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HUANENG CLEAN ENERGY RESEARCH INSTITUTE

CO_2 Storage by Mineral Carbonation

二氧化碳矿化封存

中国华能集团清能源技术研究院有限公司
Huaneng Clean Energy Resrach Institute (CERI)

王晓龙
Xiaolong Wang

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概述

CO_2矿化技术是一项二氧化碳捕集，**利用**与封存（CCUS）技术，有以下优点：

- 资源储量大、分布广
- 真正的永久性，环境友好型封存，无泄漏无后期监测
- 碳酸化反应为放热反应
- 对无法找到合适封存地层或者由于距离过远运输成本高的国家和地区有很好的适用性
- 产生多种具有经济价值的产品

技术发展

- CO_2矿化技术自1990年提出后已发展出近30种工艺；2000年后美国，芬兰，意大利，英国和澳大利亚政府投入大量资金推动技术研发，目前CO_2矿化技术总体上正处工程化前期阶段（TRL 3-4）。

- 大量研究集中在蛇纹石和镁橄榄石的工艺研究领域，目前矿石热处理技术，矿石粒径，化学试剂选择、酸浸反应动力学及参数影响、碳酸化温度压力影响等方面的研究已取得大量成果。

- 技术研究发展趋势：由高温高压直接碳化向中低温常压液相间接碳化转变，由高温热处理和精细研磨向高效化学预处理转变，由不可再生化学试剂向可再生试剂转变。

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Outline

- GHG reduction and CCS 温室气体减排与CCS
- CCS by mineral carboantion (CCSM) CO_2矿化封存
- Raw material and capacity 原料与储量
- CCSM Process routes 矿化工艺介绍
- CCSM Products 矿化产品介绍
- CCSM Projects 矿化项目介绍
- Summary 小结

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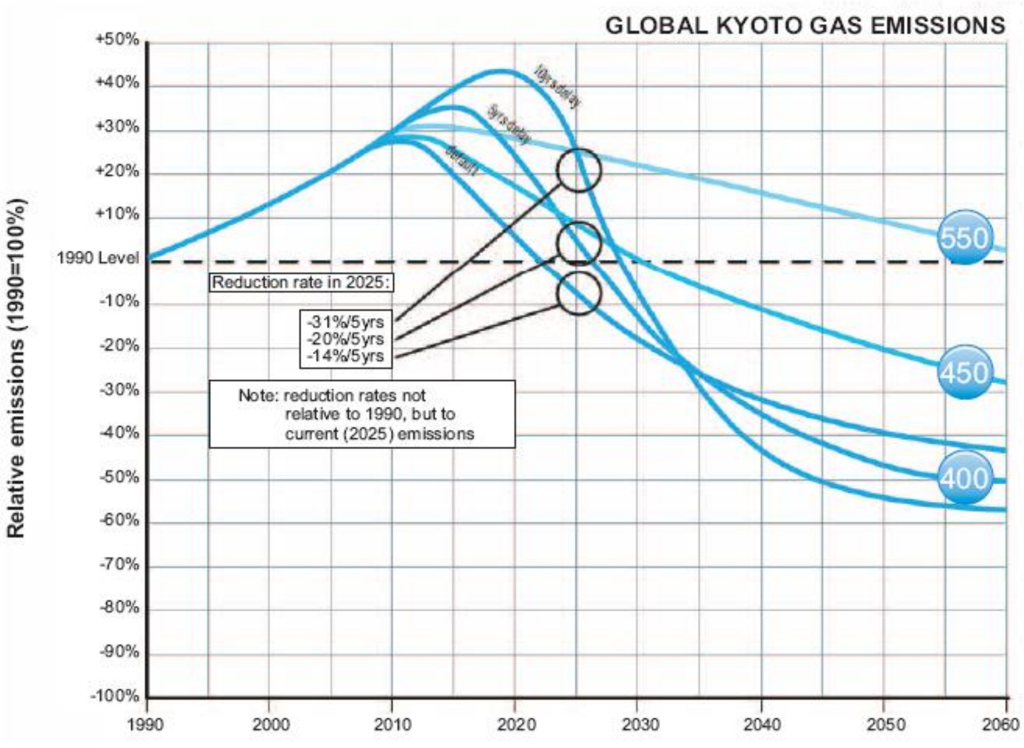
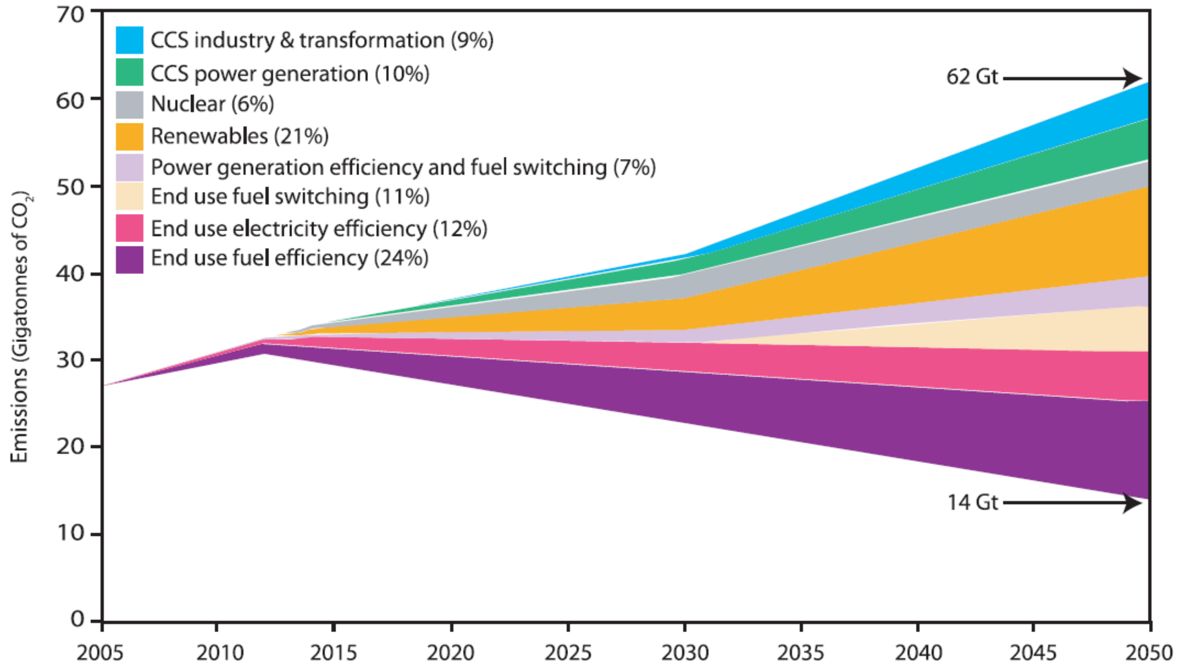
GHG reduction and CCS
Global warming and CO_2 emmision 全球变暖与CO2排放



- 2008, IPCC Fourth Assessment Report: 387ppm CO_2 concentration, global warming is caused by anthropogenic CO_2 emission with 90 % of possibilities [1].
- 2009, IEA World Energy Outlook: limit CO_2 to 450ppm, 2° C increase [2].
- 2009, Copenhagen Accord: control temperature increase to 2° C [3].

