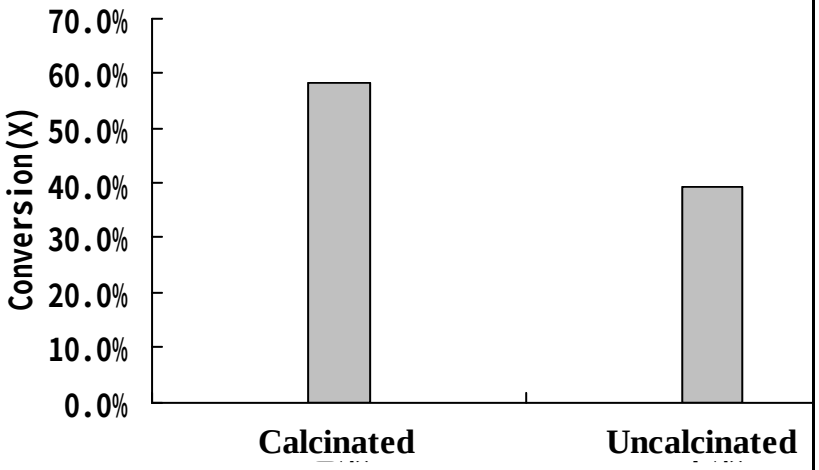
Calcined at 800℃ for 4h, then treated with HCl at pH=0 for 7h (Serpentine, olivine)



Calcined at 800℃ for 4h, then treated with HCl at pH=3 for 7h (Serpentine, olivine)

CO_2 Capture by Mineral

- CO_2 capture performance of Serpentine and olivine increase as pH decrease
- CO_2 captur performance of Serpentine better than that of olivine (treated at the same calcination temperature and pH value for acid treatment)
- Calcination Calcination pretreatment increase CO_2 mineral Sequestration performance greatly



Effect of heat treatment on Mineral captur for Serpentine
(treated with HCl acid for 7h at pH=0)

Thank You

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