CO_2 Capture and Sequestration Research in SKLCC

Professor Jianrong Qiu

State Key Laboratory of Coal Combustion
Huazhong University of Science and Technology
Wuhan, Hubei 430074, P.R.China

International Workshop on Clean Coal Technology Development
--CO_2 Mitigation, Capture, Utilization and Sequestration
August, 2005, Beijing, China

SKLCC

Outline

- Introduction of SKLCC
- Current Research and Progress
- Ongoing and Future Work

History: 1981
Faculty and Staffs: 30
Graduate Students: 150

SKLCC

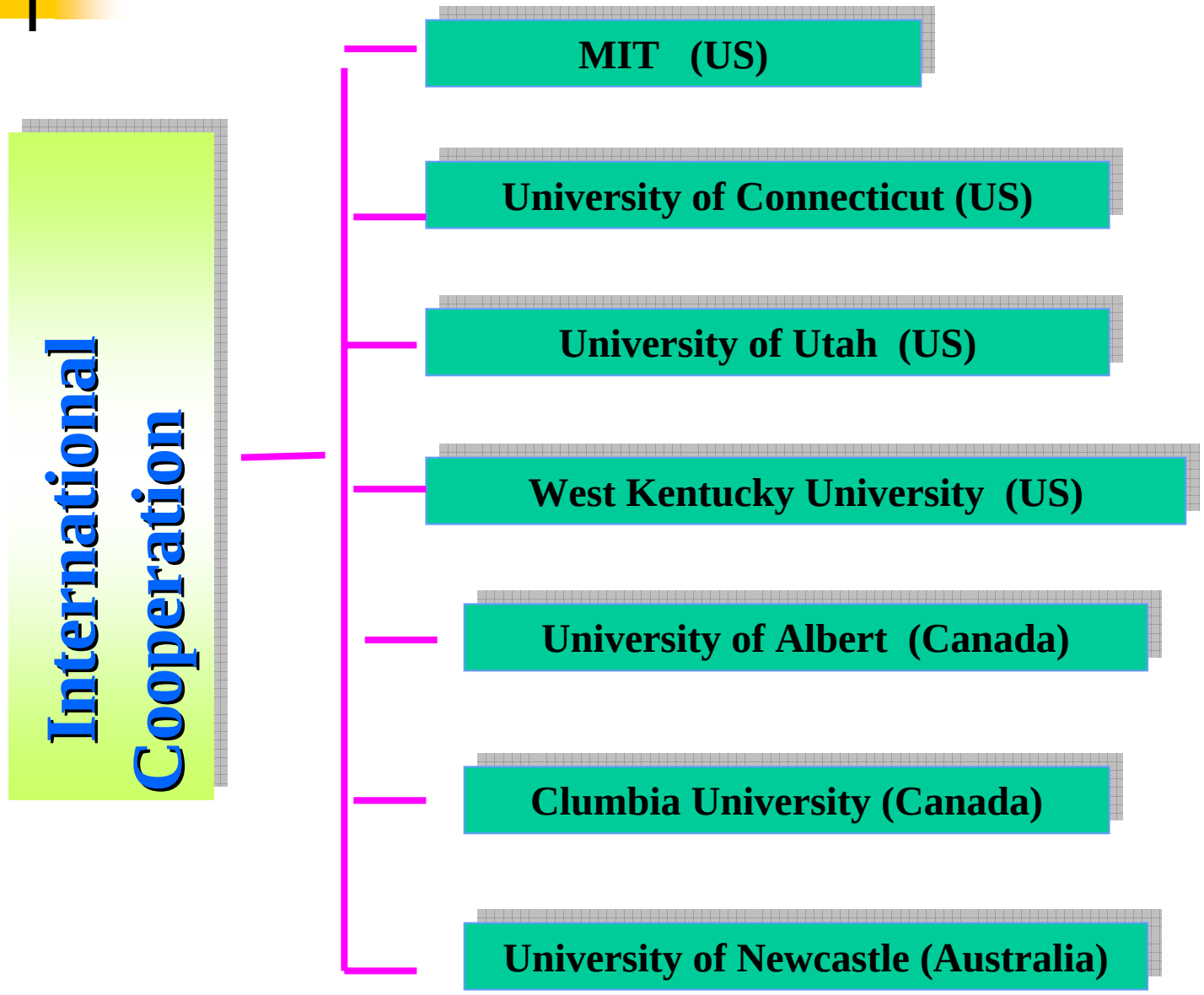
Research Areas

- Coal Combustion Science
  - Thermal Physical and Chemical Properties
  - Coal Structure and Reactivity
- Combustion Pollution and Control
  - SO_2
  - NO_x, N_2O
  - Trace Elements
  - PAHs
  - CO_2 Capture
- Combustion Model and Simulation
  - Aerodynamic Model
  - Heat Transfer
  - Combustion Model
  - Pollution Model
  - Global Simulation of Combustion Process
- Combustion Diagnosis and Application of Computer
  - Combustion Diagnosis
  - Computer Management Monitor and Control System
- Combustion Technology
  - Pulverized Coal Combustion
  - Fluidized Bed Combustion
- Advanced Power Generation Technology
  - Gasification and Flue Gas Cleaning
  - O_2/CO_2 Combustion

SKLCC

International publications: more than 200

(1997-2004)


International Cooperation
MIT (US)
University of Connecticut (US)
University of Utah (US)
West Kentucky University (US)
University of Albert (Canada)
Clumbia University (Canada)
University of Newcastle (Australia)

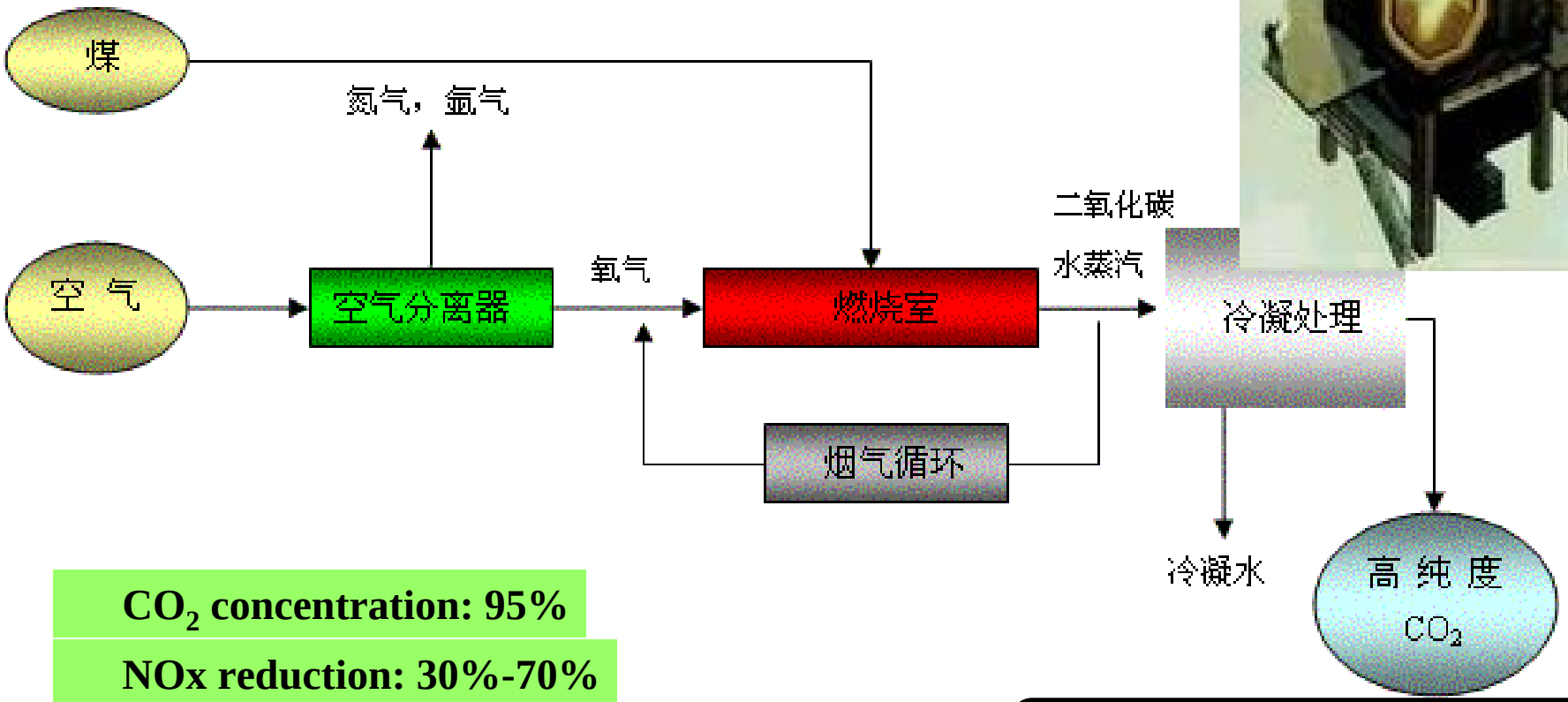
SKLCC

Current Research and Progress in SKLCC

- Oxy-fuel Combustion
- Chemical Looping Combustion
- CO_2 Capture Based on CCR
- CO_2 Sequestration by Mineral Carbonation

NSFC(1997-) (2001-)(2002-) ; 973 Program(1999-2004); 985 Program (2005-)

Oxy-Fuel Combustion



- CO_2 concentration: 95%
- NOx reduction: 30%-70%
- SO_2 removal by limestone: 40%-90%
- Thermal efficiency increase: 3%

Easy and efficient CO_2 separation, recovery

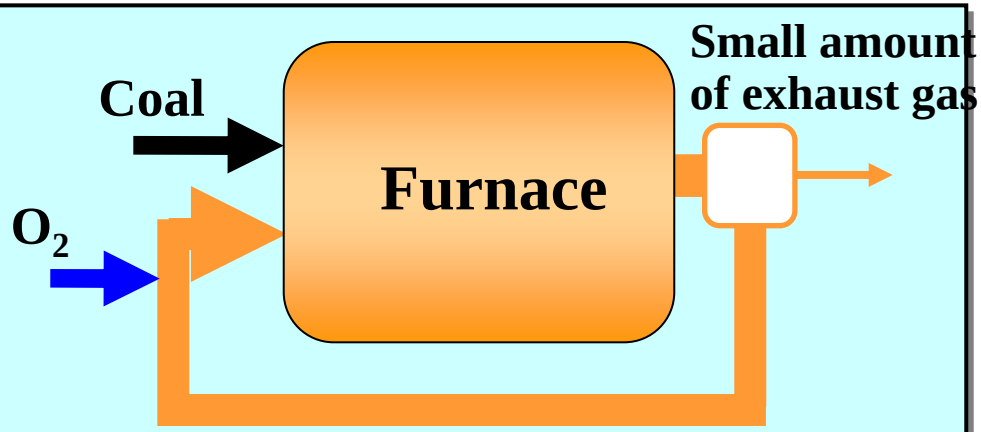
How about NO_x and SO_x emissions in O_2/CO_2 pulverized coal combustion?

Highly efficient, clean coal combustion

O_2/CO_2 Pulverized coal combustion

- **Easy and efficient CO_2 separation**
- **Extremely low NO_x emission**
- **Low SO2 emission**

Characteristics and mechanisms unknown

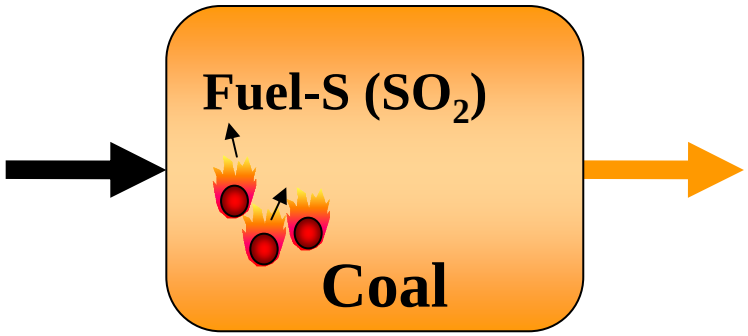


Recirculation of mass

Enrichment of mass(CO_2 , NO_x , SO_x) in furnace

Small amount of exhausted gas as a system

Conventional pulverized coal combustion

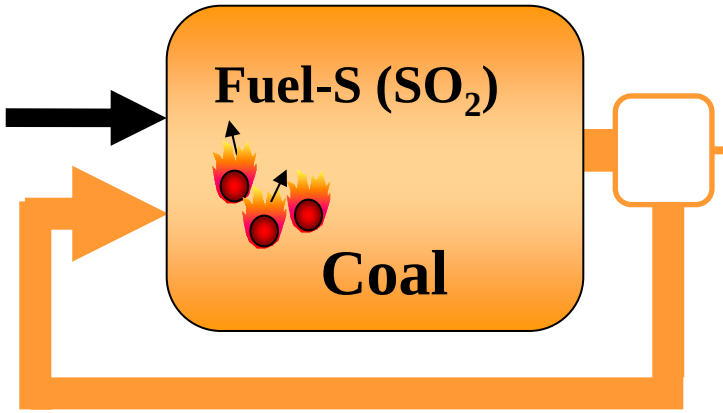


$CaSO_4$ decomposition

↓

Low desulfurization efficiency

O_2/CO_2 pulverized coal combustion



High CO_2 concentration

↓

- Enhance desulfurization reaction?
- Inhibit $CaSO_4$ decomposition?