GHG reduction and CCS

CO_2 emission abatement 温室气体加派与CCS-CO2减排路径



- ❑ CCS will contribute 3%, 10 % and 19 % at 2020, 2030 and 2050 in the portfolio of mitigation solutions, respectively [3]. CCS技术在2020,2030和2050年将分别贡献3%，10%和19%的减排量在整个减排措施组合中。
- ❑ IEA report that the total cost of emission abatement by 2050 will increase 70% without implementing CCS [3]. IEA报道如不采用CCS到2050年减排的总费用将增加70%。

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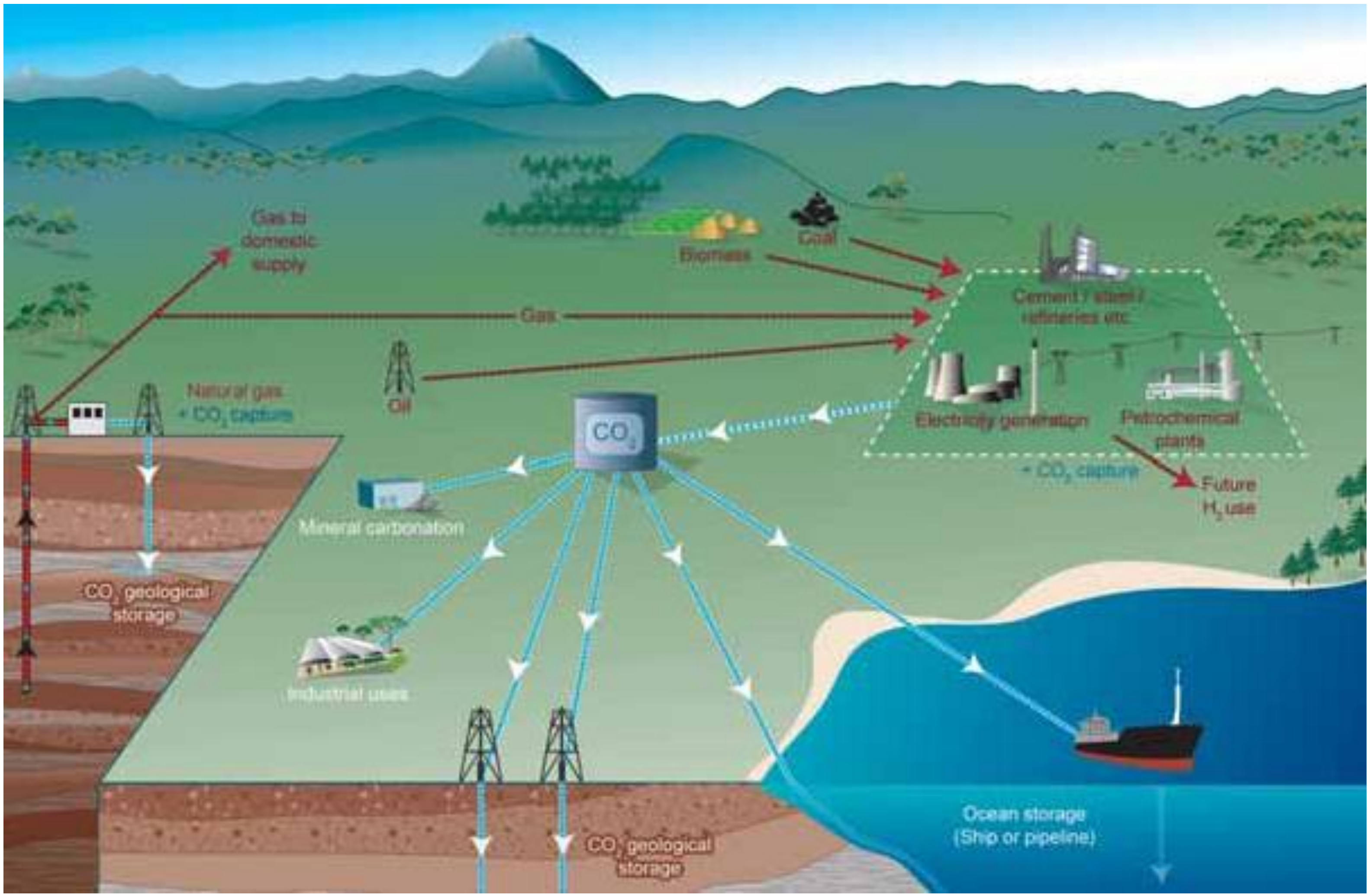
GHG reduction and CCS

Carbon Capture and Storage



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GHG reduction and CCS

Development stages of CCS technologies 不同CCS技术发展阶段

CCS component	CCS technology	Research phase [13]	Demonstration phase [7]	Economically feasible under specific conditions [5]	Mature market [6]
Capture	Post-combustion			X	
	Pre-combustion			X	
	Oxyfuel combustion		X		
	Industrial separation (natural gas processing, ammonia production)				X
Transportation	Pipeline				X
	Shipping			X	
Geological storage	Enhanced Oil Recovery (EOR)				X[a]
	Gas or oil fields			X	
	Saline formations			X	
	Enhanced Coal Bed Methane recovery (ECBM)		X		
Ocean storage	Direct injection (dissolution type)	X			
	Direct injection (lake type)	X			
Mineral carbonation	Natural silicate minerals	X			
	Waste materials		X		
Industrial uses of CO_2					X

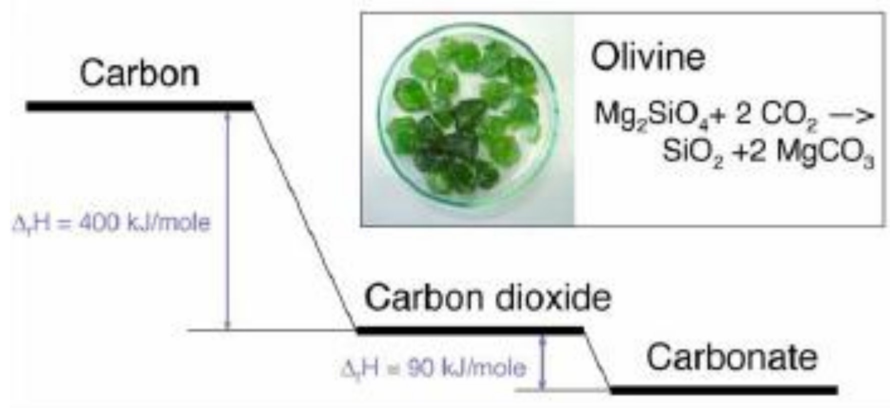
❑ CCS is the combination of technologies, individual technology develops at different stage [4]. CCS是多种技术的组合，而其中不同的技术处于不同的阶段。

CCS by mineral carboantion

Foudemtnal chemistry CO_2矿化的基本化学机理

$$MO+CO_2 \longrightarrow MCO_3 + Heat$$

M= Calcium, Magnesium, Iron

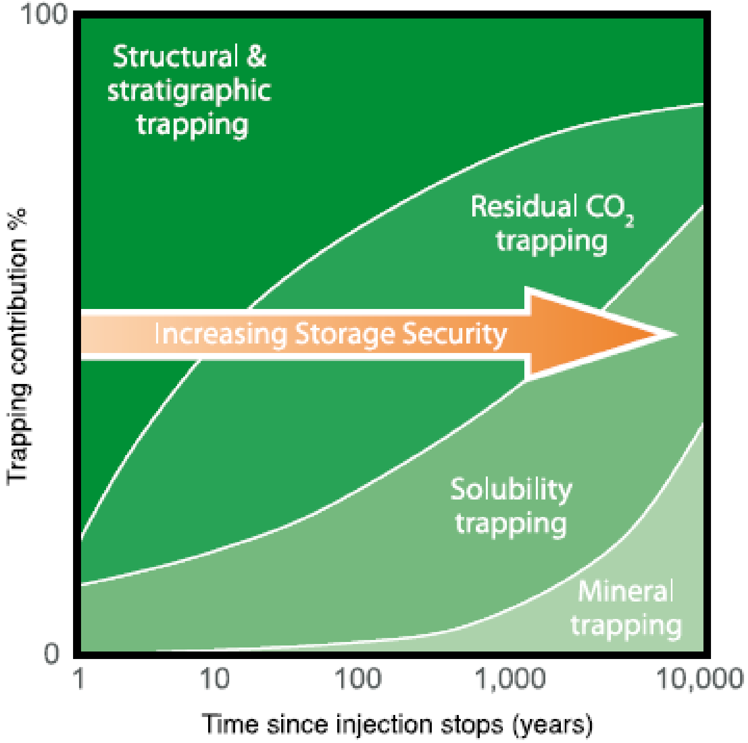


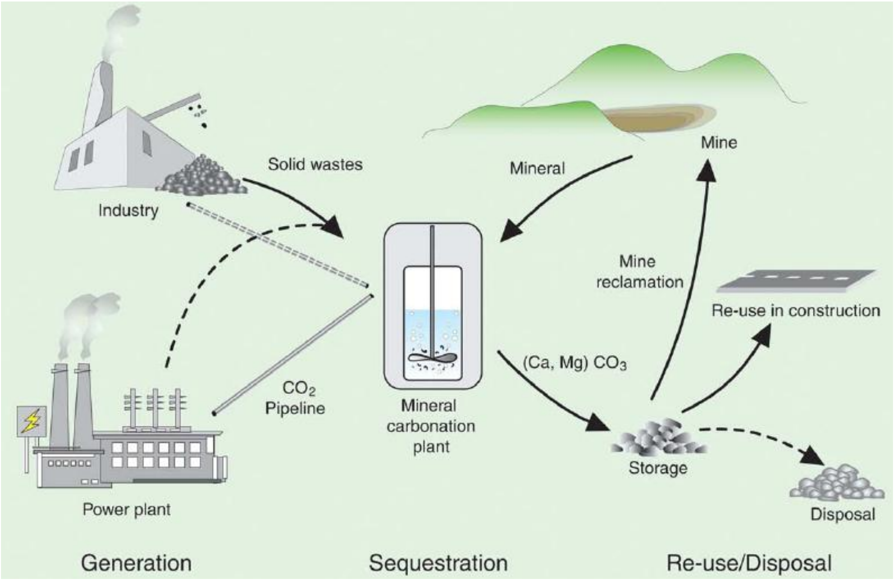
Issues:

- Stability of carbonation
- Availability of alkalinity source
- Reactivity of alkaline materials
- 碳酸盐稳定性
- 碱土矿石资源广泛性
- 碱土资源的反应活性

CCS by mineral carboantion

In-situ and ex-situ





Two types of mineral carbonation:

- In-situ mineral carbonation (Underground) 原位的矿化（地下）
- Ex-situ Mineral carbonation (Above ground) 移位的矿化（地上）

CCS by mineral carboantion

Definition

Mineral Carbonation – the chemical fixation of CO_2 in minerals to form geologically stable mineral carbonates 通过化学反应将CO_2同矿石反应生成稳定碳酸盐的过程。

Olivine橄榄石

Serpentine蛇纹石

+ CO_2 →

Mineral carbonates

- ❑ Construction products
- ❑ Aggregates
- ❑ Mine void filler

碳酸盐产品

- ❑建筑材料
- ❑混凝土
- ❑填料

Waste concrete

废旧水泥

Slag 钢渣

Industrial by-products may make process more sustainable

CCS by mineral carboantion

Advantages 优 势

- Carbon Capture, Storage and Utilization (CCSU) is more economical and acceptable than CCS; 更经济且易于接受
- The leakage risk of geological storage (Recent news about CO_2 leakage from Weyburn project, unproven [5]) and envrironmental impacts;没有泄露危险，环境影响小
- The technology selection in some countries due to lack of storage formation, such as Finland, Oman and Singapore; 适于一些没有合适地质封存场所的国家和地区，芬兰，也门，新加坡
- For small point emission sources; 适合于小规模的点源
- Potencial profits from by-product, abstract investment from private shakeholders. 生产多种副产品，吸引私人投资

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Raw material and capacity 原料与储量

Mg/Ca silicates are abundant and worldwidely available.

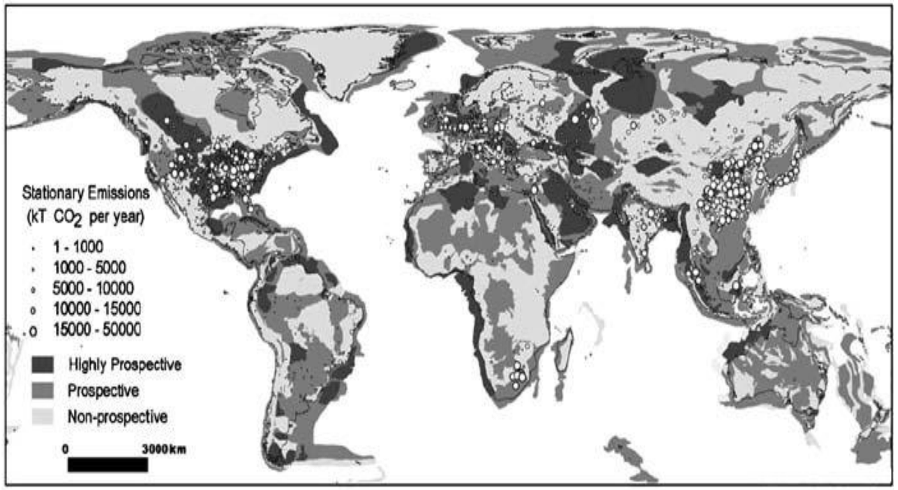
- Olivine: $Mg_2SiO_4 + CO_2 — 2MgCO_3 + SiO_2$
- Serpentine: $Mg_3Si_2O_5(OH)_4 + 3CO_2 — 3MgCO_3 + 2SiO_2 + 2H_2O$
- Wollastonite: $CaSiO_3 + CO_2 — CaCO_3 + SiO_2$

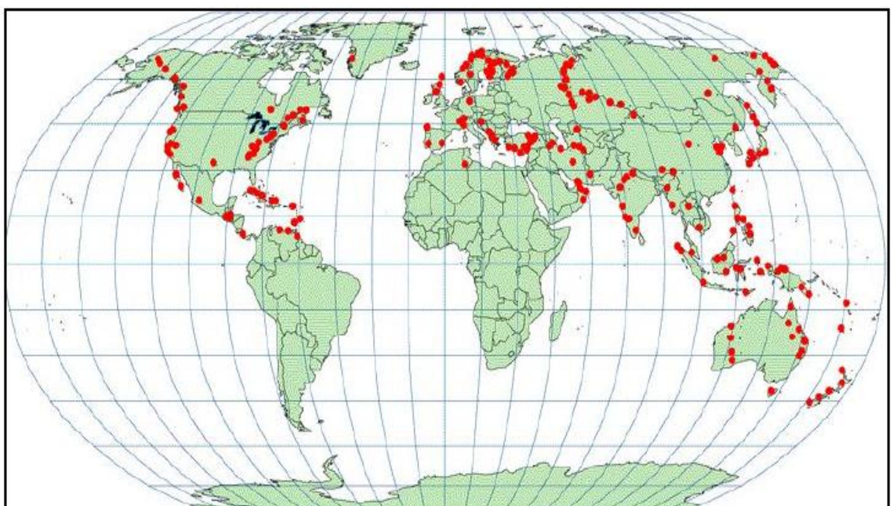
Olivine

Sepentine

Raw material

Minerals 天然矿石





Material	MgO [wt%]	CaO [wt%]	FeO [wt%]	R_{CO2} [kg/kg]	Capacity
Olivine	45-50	0.1-0.5	6-10	1.8	10000 Gt
Serpentine	38-45	0	5-8	2.3	10000 Gt
wollastonite	-	35-48	-	3.6	Small

Raw material

Waste materials 大宗废弃物

- Steel industry (60-80Mt CO_2/y)
  - •Steel slag
  - •AOD process slag
  - •Steel converter slag
- Energy Sector
  - •Lignite fly ash
  - •APC fly ash
  - •MSWI ash
  - •PF ash
- Cement industry
  - •Waste cement
  - •Cement dust