↓

Possibility of high in-furnace desulfurization efficiency

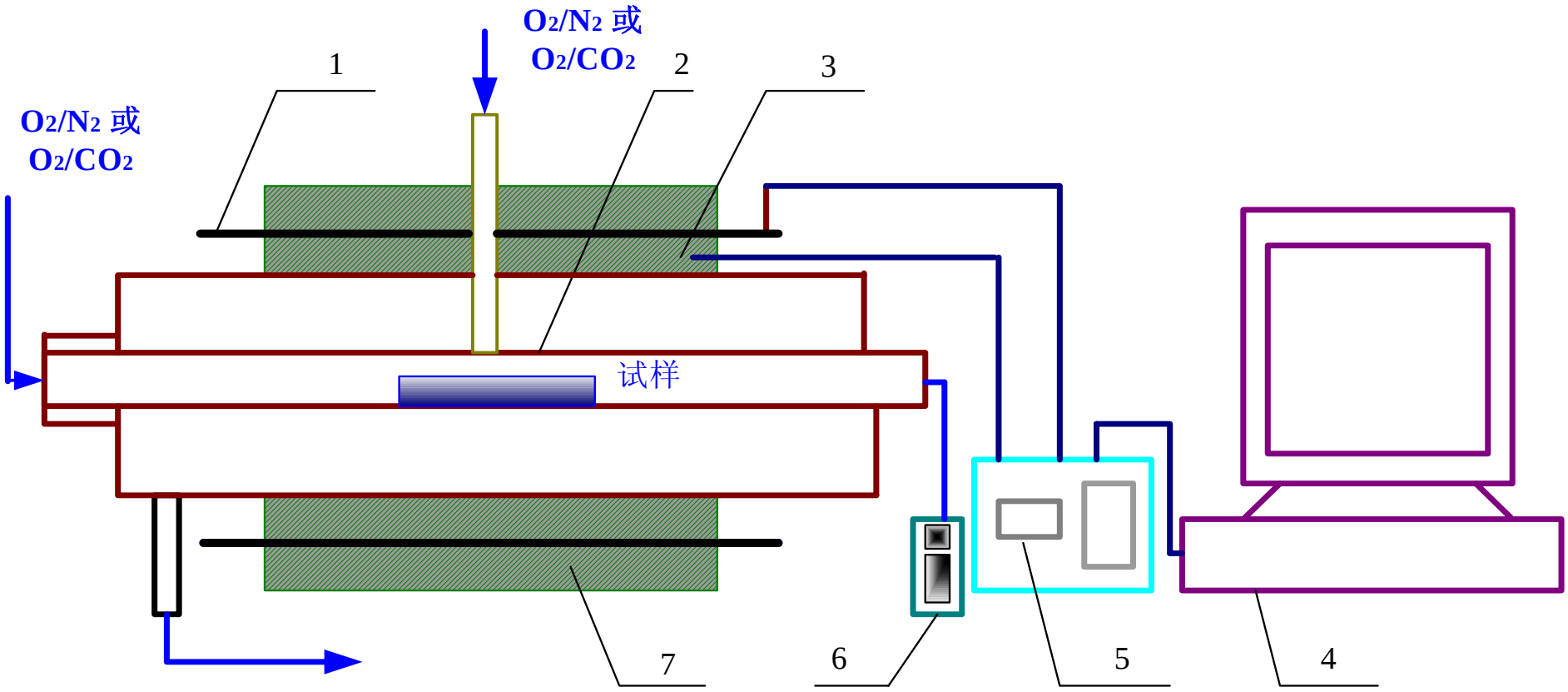
↓

Characteristics and mechanisms: unknown

SKLCC's Progress

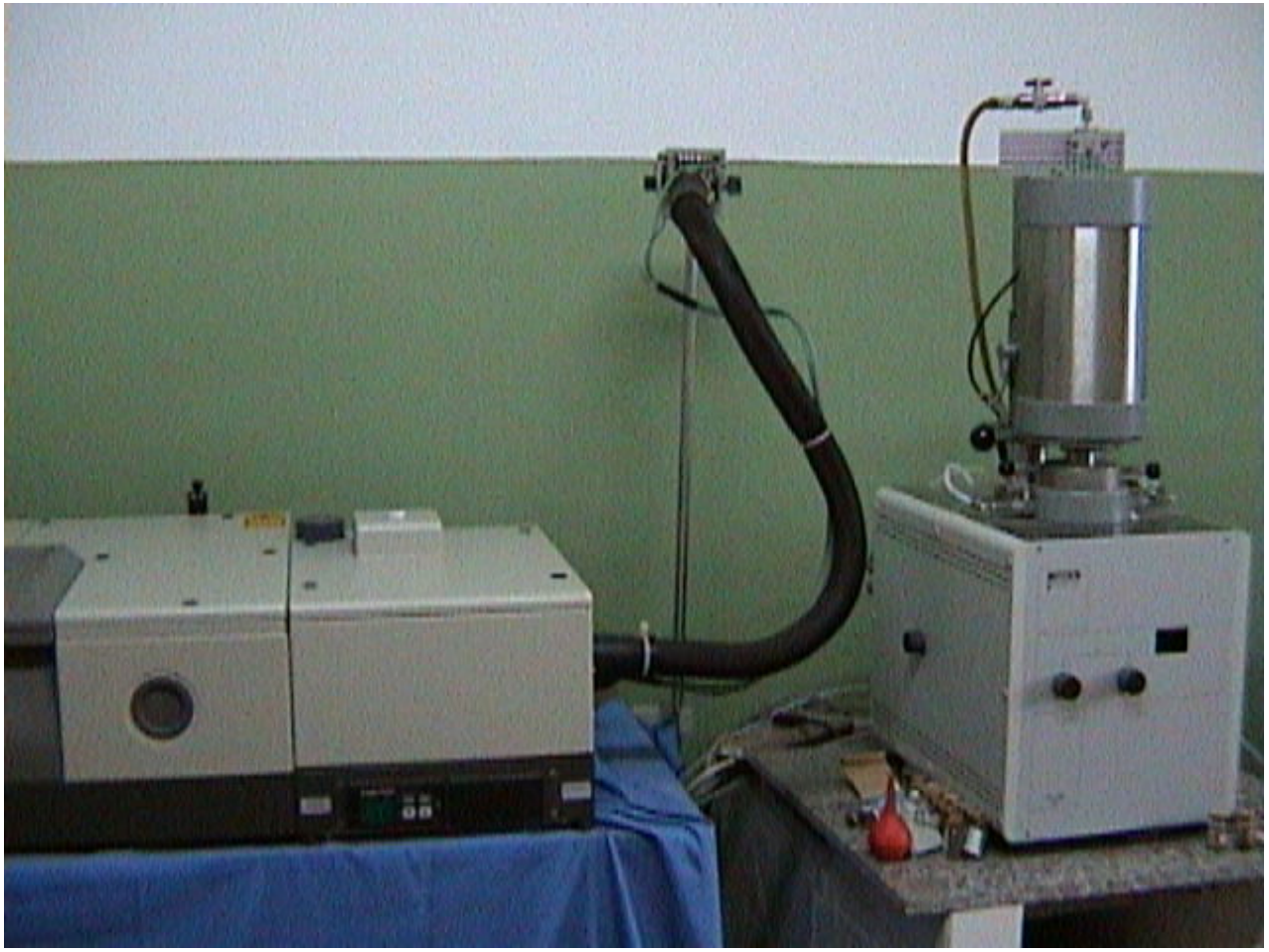
- **Flame Characteristics and Combustion behavior**
- **The mechanism of SO_2 and NOx reduction**
- **Limestone desulfurization reaction mechanism in O_2/CO_2**