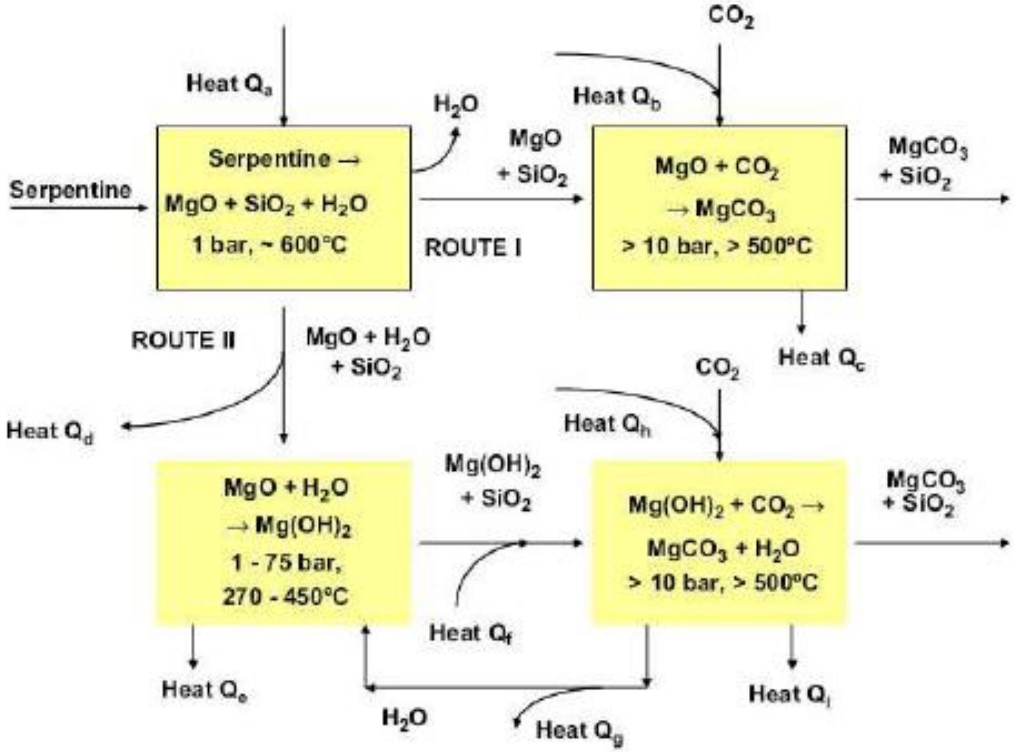
100 Mt CO_2/y

Process routes 工艺路线

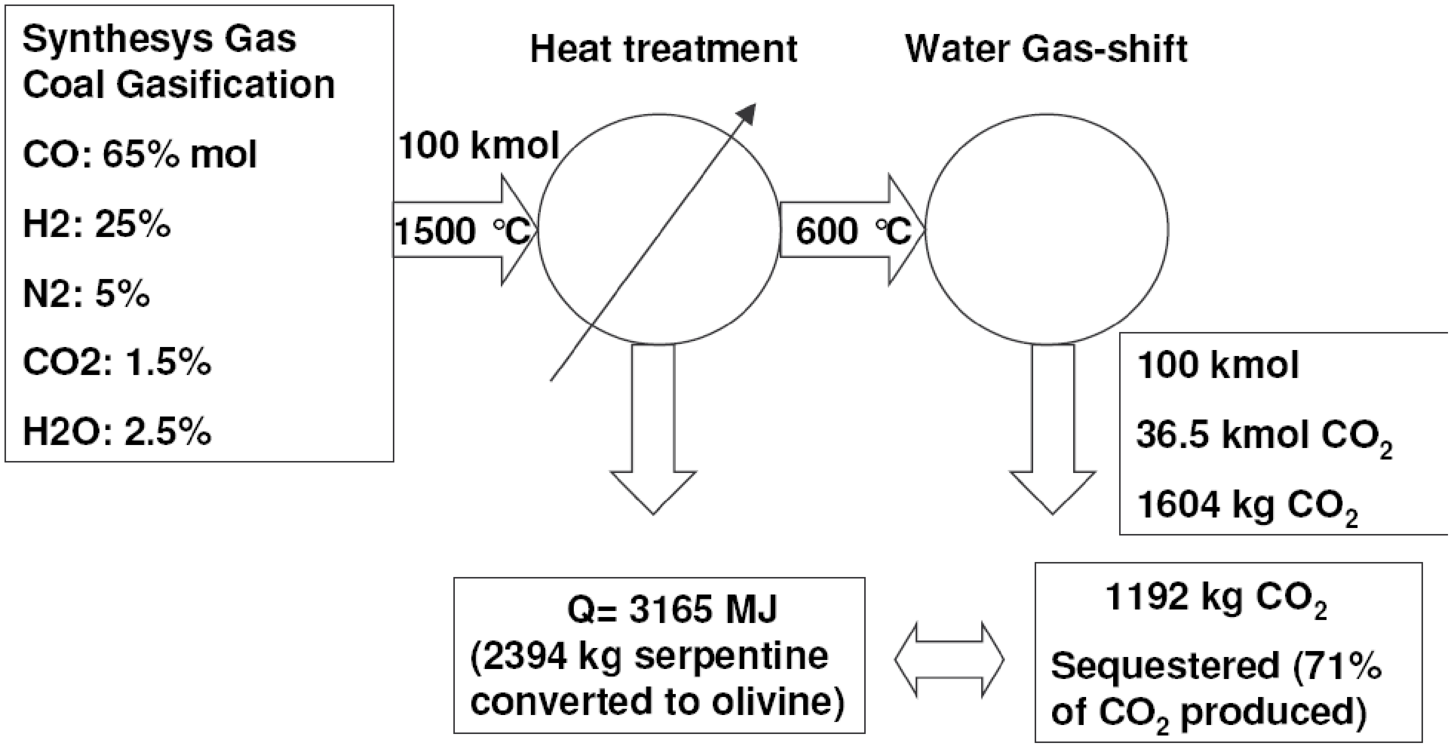
- Gas-solid
  - Single-step
  - Multi-step
- Aqueous
  - Single-step
    - Without chemicals
    - With chemicals
      - Salts
      - Bicarbonate
  - Multi-step (pH-swing)
    - Acid/base swing
    - P/T swing
    - Chelant

Multi-step Gas-solid 分步气固法

- Zevenhoven et al., 2008
  - Step 1: Production of free $MgO/Mg(OH)_2$
  - Step 2: Carbonation of $MgO/Mg(OH)_2$ to $MgCO_3$



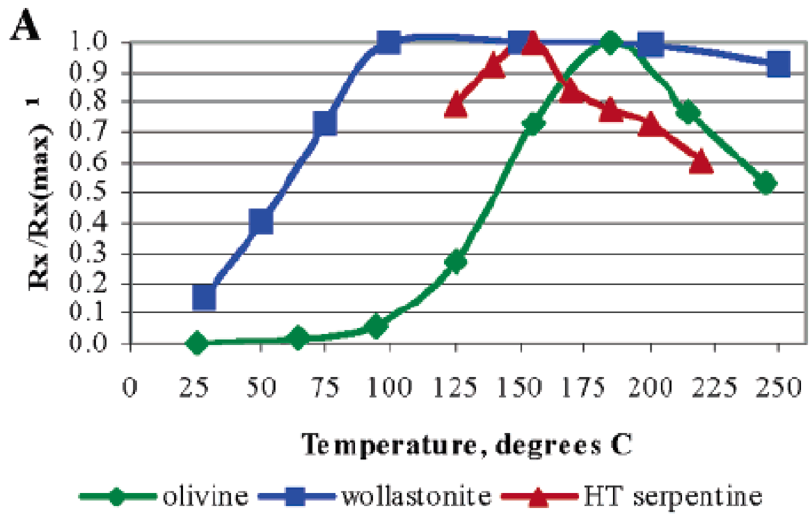
Aqueous route Single-step 一步液相法



Geerling et al., 2007

- Materials: olivine, forsterite, wollastonite, serpentine
- Particle size: 200 μm Reactor: slurry bubble column
- CO2 pressure: 1-50bar; total pressure: 1-150 bar

Aqueous route Single-step一步液相法



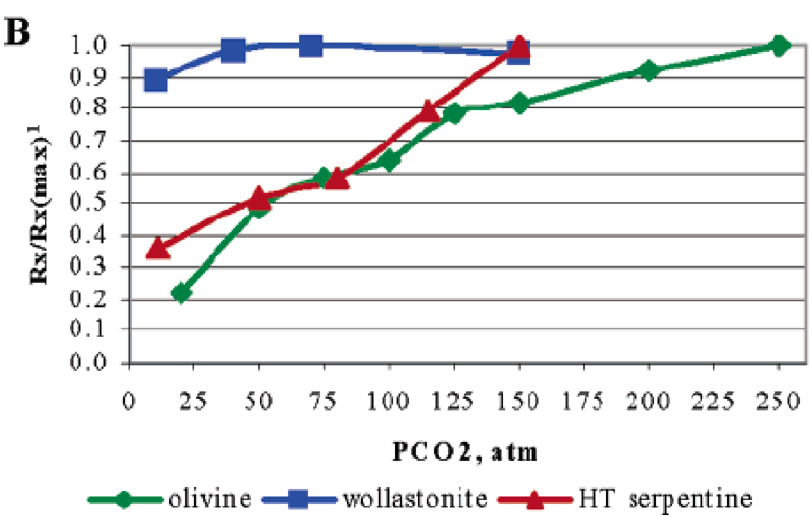


TABLE 1. Optimum Carbonation Conditions, by Mineral

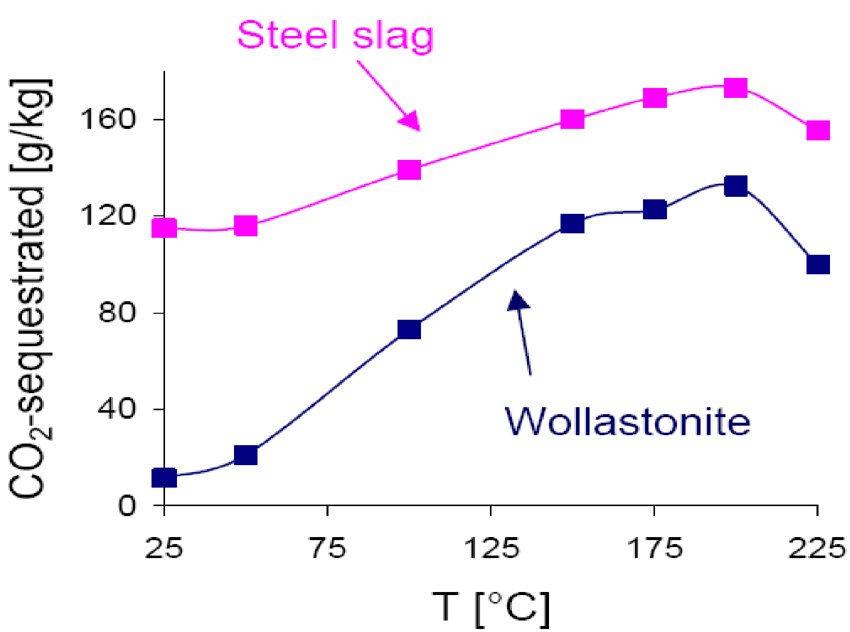
	carbonation conditions		
mineral	*T*, °C	P_{CO_2}, atm	carrier solution
olivine	185	150	0.64 M $NaHCO_3$, 1 M NaCl
wollastonite	100	40	distilled water
HT serpentine	155	115	0.64 M $NaHCO_3$, 1 M NaCl

Gerdemann et al. and O'Conor 2007

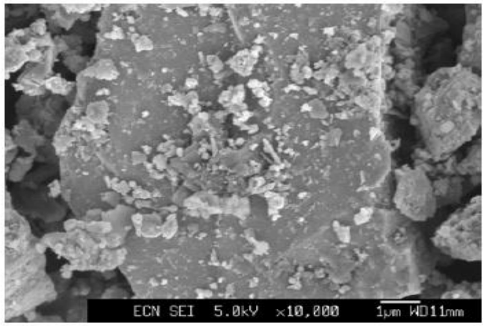
- Grinding to < 75 μm
- Rx= extent of reaction in 1 h, Rx(max)= maximum extent of reaction in 1 h
- Olivine: 49.5%
- Wollastonite: 81.8%
- HT serpentine: 73.5%

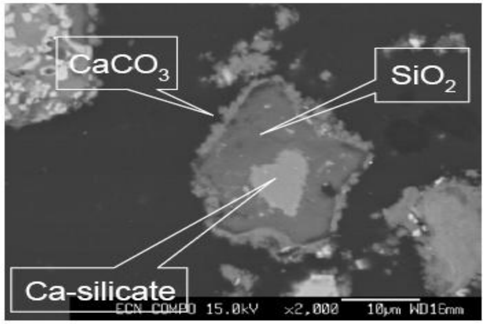
Aqueous route Single-step一步液相法

1) $CO_2\ (g) + H_2O\ (l) \rightarrow HCO_3^-\ (aq) + H^+\ (aq)$
2) $CaSiO_3\ (s) + 2\ H^+\ (aq) \rightarrow Ca^{2+}\ (aq) + SiO_2\ (s) + H_2O\ (l)$
3) $Ca^{2+}\ (aq) + HCO_3^-\ (aq) \rightarrow CaCO_3\ (s) + H^+\ (aq)$



$d < 106\ \mu m,\ p_{CO2} = 20$ bar

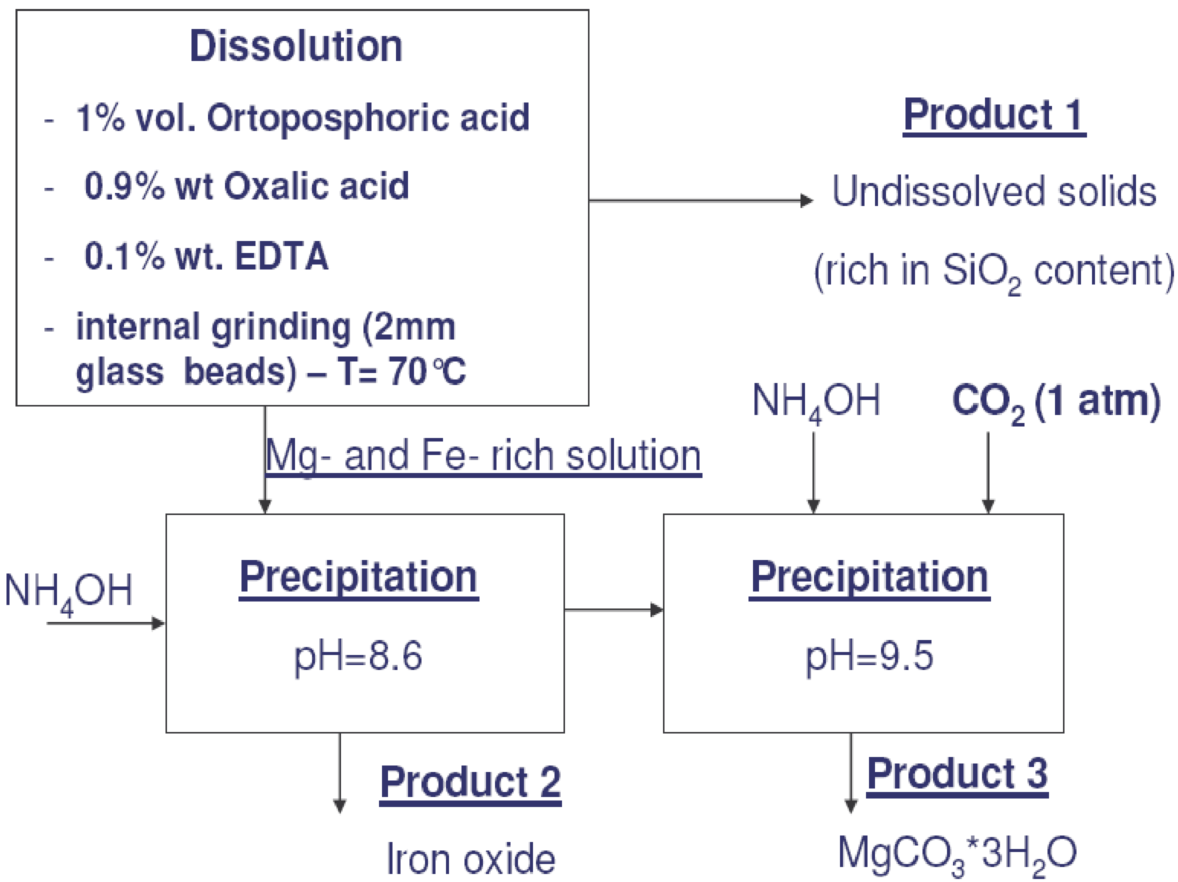




Huijgen et al., 2005

- Materials: steel slag and wollastonite
- Particle size: <38 μm; <106 μm; <500 μm