Experimental Facility

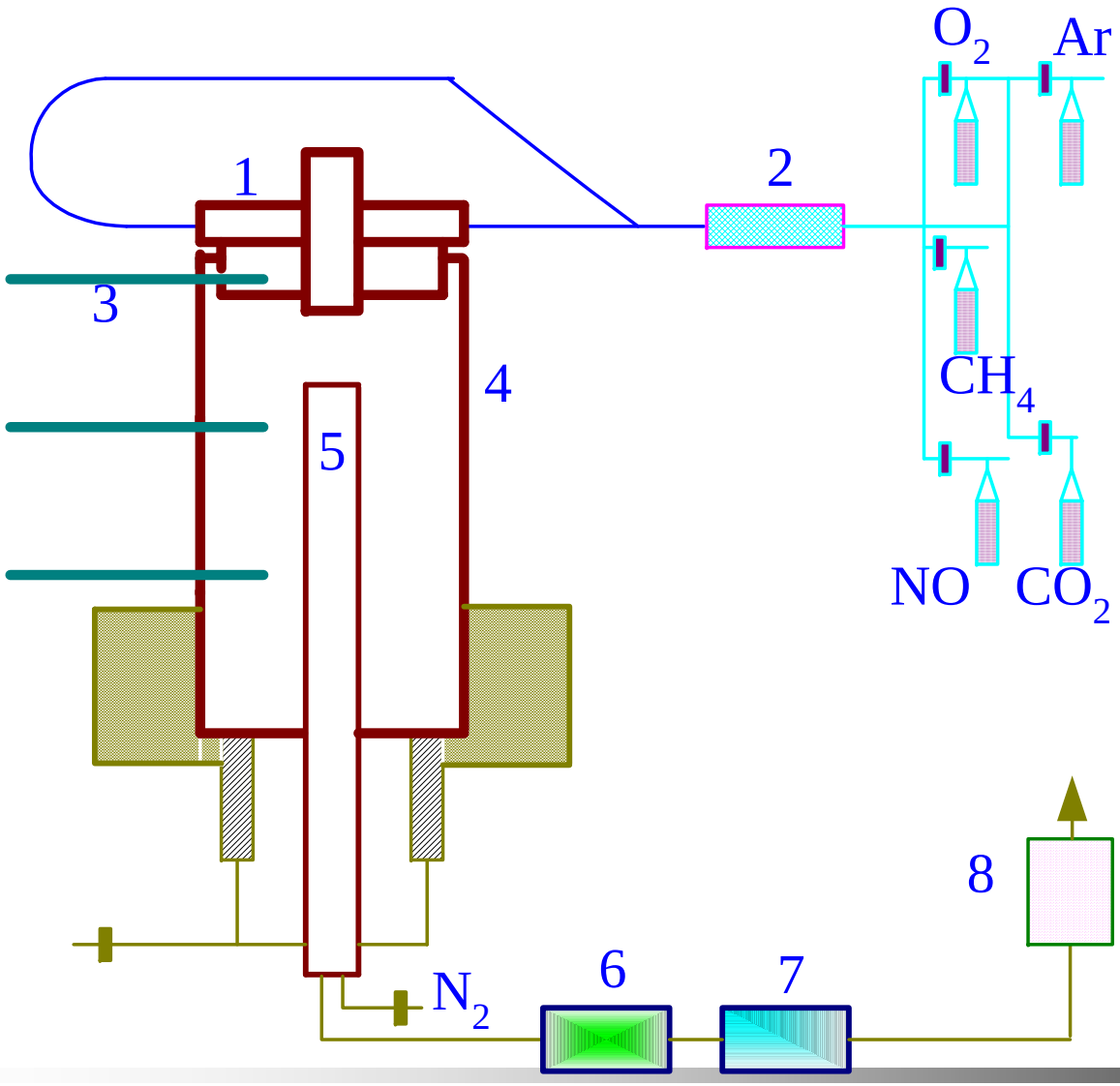


1 硅炭管　2 石英管　3 热电偶　4 计算机　5 温控仪　6 烟气分析仪　7 保温带

TGA-FTIR

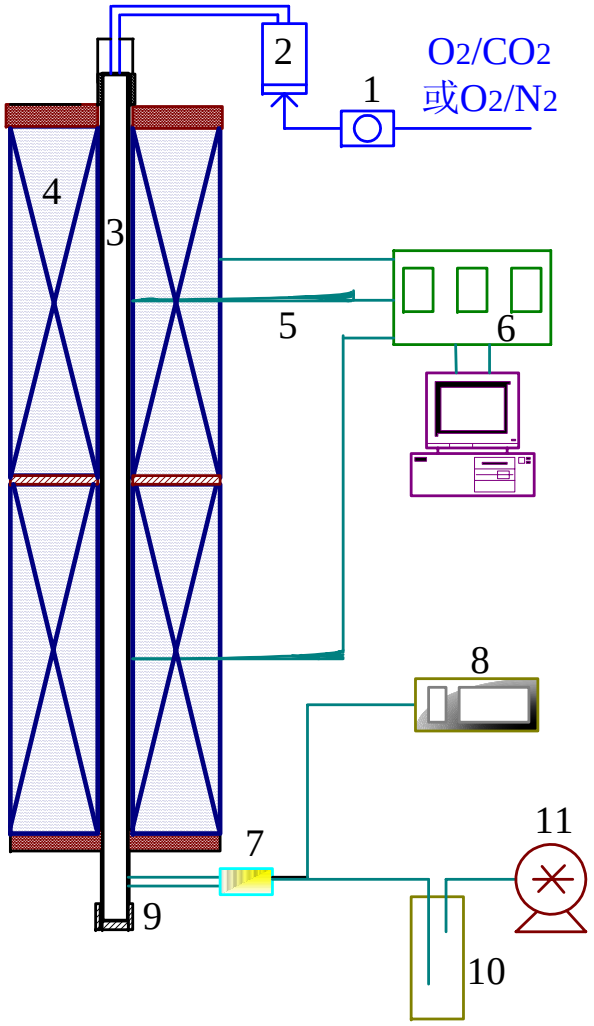


CH4 combustion device

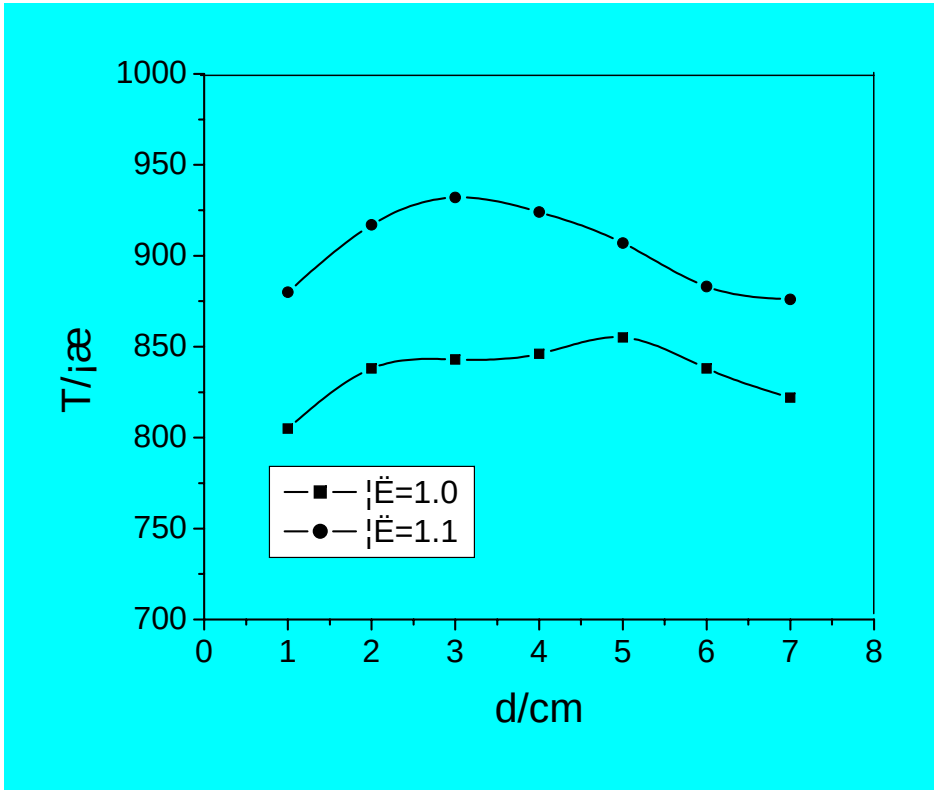


1 点火器
2 混气器
3 热电偶
4 反应器
5 取样管
6 过滤器
7 干燥器
8 烟气分析仪

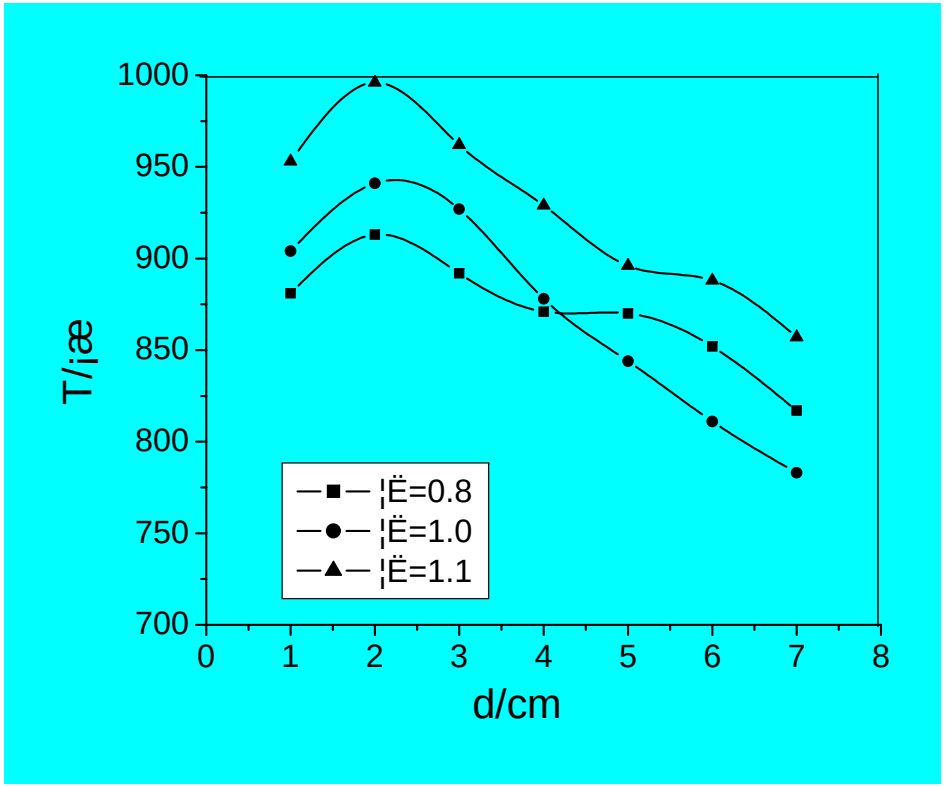
O2/CO2 Coal Combustion Furnace



Flame Characteristics

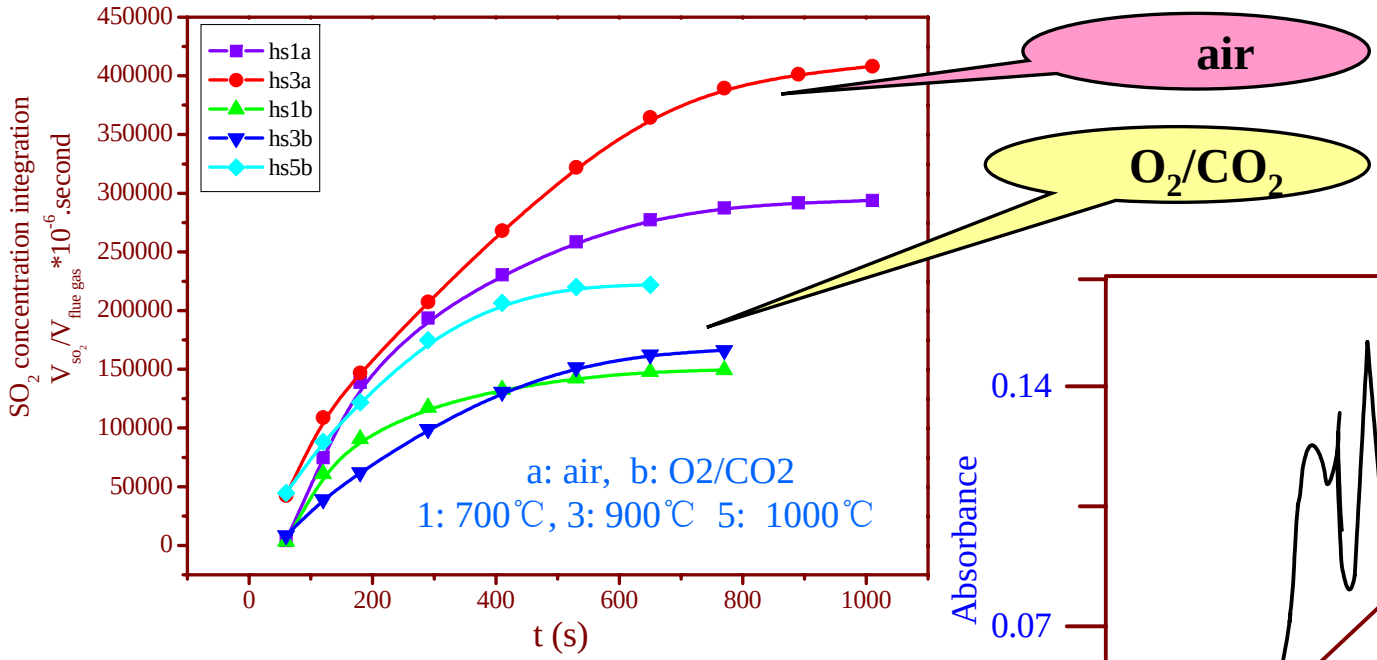


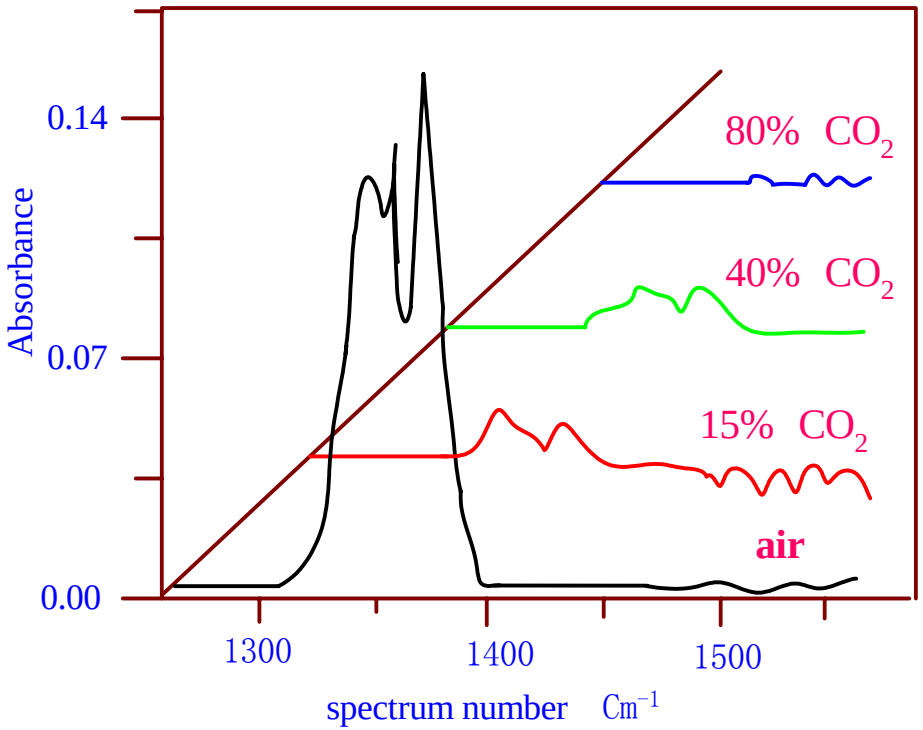
60%CO_2



40%CO_2

SO_2 Emission





$$C + CO_2 \rightarrow 2CO$$

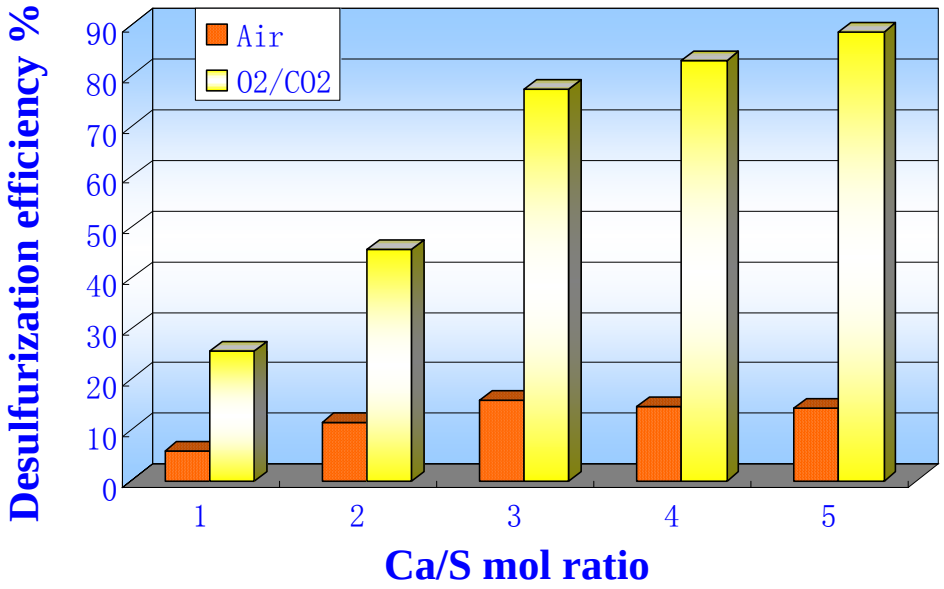
$$2CO + SO_2 \rightarrow CO_2 + S$$

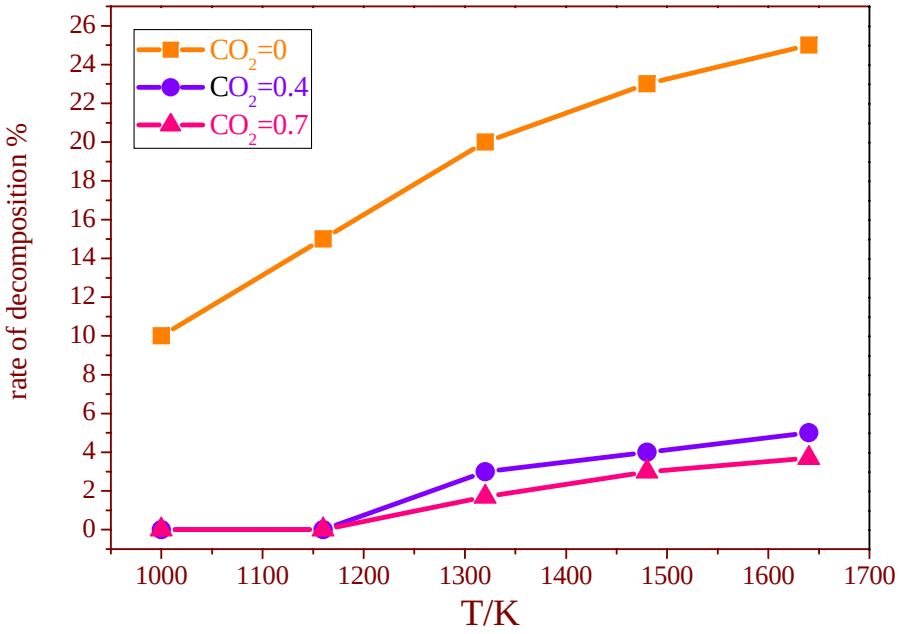
$$CO + S \rightarrow COS$$

$$SO_2 + 2COS \rightarrow 2CO_2 + \frac{3}{2}S_2$$

SO_2 emission decreased about 30-60% for different coals at different temperatures