Aqueous route Multi-step 多步液相法



Park and Fan, 2005

- pH swing
- Material: serpentine
- Slurry fluidized bed reactor
- Particle size: 100-500 μm
- Step 1: dissolution with weak acid
- Step 2; precipitation of iron oxide
- Step 3: precipitation of $MgCO_3$

Aqueous route Multi-step多步液相法

Maroto-Valer et al., 2004;2005

- Materials: olivine, serpentine; 70-150 μm
- Step 1: chemical activation with an acid: T=15-75 ° C; 3-12 h

$Mg_3Si_2O_5(OH)_4 + 3H_2SO_4$ — $3MgSO_4 + 5H_2O + 2SiO_2$

- Step 2a: use of base (KOH, NaOH, NaHCO3, Acetates, pH=7-14)

$MgSO_4 + 2NaOH$ — $Mg(OH)_2 + Na_2SO_4$

- Step 2b: addition of $Ca(NO_3)_2$

$MgSO_4 + Ca(NO_3)_2 + 2H_2O$ — $CaSO_4{\cdot}2H_2O + Mg(NO_3)_2$

$Mg(NO_3)_2 + Ca(OH)_2$ — $Mg(OH)_2 + Ca(NO_3)_2$

- Step 3: Mg carbonate precipitation

$Mg(OH)_2 + CO_2$ — $MgCO_3 + H_2O$

Aqueous route Multi-step多步液相法

Blencoe et al., 2004

- Step 1: $Mg_2SiO_4 + 2NaOH + H_2O — 2Mg(OH)_2\downarrow + Na_2SiO_3$
- Step 2: $Na_2SiO_3 + 2\ CO_2 + H_2O — 2NaHCO_3 + SiO_2\downarrow$
- Step 3: $2Mg(OH)_2 + 2NaHCO_3 — 2MgCO_3\downarrow + 2NaOH + 2\ H_2O$

- Particle size: 100 µm
- Pressure: slightly below vapor pressure of water (Step 1)

  10-30 bar above vapor pressure of water at the operating T (Step 2/3)

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Aqueous route Multi-step多步液相法

Gorset et al., 2007

- Material: olivine
- Pressure /Temperature swing
- No chemicals addition
- R1: dissolution

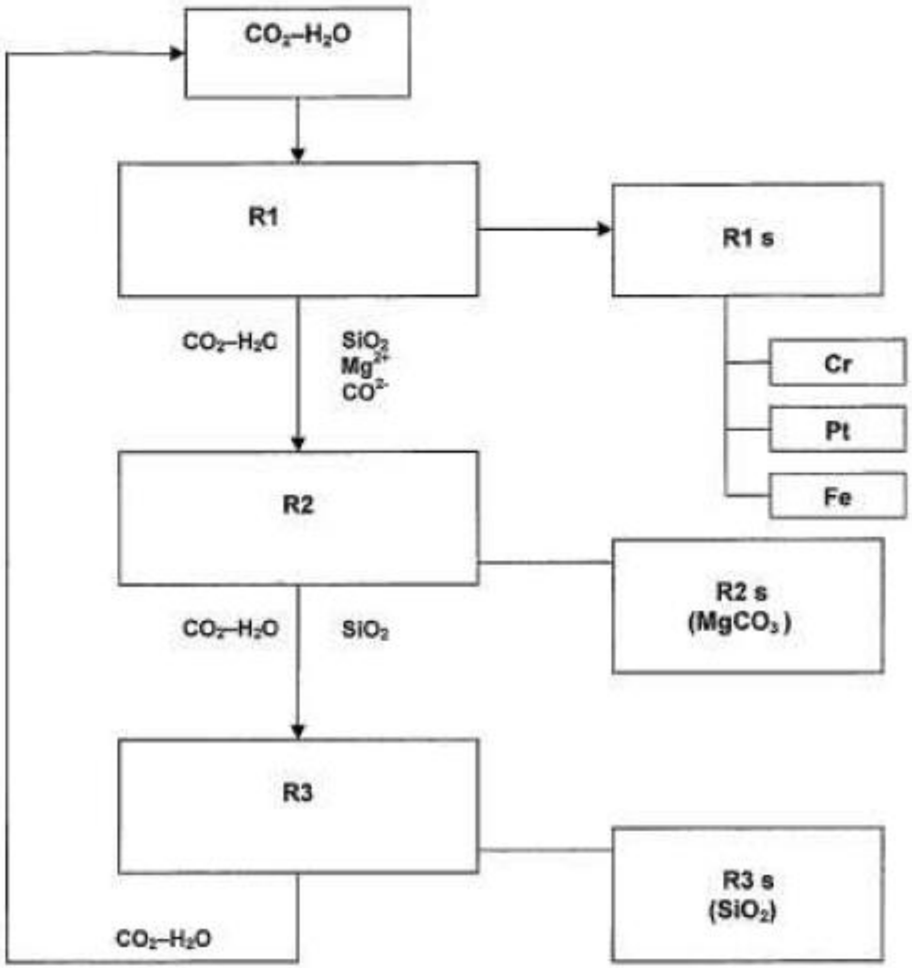
pH=3-5 P=50-150 bar / T=100-170 ° C

- R2: MgCO3 precipitation

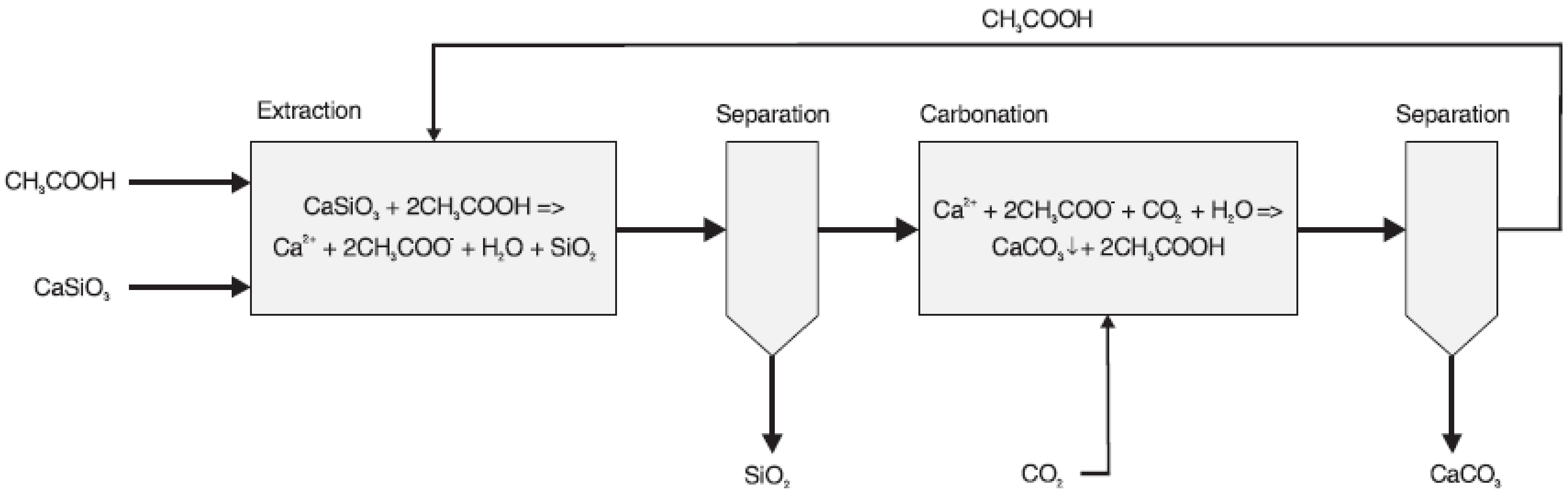
pH>> P=50-80 bar / T =140-250 ° C

- R3: SiO2 precipitation

T lower than in R2

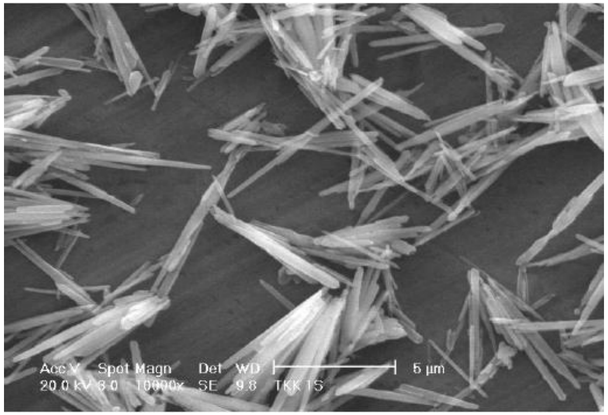


Aqueous route Multi-step



Teir et al., 2007

- Material: wollastonite and steel slag
- Temperature: 70 ° C (dissolution); 30 ° C (Carbonation)



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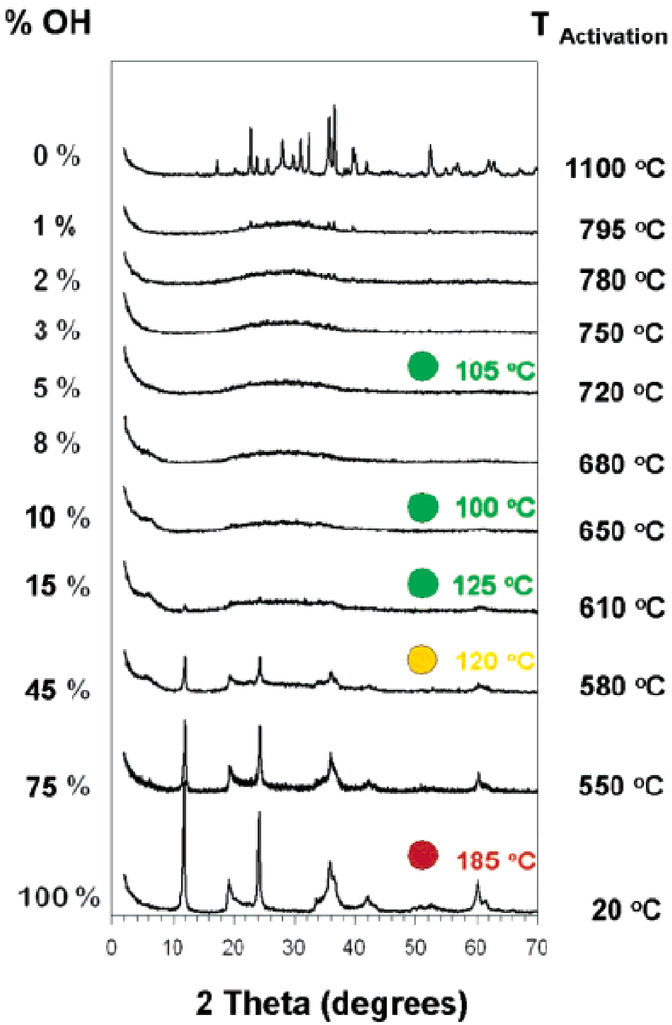
Aqueous route – Heat activation 热处理



McKelvy et al., 2004

- Thermal treatment of serpentine
- Amorphous meta-serpentine is formed
- Serpentine shows no reaction up to 185 ° C
- 650 ° C 10% Hydroxide residual
- 1100 ° C serpentine change to olivine totally

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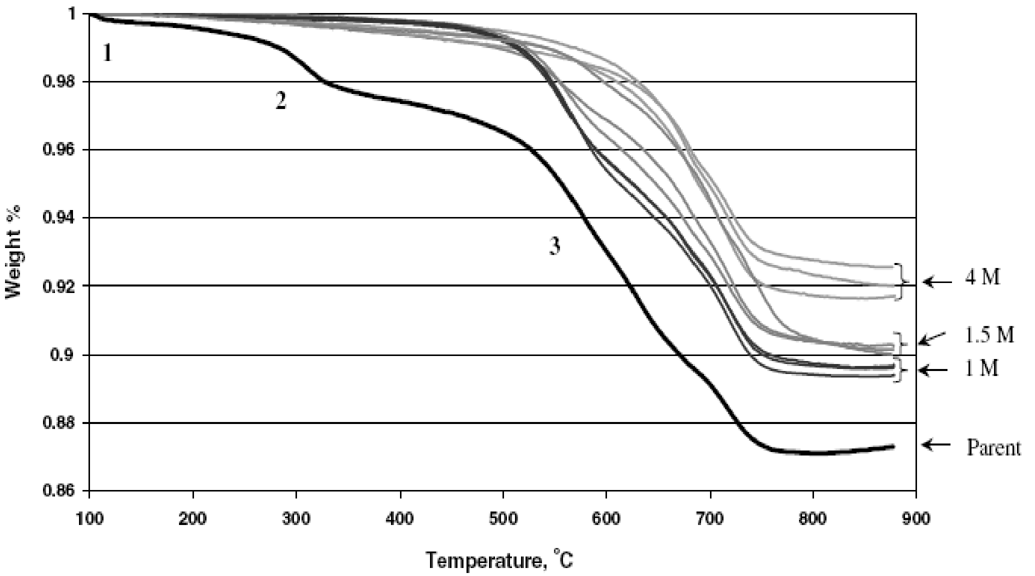
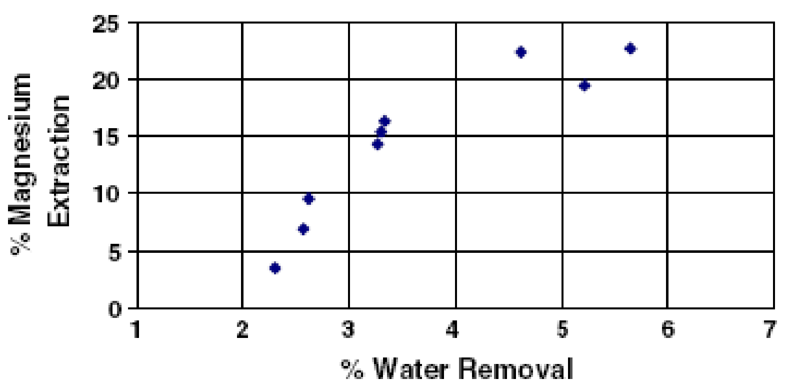
Aqueous route – Chemical activation 化学激活