SO_2 Removal by Limestone





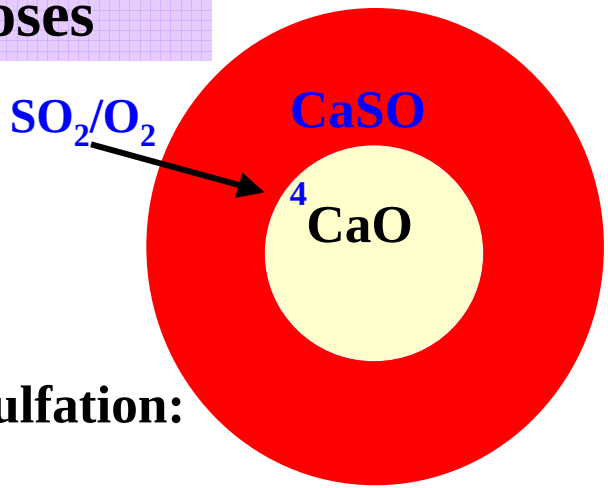
CaSO4 decomposition

➢ **The presence of high concentration CO_2 can improve the SO_2 removal efficiency with limestone injection.**

Fundamental Mechanisms

Low CO_2 concentration

$CaCO_3$ decomposes



Indirect sulfation:

$$CaCO_3 = CaO + CO_2$$

$$CaO + (1/2)O_2 + SO_2 = CaSO_4$$

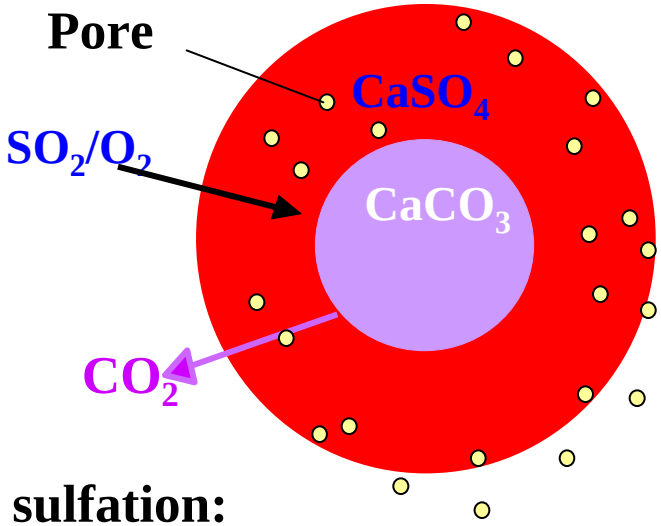
CaO Sintering

SO_2 is difficult to get into the particle

Low reaction rate

High CO_2 concentration

$CaCO_3$ does not decompose



Direct sulfation:

$$CaCO_3 + (1/2)O_2 + SO_2 = CaSO_4 + CO_2$$

Sintering is mitigated

CO_2 formation and diffusion results in a porous product layer

SO_2 is easy to get into the particle

SO_2 reduction mechanism in Oxy-fuel recycle combustion system

Small amount of SO_2 emission

Small amount of exhausted gas

COS formation

SO_2 retention by CaO in the coal

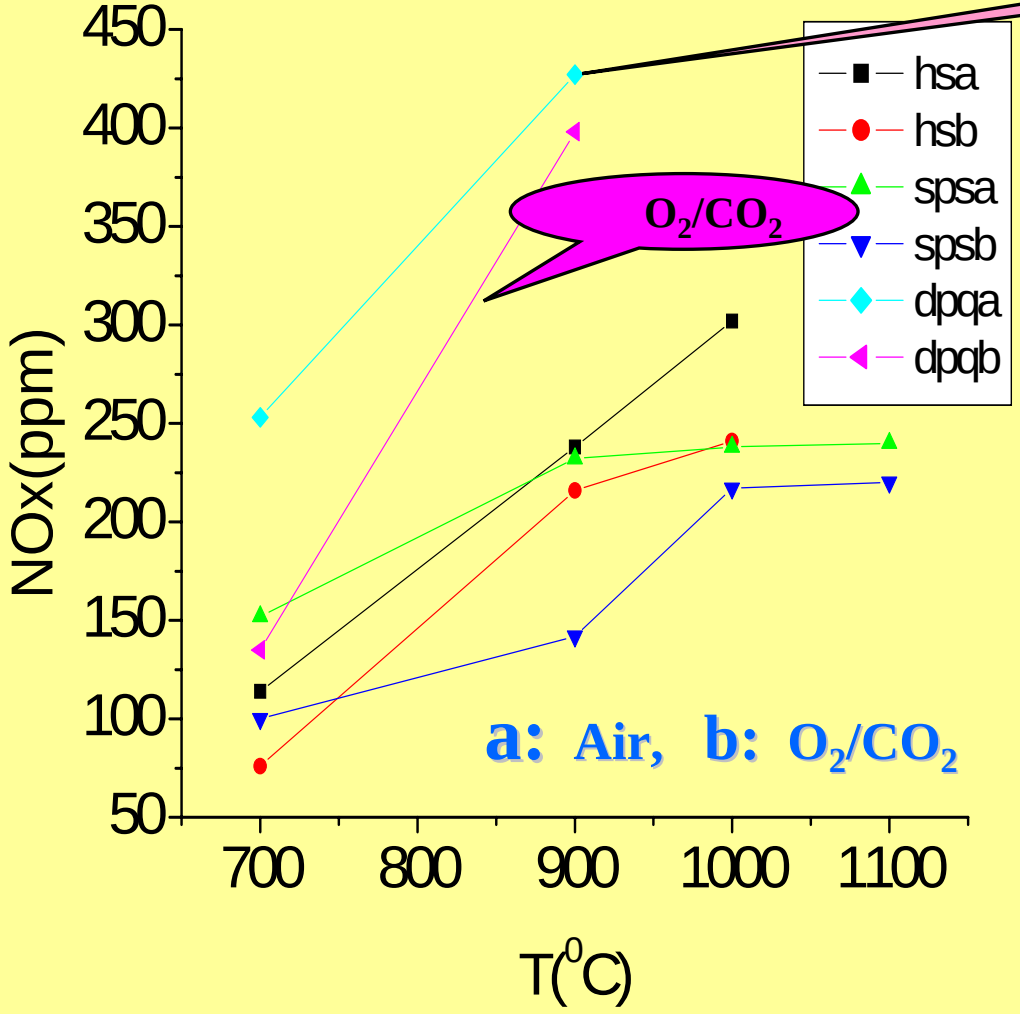
Higher Limestone desulfurization efficiency

Increase of η due to inhibition of CaSO4 decomposition

Increase of η due to recirculation of flue gas (sorbents)

About four times longer than in conventional coal combustion owing to gas recirculation

NOx Emission



$C+CO2 \rightarrow 2CO$

$NO+CO \rightarrow CO2+1/2\ N2$

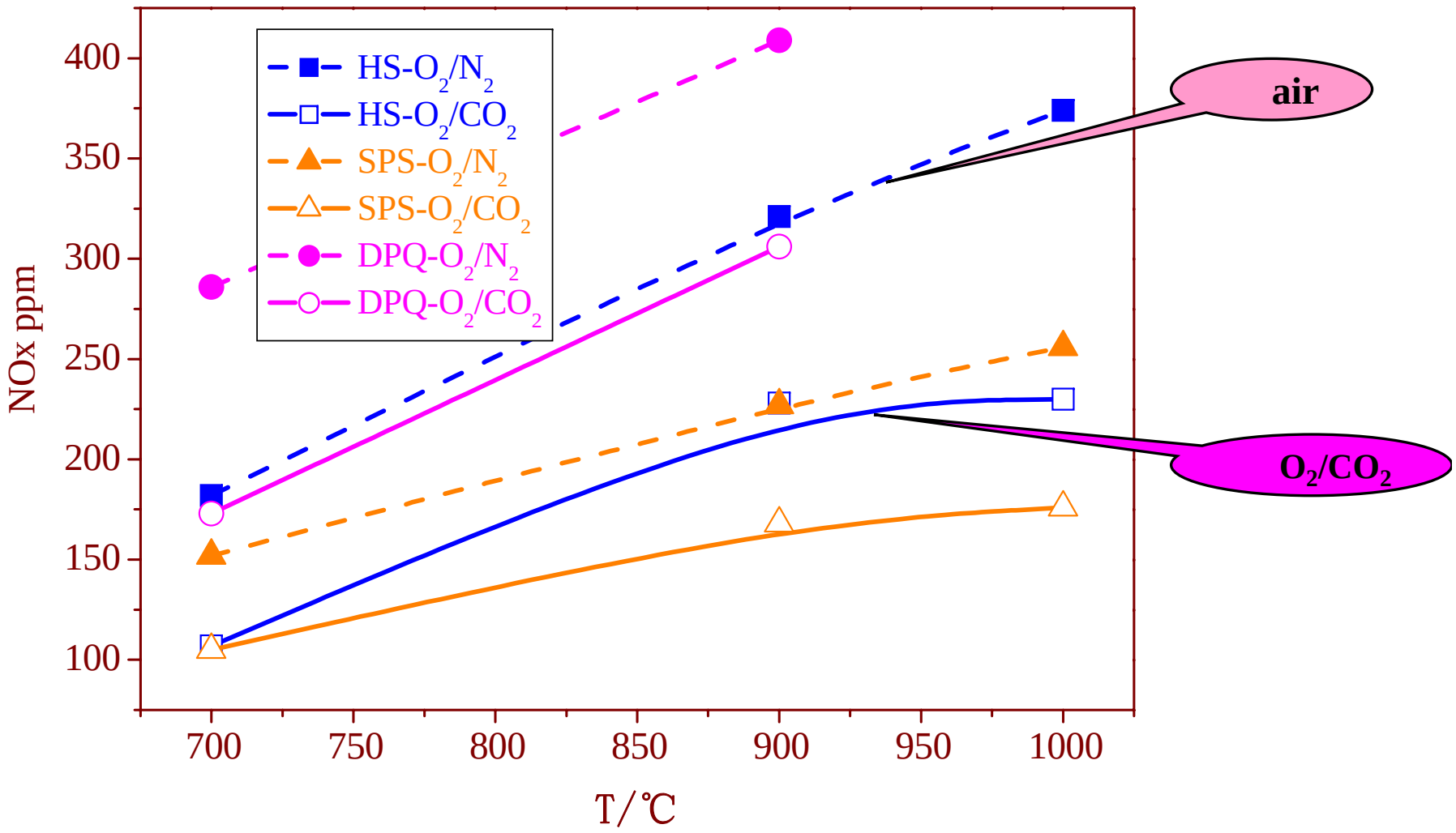
$C+2NO \rightarrow CO2+N2$

$2C+2NO \rightarrow 2CO+N2$

煤中矿物质尤其是Fe和Ca的存在对半焦与NO的反应有催化作用.

NOx emission decreased about 10-40% for different coals at different temperatures

NOx Emission in Desulfurization



CaCO3的存在对CO与NO的表面反应有催化作用.

NO reduction mechanism in Oxy-fuel recycle combustion system

Small amount of NO emission

Small amount of exhausted gas

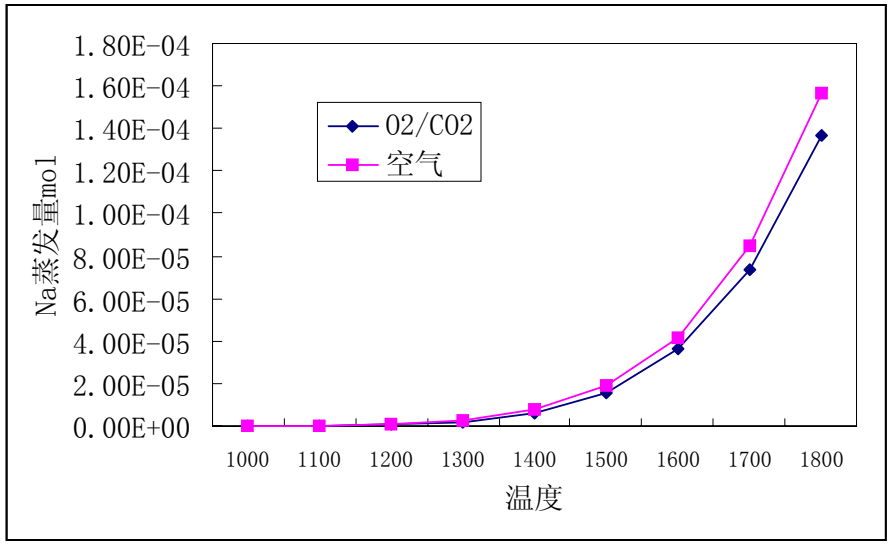
No thermal NO

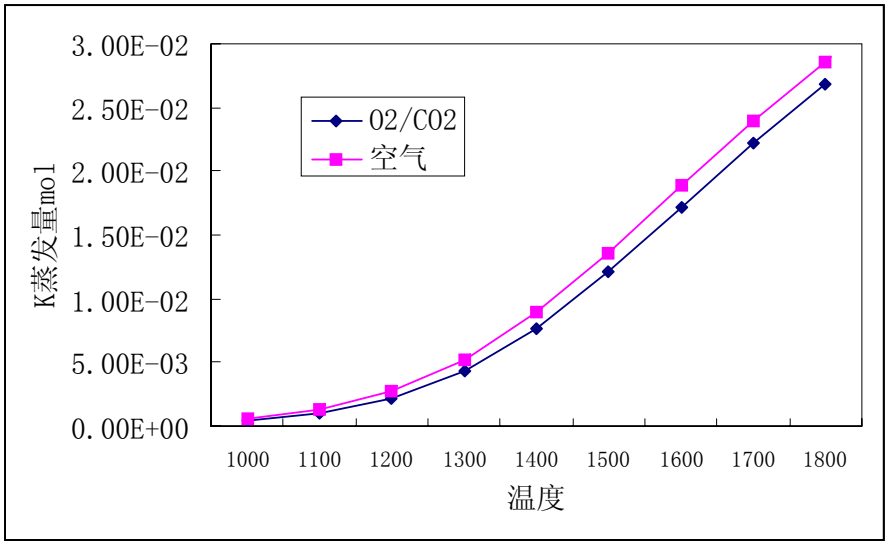
Decrease of N conversion due to increase of CO_2 concentration

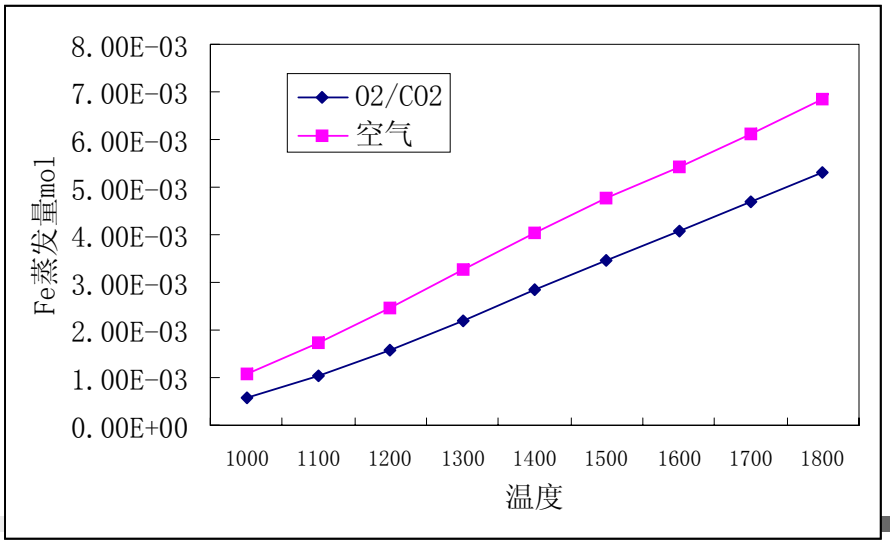
Reduction of recycled NO in the furnace

Interaction between fuel-N and recycled NO

Mineral Transformation







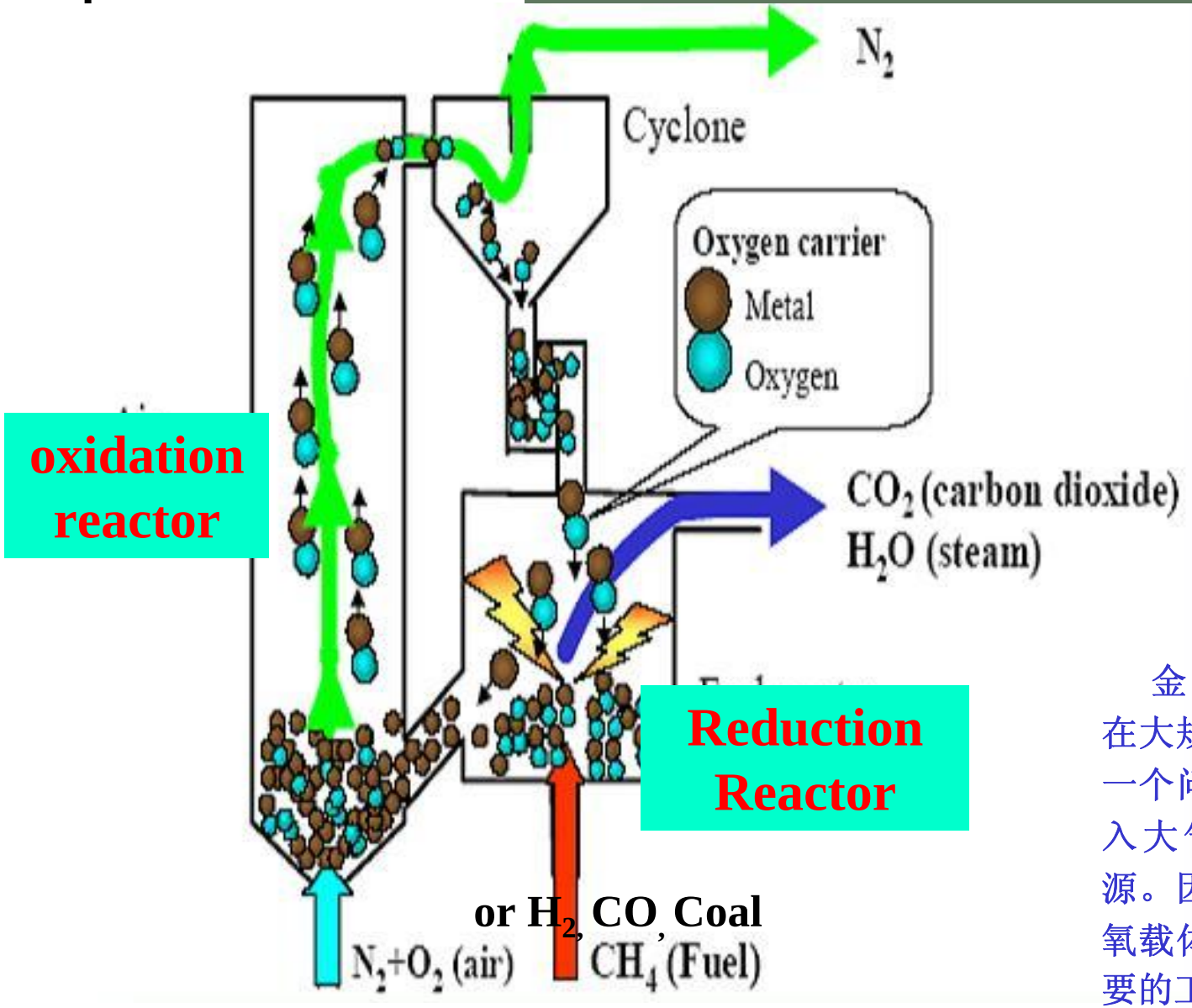
SKLCC

Current Research and Progress in SKLCC

- Oxy-fuel Combustion
- Chemical Looping Combustion
- CO_2 Capture Based on CCR
- CO_2 Sequestration by Mineral Carbonation

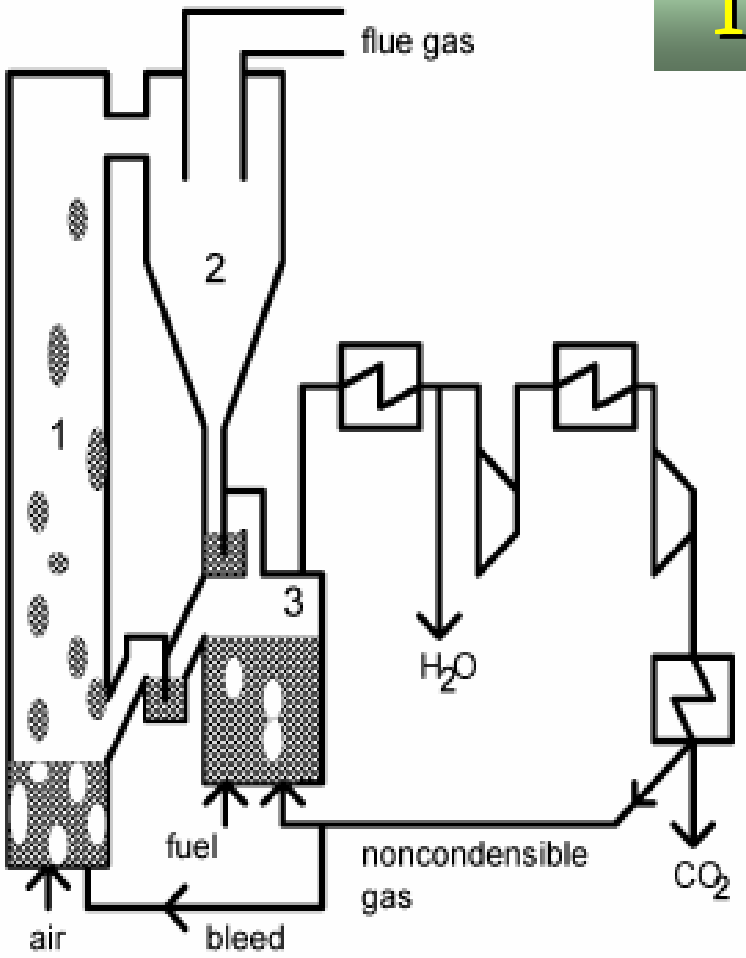
NSFC(1997-) (2001-)(2002-) ; 973 Program(1999-2004); 985 Program (2005-)

Chemical Looping Combustion



金属氧化物作为氧载体在大规模应用中必须考虑的一个问题是金属氧化物会进入大气环境，为新的污染源。因此，探索新的非金属氧载体物质也是一项非常重要的工作。

New Oxygen Carrier

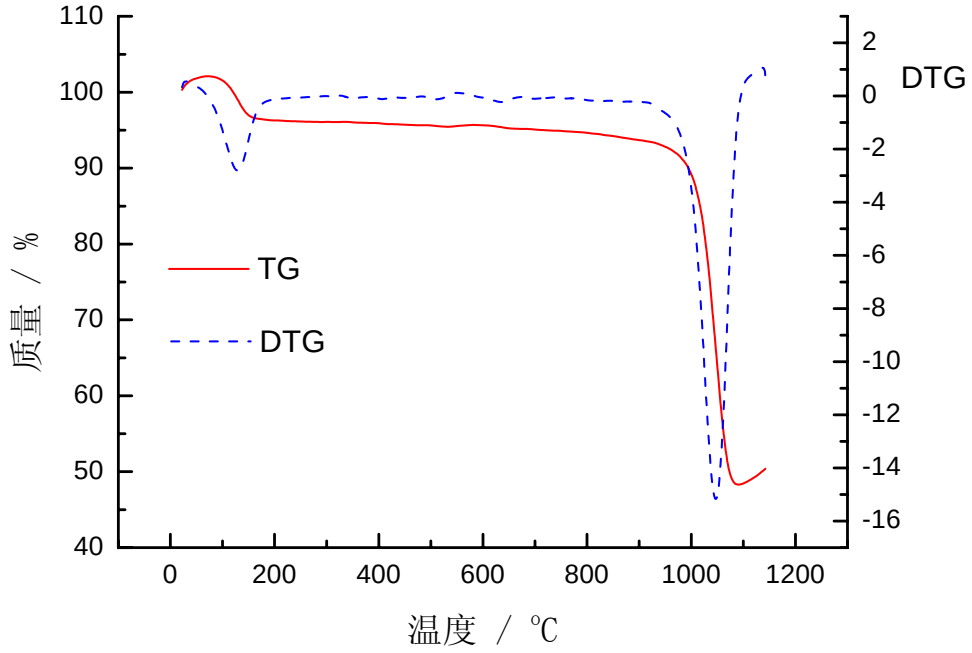


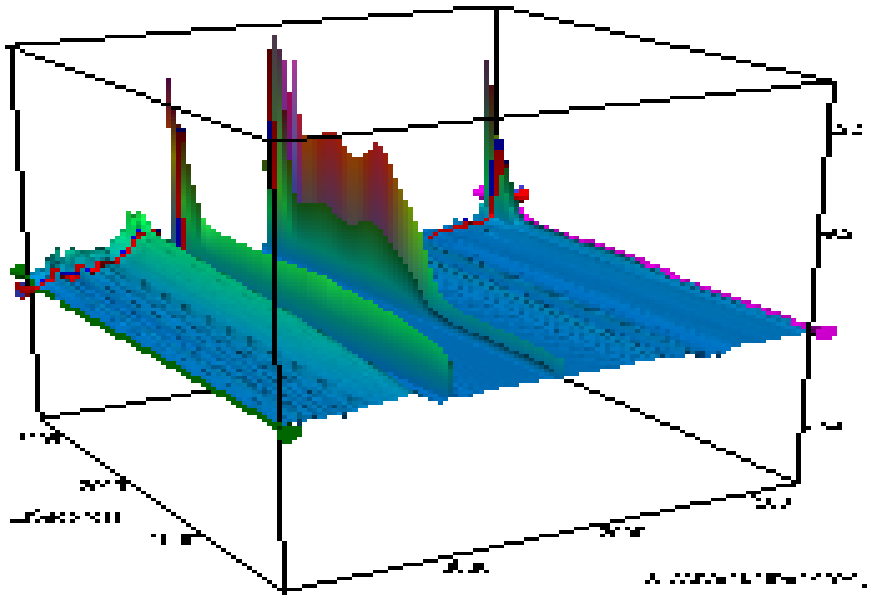
New Oxygen Carrier is developed instead of metal Oxygen Carrier (NiO/Ni, Fe_2O_3/Fe_3O_4, CoO/Co, CuO/Cu, Mn_3O_4/MnO etc.)