Alexander et al., 2007

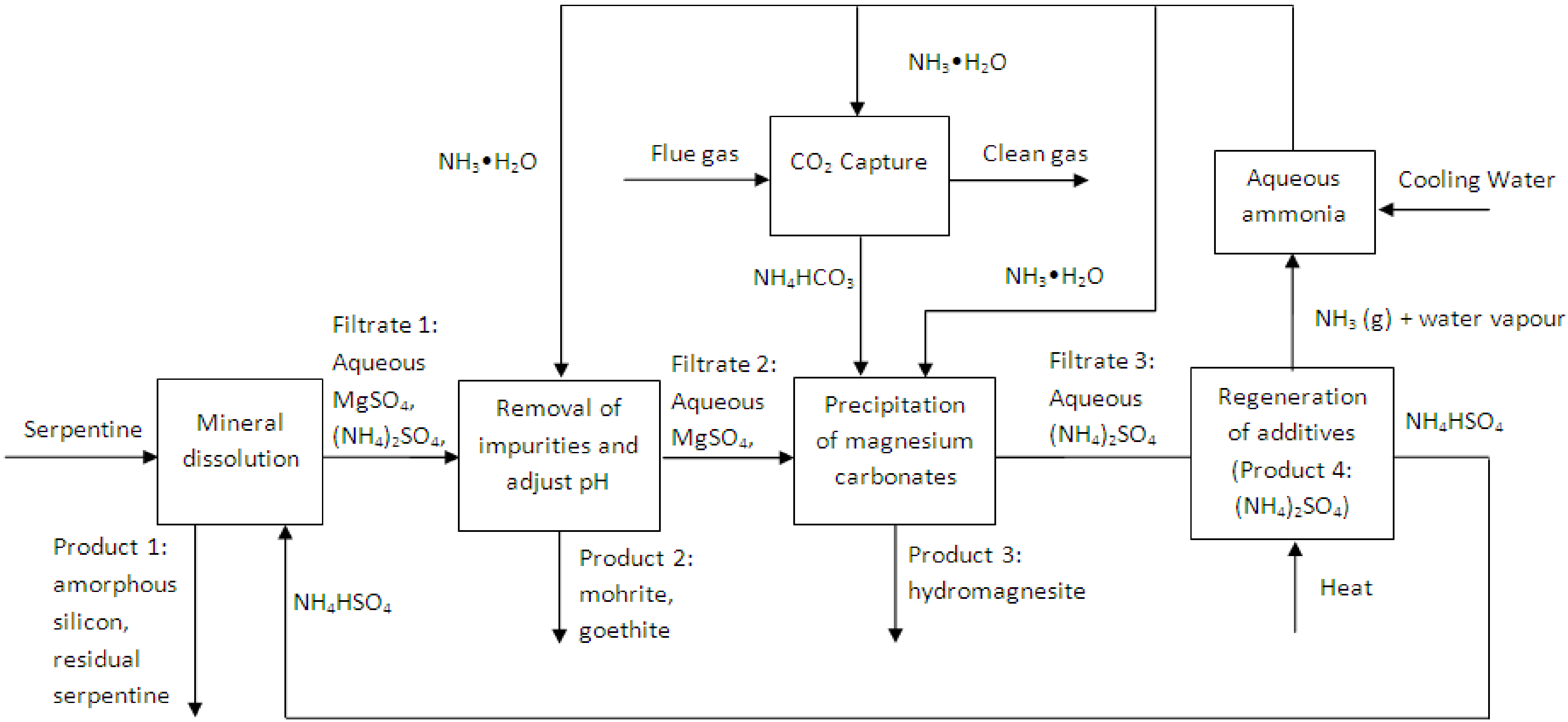
Serpentien from Cedar Hills quarry

- Activation with sulfuric acid

1. loss of adcorbed water
2. losss of crystallized water
3. loss of OH groups

- Reduction of water content is correlated with Mg extraction

CCSM research in CERI 清能院开发的工艺



CCSM process with recyclable ammonium salts

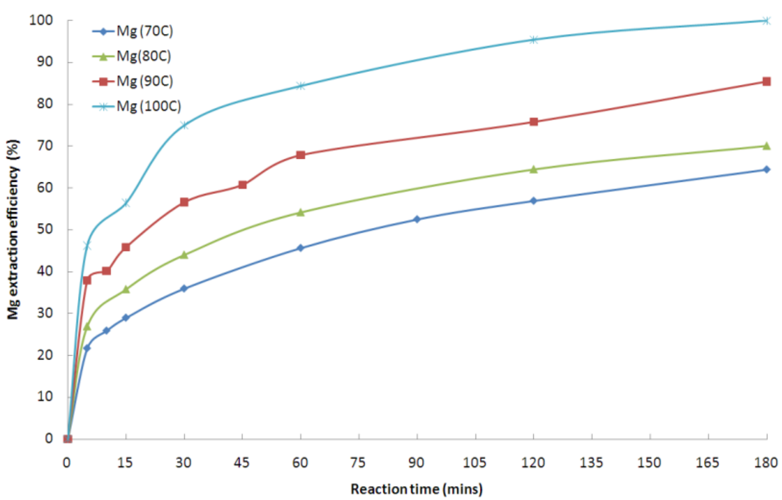
CCSM research in CERI清能院开发的工艺

Dissolution

• High dissolution efficiency using ammonium bisulfate;

• Effect of T, t, p, con. and S/L;

• Rate limiting mechanism: Chemical reaction control and product layer diffusion control.



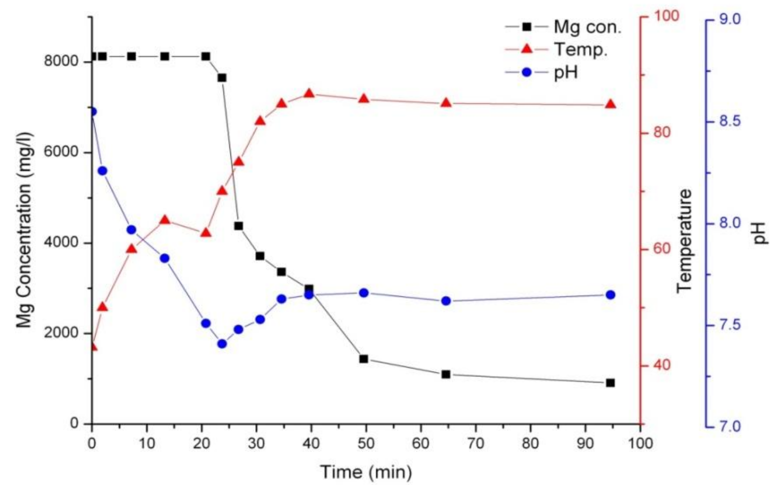
Carbonation

• High conversion and fast rate;

• The effect of Mg:NH_4HCO_3:NH_3 ratio;

•Improve carbonation by adding of NH_3;

• Multi-products: Si rich residue, Fe rich residue and hydromagnesite.



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CCSM products 矿化产品

Products	Purity	Market size	Applications	Value
PCC	>97% ($CaCO_3$ %)	13 Mt	Filler and coating pigment in plastics, rubbers , paints and papers	145-402 US$/t (fine grade)
Magnesite or hydromagnesite	>90% ($MgCO_3$ %)	18.3 Mt	paper industry, cement industry, civil engineering and production of fire retardant, a reinforcing agent in rubber, a drying agent, a laxative, supplement in food	200-1200 US$/t (technical grade-pharma grade)
Silica	82-88% (SiO_2)	112 Mt	electronic, automotive, chemical, and ceramic industries	10-134 £/t (grain-fine ground grade)
Iron oxide	24-36% (FeO)	1.4 Mt (pigment) 1414 Mt (crude steel production)	iron industry and the manufacture of pigments	219-235 US$/t (pigment) 2.12 US$/t (iron ore)

CCSM projects 矿化封存项目

Projects:

- Skymine project, funded by DOE, 2.5 M$ in July2010
- Calera project, funded by DOE, 1.9 M$ in July 2010
- Alcoa project, funded by DOE, 1.1 M$ in July 2010
- ETI project (Caterpillar, Shell and Forster Wheeler)

Funded research project:

- Newcastle University, AU, 9 M $, 2011-2015
- Abo University, Finland, 2 M Euro, 2010-2013
- Huanneg Clean Energy Research Insitute, 2.5 M RMB, 2013-2014

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Summary 小结

Pro:

- CO_2 stored in a safe manner 安全
- CO_2 storage potential basically unlimited 储量大
- Ca-silicates/residues carbonation at relatively mild conditions 温和条件

Cons:

-Energy penalty and associated cost still too high 耗能，成本高

-Mg-silicate carbonation needs energy intensive pre-treatment

需前处理

-Lack of demonstration units 缺乏示范

Future development

a)Dissolution and precipitation steps handling and coupling协调溶解沉淀

b) single-step: methods to match proper dissolution and precipitation

-More fundamental study on dissolution and precipitation 更多基础研究

c) Two-steps: methods for switching conditions and the issue of chemicals recycle pH值转换以及化学试剂循环利用

- Investigation on new routes with new catalyst 使用新催化剂工艺路线

References 文献

[1] IPCC fourth assessment report, 2007

[2] Copenhagen Accord, 19 December 2009, viewed on 25 December 2010, <http://unfccc.int/files/meetings/cop_15/application/pdf/cop15_cph_auv.pdf>.

[3] IEA, World Energy Outlook 2009, Paris: France, 2009.

[4] IPCC special report on carbon capture and storage, 2005

[5] Experts Criticize Evidence Used to Diagnose a Suspected Leak at One of the World's Largest CO2 Storage Sites, viewed on 19 January 2011, http://www.scientificamerican.com/article.cfm?id=weyburn-carbon-storage-alleged-leak

[6] Secretary Chu Announces Six Projects to Convert Captured CO_2 Emissions from Industrial Sources into Useful Products, viewed on 10 September 2010, http://www.energy.gov/9247.htm