$$CH_4(CO,H_2) + N\text{-}MeOx \rightarrow CO_2 + H_2O + N\text{-}Me$$

$$N\text{-}Me + 2O_2 \rightarrow NMeOx$$

A Novel non-metal oxides: no secondary pollution





TG--FTIR experiment for reaction system of non-metal oxides with CH_4

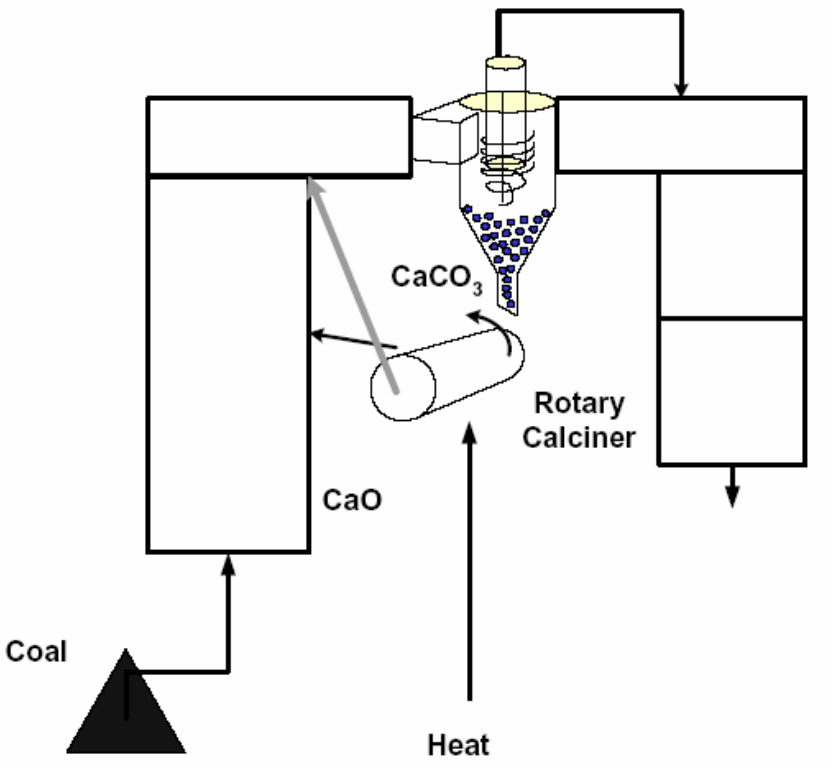
Current Research and Progress in SKLCC

- Oxy-fuel Combustion
- Chemical Looping Combustion
- CO_2 Capture Based on CCR
- CO_2 Sequestration by Mineral Carbonation

NSFC(1997-) (2001-)(2002-) ; 973 Program(1999-2004); 985 Program (2005-)

CO_2 Capture Technology Based on Carbonation/Calcination Reactions

I — CO_2 Capture During Combustion



Capture: $CaO + CO_2 \rightarrow CaCO_3$

Regeneration: $CaCO_3 \rightarrow CaO + CO_2$

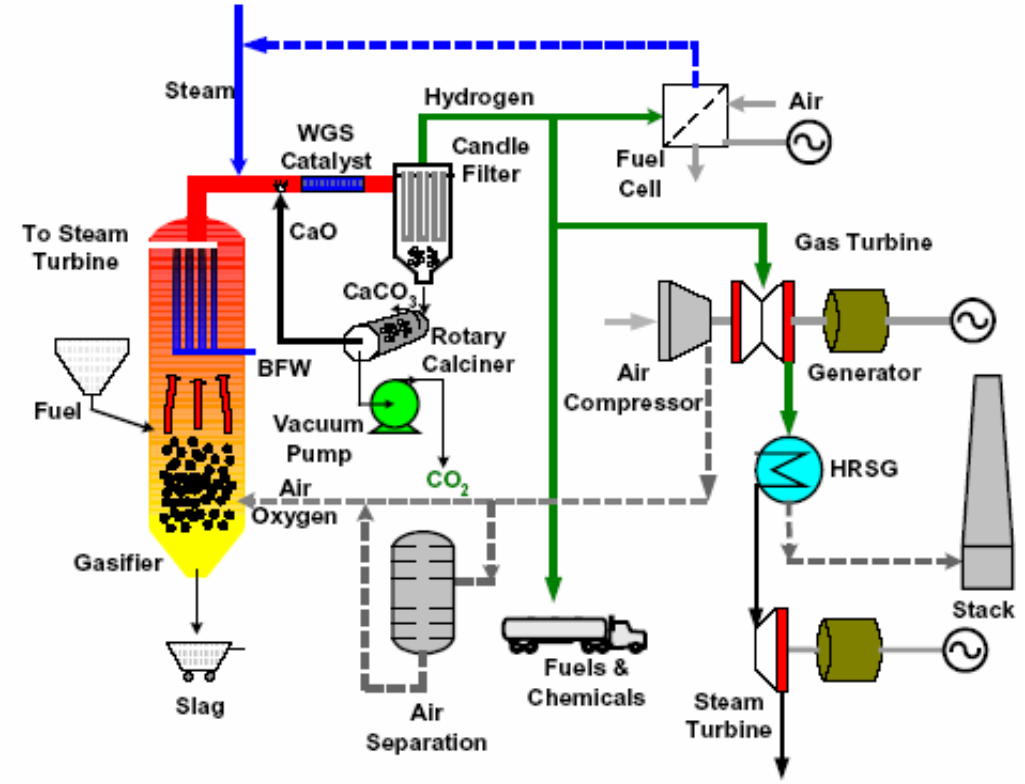
Separation Energy:

CCR process 84 kWh/ton CO_2

MEA process 203 kWh/ton CO_2

CO_2 Capture Technology Based on Carbonation/Calcination Reactions

II — CO_2 Capture During Gasification



1) Syngas CO/H_2

Water Gas Shift Reaction:

$CO + H_2O \rightarrow CO_2 + H_2$

$CaO + CO_2 \rightarrow CaCO_3$

$CaCO_3 \rightarrow CaO + CO_2$

2) $CH_4 + 2H_2O + CaO \rightarrow$

$CaCO_3 + 4H_2$

$CaCO_3 \rightarrow CaO + CO_2$

SKLCC

Two-Core Reactions

☆ CO_2 Capture: $CaO + CO_2 \rightarrow CaCO_3$

☆ Regeneration: $CaCO_3 \rightarrow CaO + CO_2$

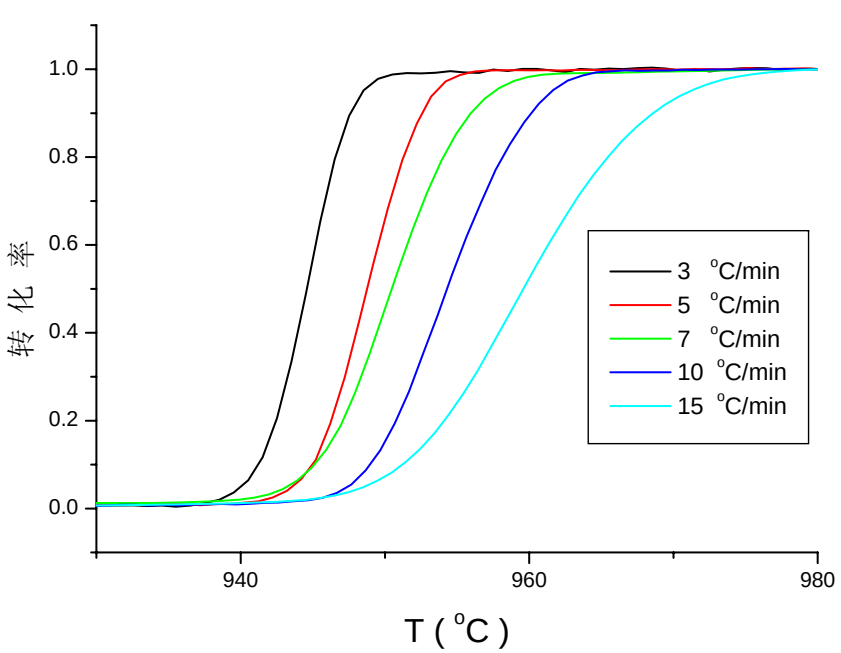
— Experimental Research

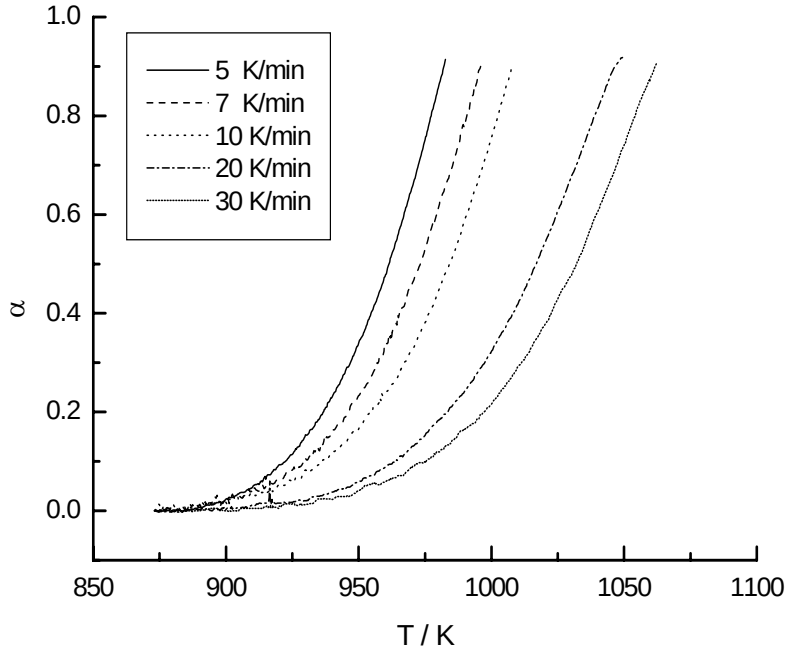
- Calcination Kinetics at CO_2 and N_2 atmosphere
- Carbonation Reaction

— Numerical Simulation

- Calcination model for dispersed limestone particle(弥散石灰石煅烧模型)
- Fractal model for dispersed limestone decomposion (石灰石分解的分数维模型
- Freedom pore model for carbonation of CaO under high pressure (高压下的随机孔模型)

Calcination Kinetics at CO_2 and N_2 Atmosphere



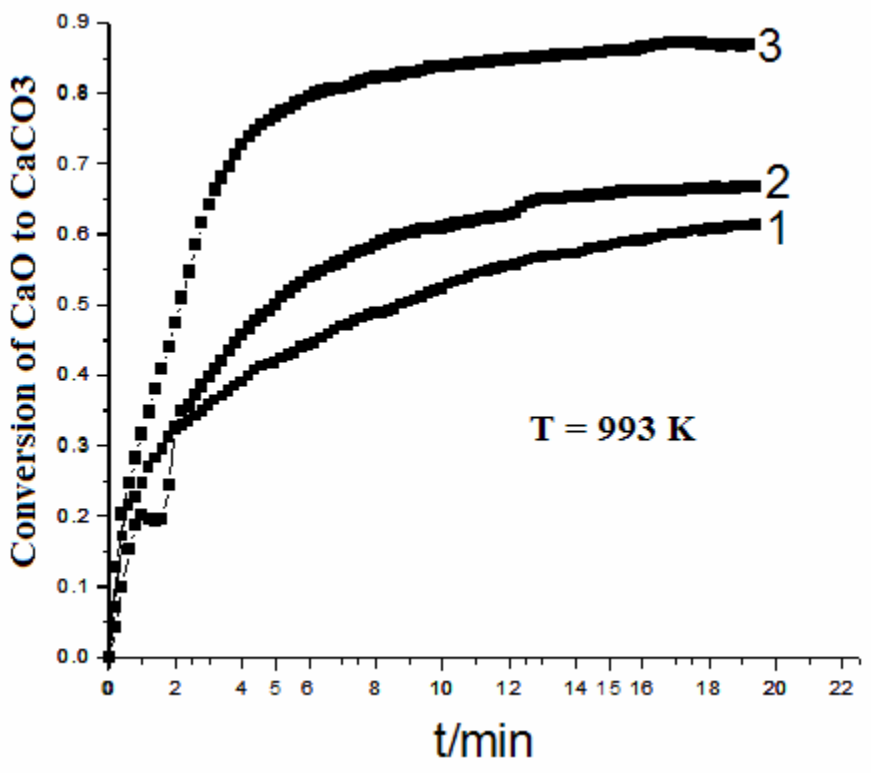


CO_2 N_2

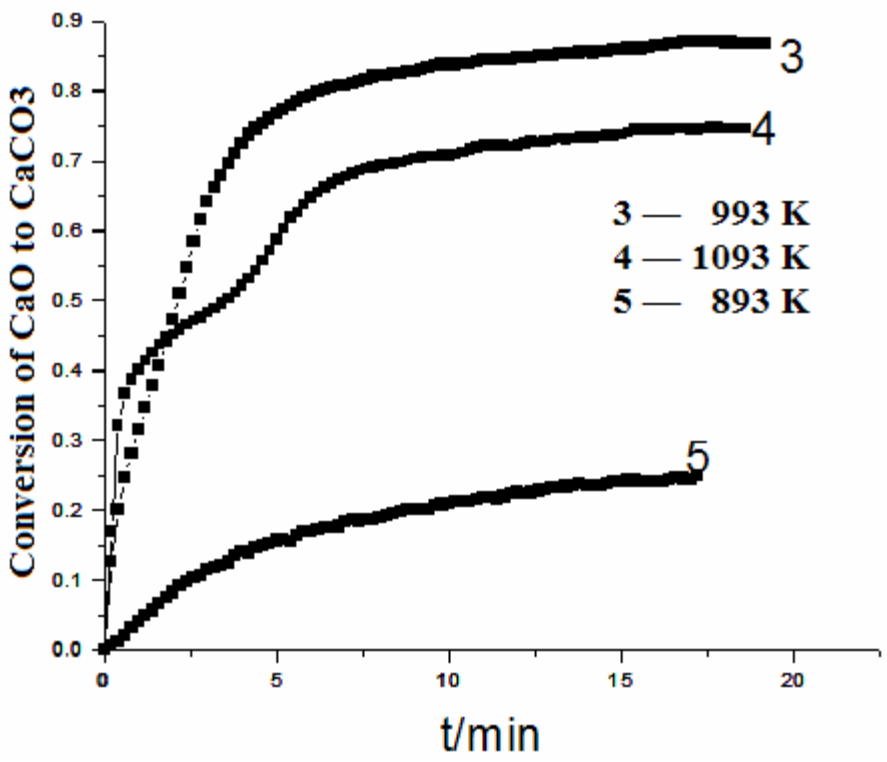
n=2/3，mechanistic function ，

CO_2 atmosphere，$E_{\alpha\to0}$=975.38kJ/mol; N_2atmosphere，$E_{\alpha\to0}$=243.62kJ/mol

Carbonation Characteristic of CaO



CaO conversion ratio vs. CO_2 concentration



CaO conversion ratio vs. temperature

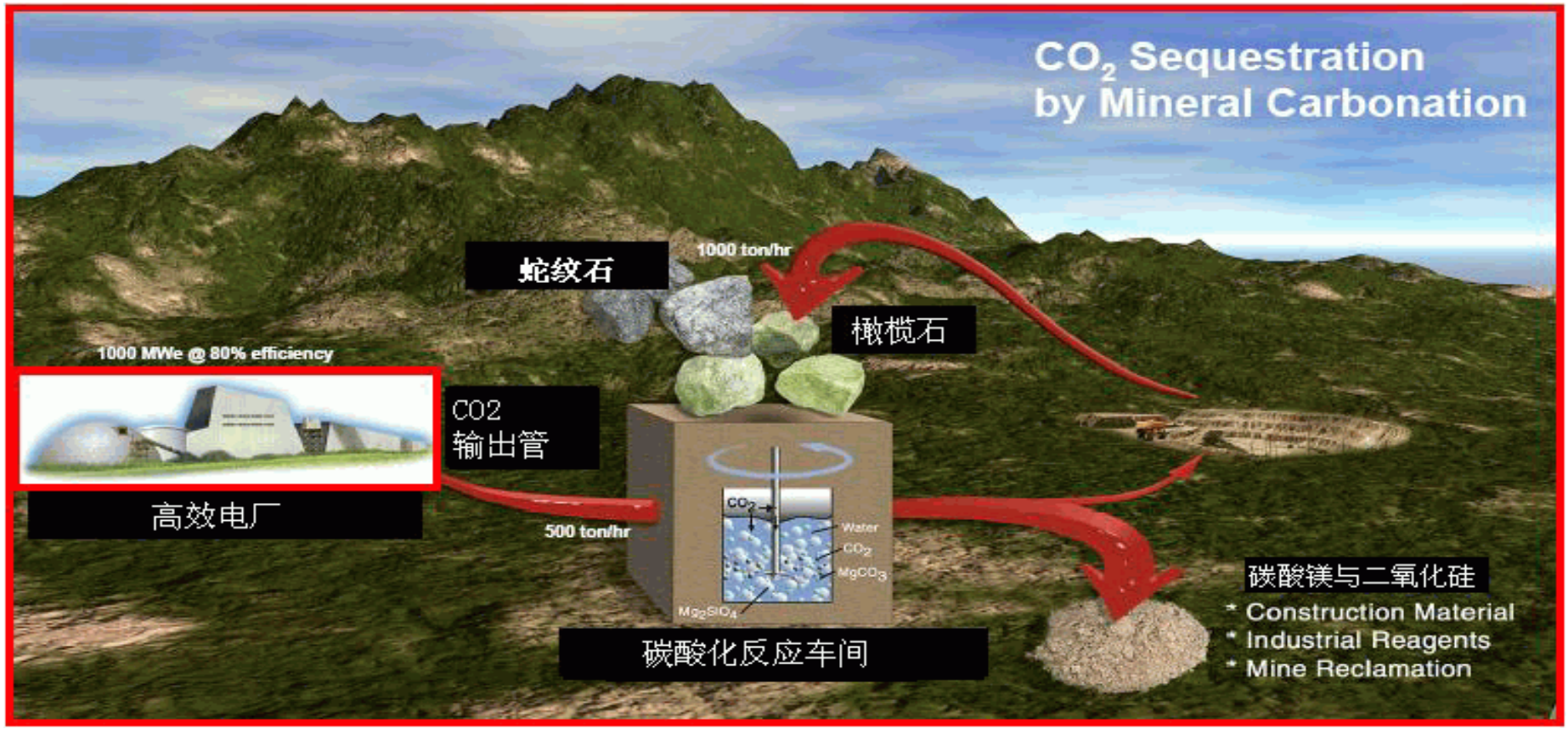
SKLCC

Current Research and Progress in SKLCC

- Oxy-fuel Combustion
- Chemical Looping Combustion
- CO_2 Capture Based on CCR
- CO_2 Sequestration by Mineral Carbonation

NSFC(1997-) (2001-)(2002-) ; 973 Program(1999-2004); 985 Program (2005-)

CO_2 Sequestration by Mineral Carbonation



该技术原理是基于CO_2与矿物在一定条件下反应生成稳定、无污染的碳酸盐，以实现二氧化碳的储存。例如CO_2与硅酸盐矿物反应生成碳酸盐，二氧化硅和水并且放出热量。

SKLCC

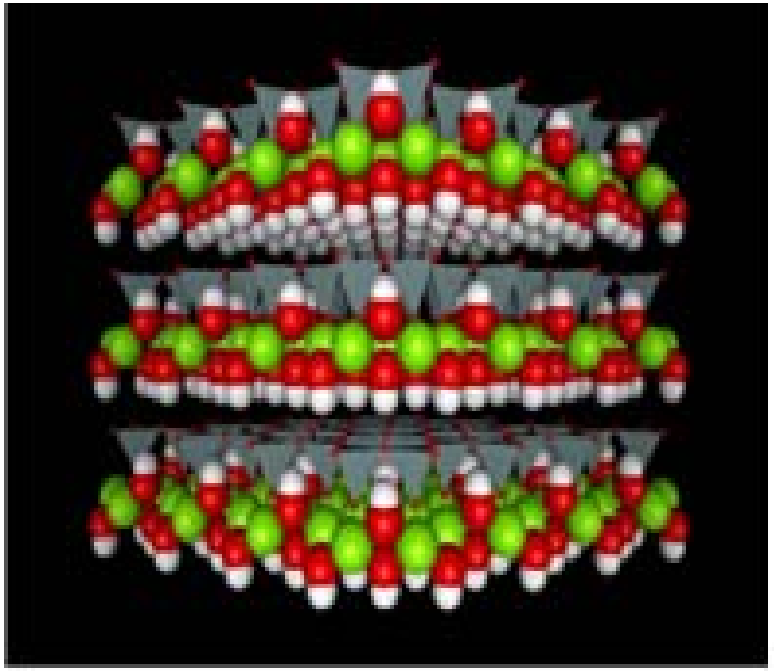
CO_2 Mineral Carbonation

The family of reactions:

$(Mg, Ca)xSiyOx + (2y+z)\,H_2 + (z+x)\,CO_2 \rightarrow x(Mg,Ca)CO_3 + ySiO_2 + zH_2O$

Serpentine:

- MgO38-45%(wt%）
- Fe_2O_{35-8} %(wt%）
- H_2O13 %(wt%）
- Reaction releases heat： + 64 kJ/mole
- One ton of serpentine can dispose of approximately one-half ton of CO_2

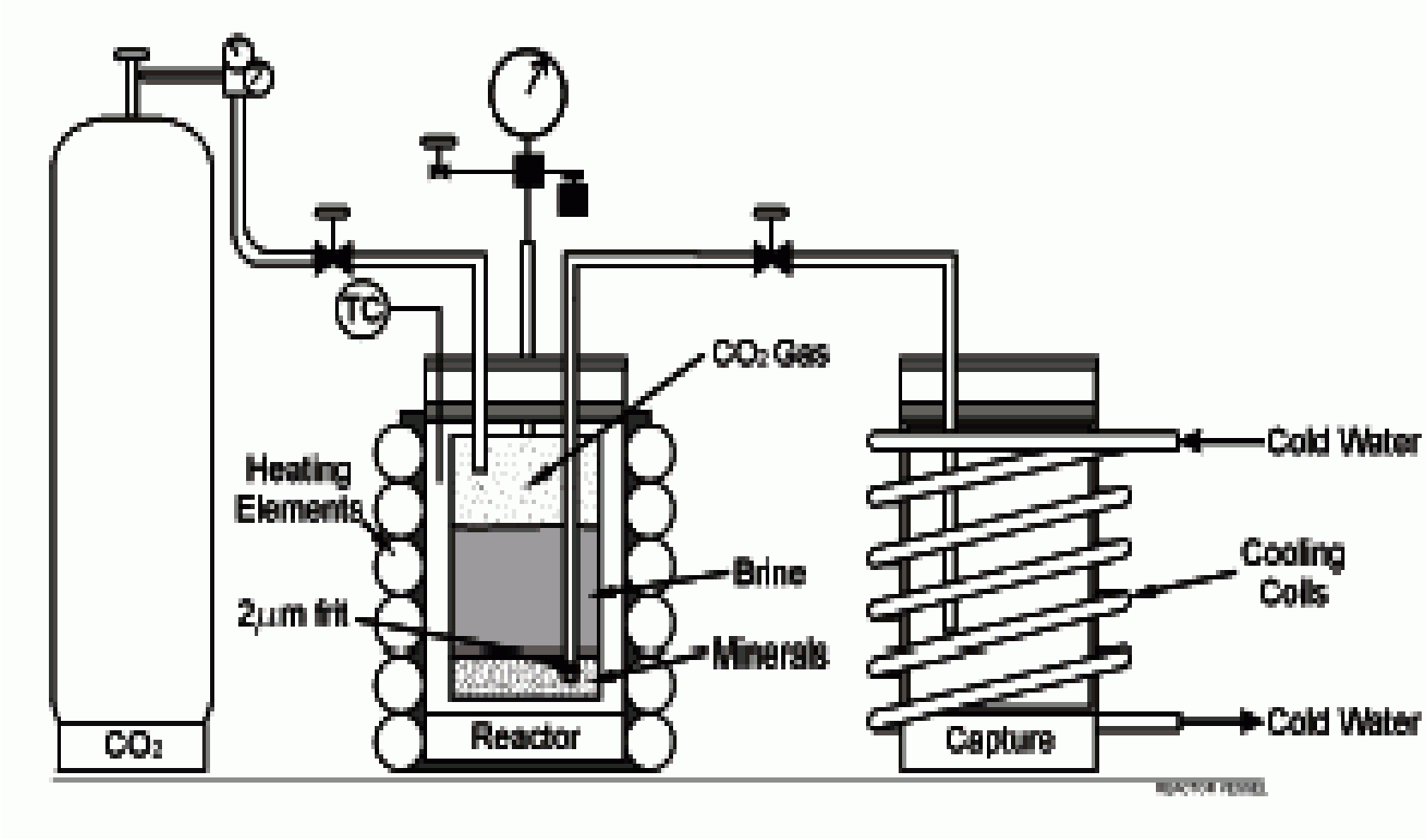


The structural model of Serpentine (antigorite)

Olivine:

- MgO45-50%(wt%）
- Fe2O3 6-10%(wt%）
- Reaction releases heat： + 95 kJ/mole
- One ton of olivine can dispose of approximately two-thirds of a ton of CO_2

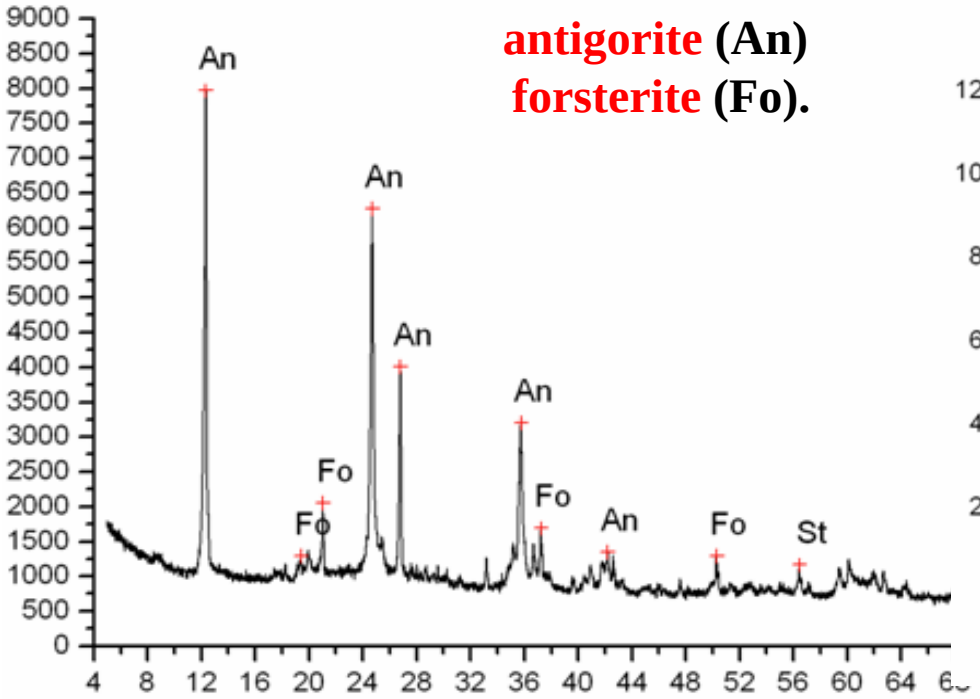
Experimental Facility



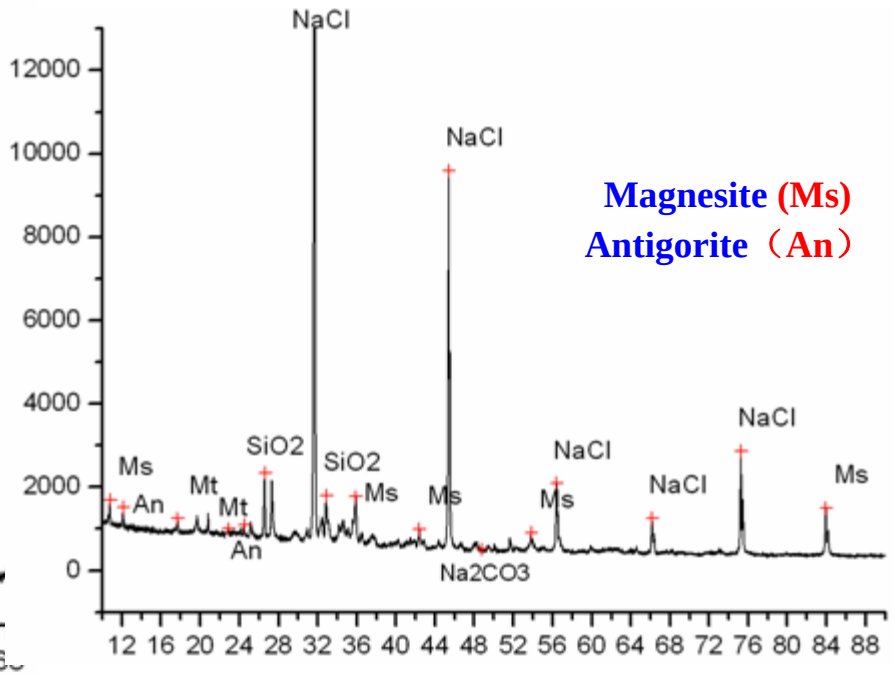
※ 问题：　1）碳酸化速率太慢；　2）能耗高，隔离成本大。

※ 解决途径：　减小颗粒粒径、添加催化溶液、表面预处理。

XRD Analysis



antigorite (An)
forsterite (Fo).



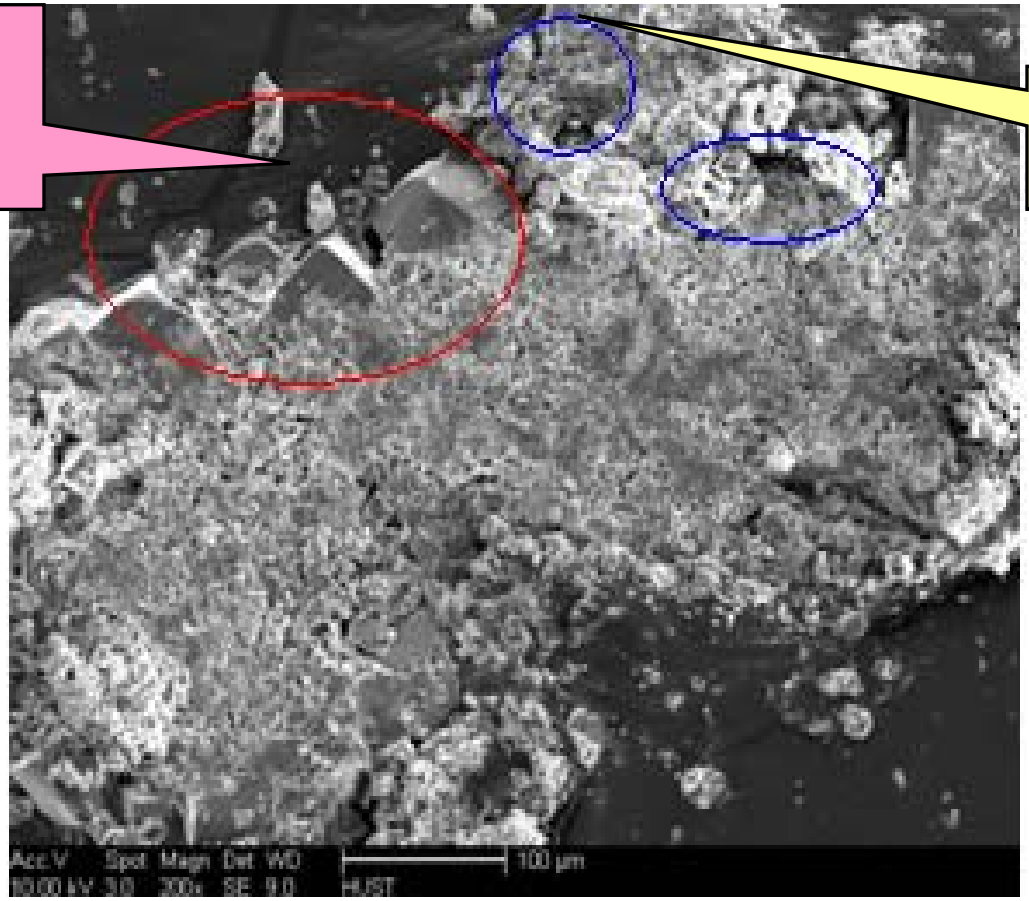
Magnesite (Ms)
Antigorite（An）

X-ray diffraction pattern for serpentine HT 650 feed ample and reaction

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O + 192kj/mole$$

Serpentine HT-650 reaction products

rhombohedral magnesite crystals（菱铁矿）



serpentine（蛇纹石）

- Sample was from an experiment in which the serpentine (heat treated at 650℃ for
- 2 hrs) was exposed in a stirred autoclave to an aqueous solution of sodium
- bicarbonate and sodium chloride for one-half hour at T=155℃ and Pco_2=100 atm.

SKLCC

Outline

- Introduction of SKLCC
- Current Research and Progress in SKLCC
- Ongoing and Future Work

SKLCC

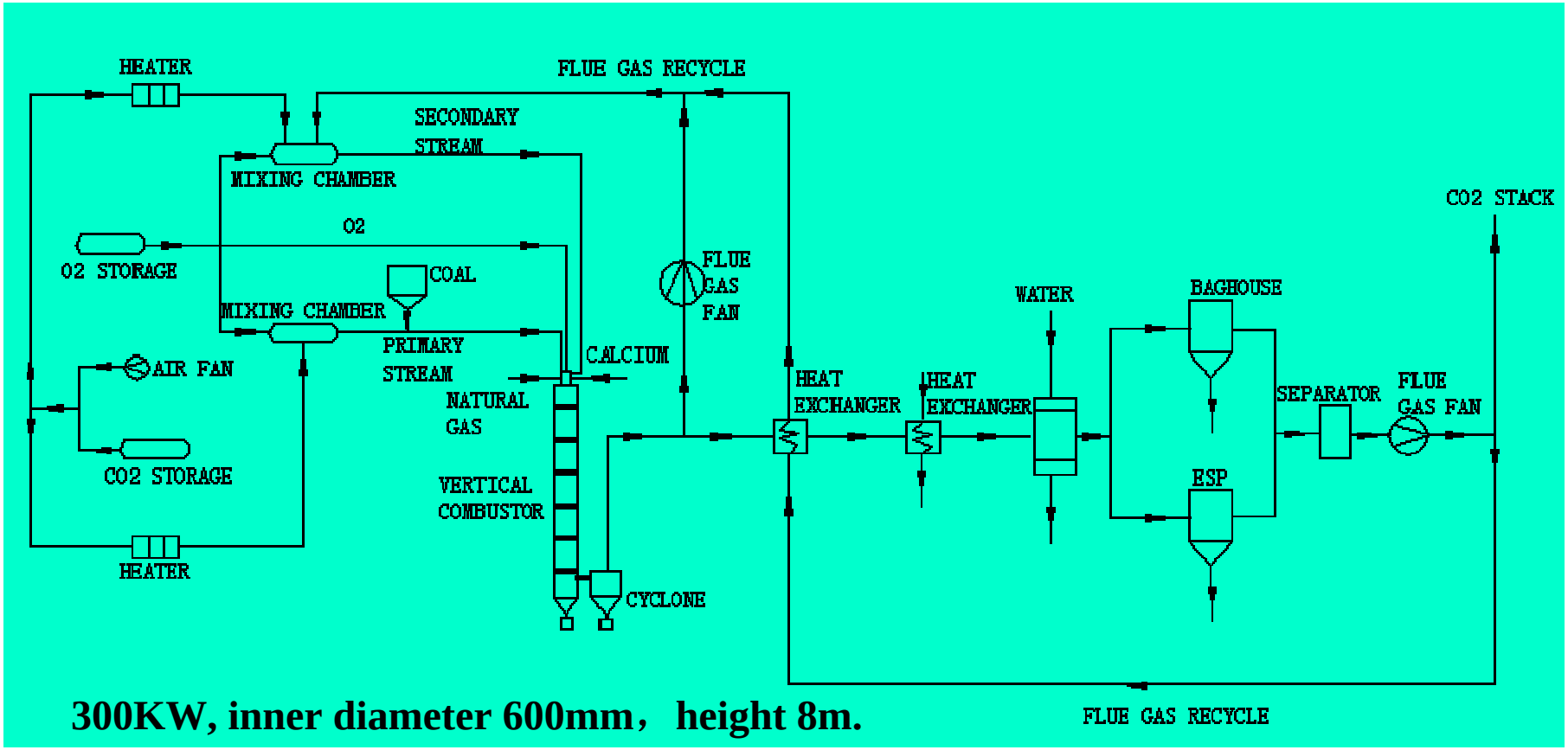
Ongoing and future works

- Oxy-fuel recycle combustion
- Chemical Looping Combustion fueled by coal
- Explore other CO_2 capture and Sequestration method

Grant: 985 Program---Clean Combustion & Thermal Energy Conversion
Funding: RMB 12 Million

Oxy-fuel recycle combustion system

- **Pilot-Scale flow chart (under construction)**



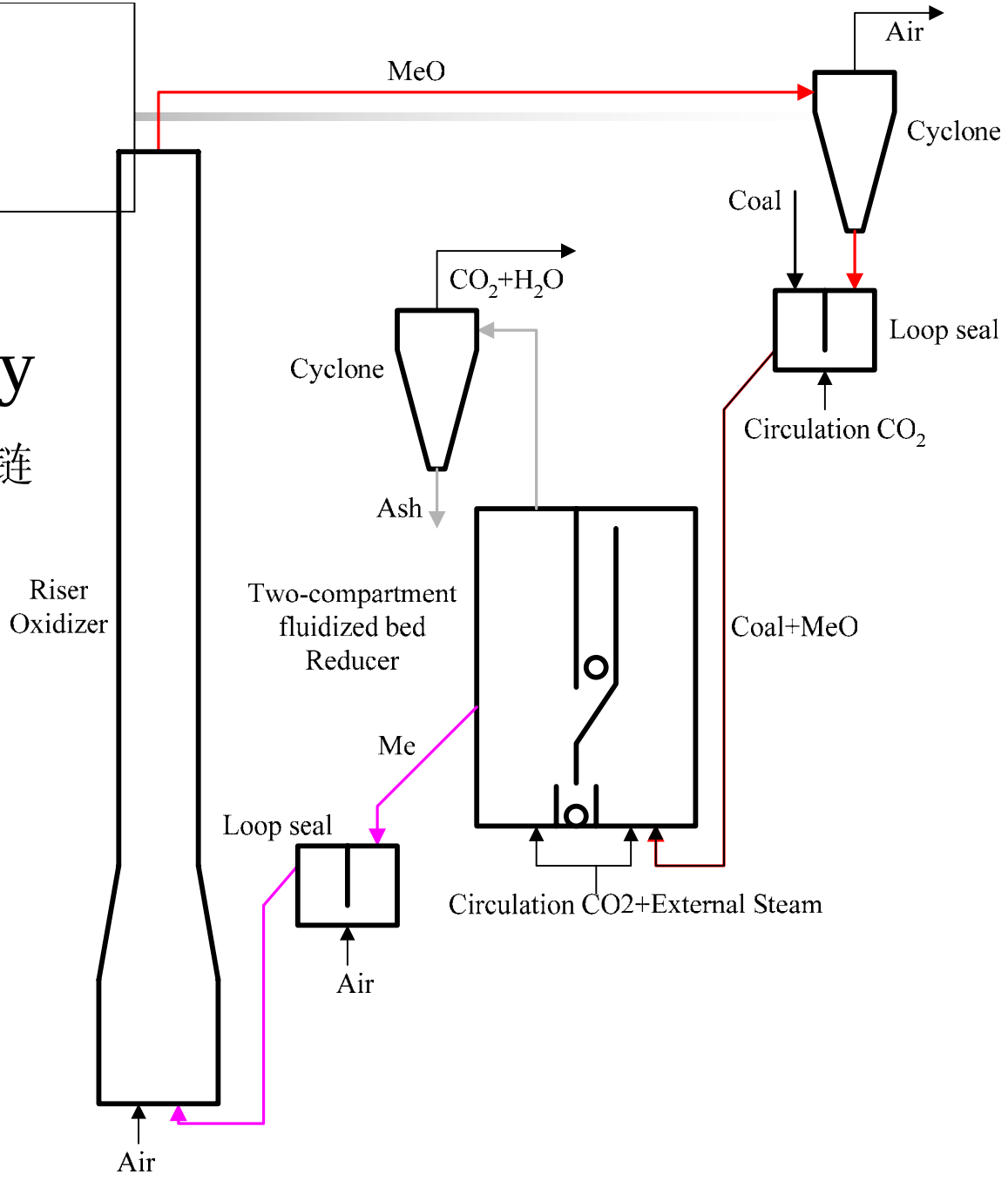
300KW, inner diameter 600mm， height 8m.

Detect CO2 concentration . (recycle ratio)
Combustion behavior for typical Chinese coals (is feasible for retrofit application?)
SO2/NOx emission and Control, ash deposition

Future work

Chemical Looping Combustion fueled by coal(以煤直接为燃料的化学链燃烧系统)

a riser type oxidizer rector, a bubbling, two-compartment, pressurized fluidized reduction reactor



Thank You!