NATIONAL ENERGY TECHNOLOGY LABORATORY

NETL

Theoretical Screening of Solid Sorbents for CO_2 Capture Applications

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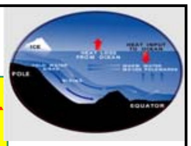
12th Int. Conf. on CO_2 Utilization

(June 24, 2013, Alexandria, VA)

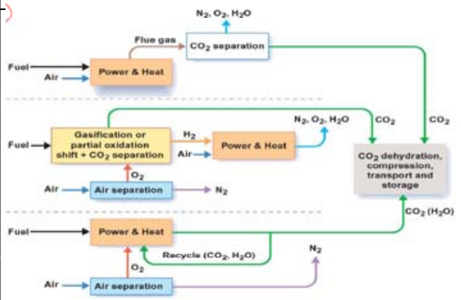
Motivation

- CO_2 emission causes Global Warming.

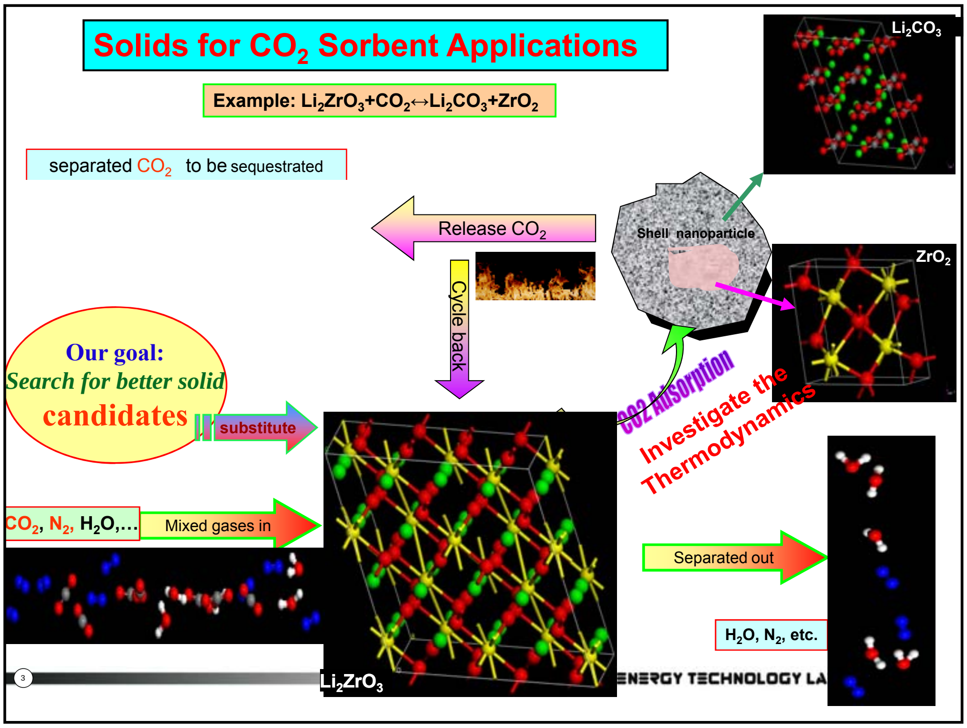
stop



CO_2 Capture Technology for Power Plants

Process	Schematic	Main separating Gas	Desired working T (°C)	P_{CO2} (atm)	Possible technology	Capture goal
Post-combustion		CO_2/N_2	<100 or >600	0.1~0.2	Solvent: MEA Solid: CaO membrane	Capture >90% Cost <35%
Pre-combustion		CO_2/H_2	40~260 (post WGS) 260~500 (concurrent WGS-separation)	10-20	Solid: salts, oxides Solvent: Selexsol Membrane Chemical-looping	Capture >90% Cost: <10%
Oxyfuel		O_2/N_2		0.2 (P_{O2})	Cryogenics OTM IGCC	

- Current CO_2 sorbents have big limitations due to large energy usage → high operating costs. Need to identify CO_2 sorbents with optimal energy usage. Theoretical simulations are powerful tools for selecting good candidates of CO_2 sorbents.



Solids for CO_2 Sorbent Applications

Example: $Li_2ZrO_3+CO_2 \leftrightarrow Li_2CO_3+ZrO_2$

separated CO_2 to be sequestrated

Release CO_2

Cycle back

Shell nanoparticle

Li_2CO_3

ZrO_2

Our goal:

Search for better solid

candidates

substitute

CO2 Adsorption

Investigate the Thermodynamics

CO_2, N_2, H_2O,…

Mixed gases in

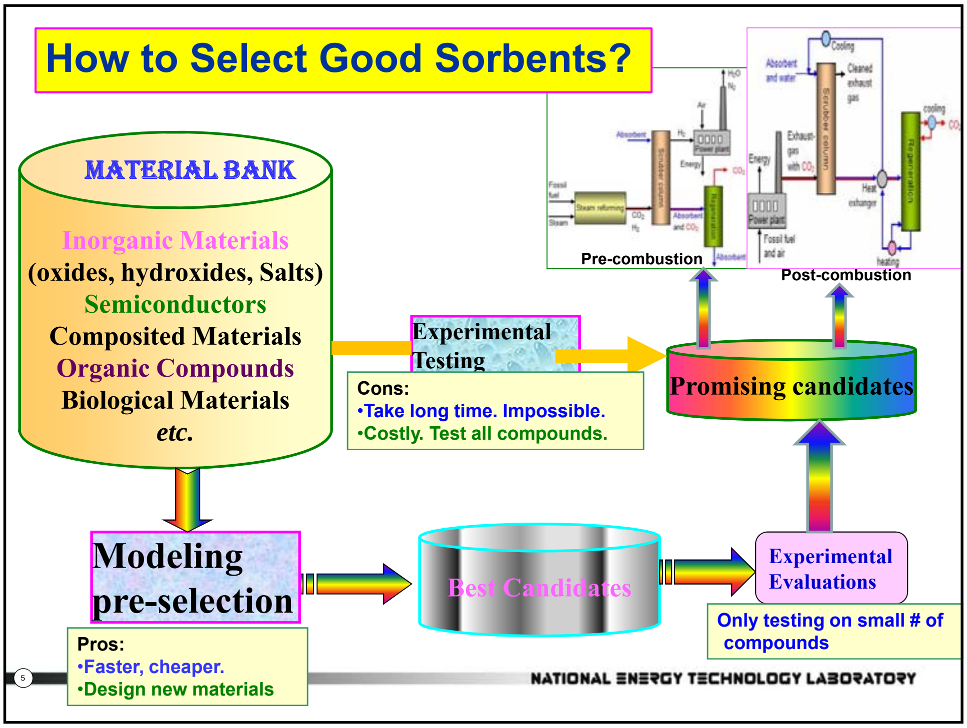
Li_2ZrO_3

Separated out

H_2O, N_2, etc.

Objectives

- Establishing ***a theoretical procedure*** to identify most potential candidates of CO_2 solid sorbents from a large solid material databank.
- To explore the optimal working conditions for the promised CO_2 solid sorbents and provide guidelines to the experimentalists.



How to Select Good Sorbents?

MATERIAL BANK

Inorganic Materials
(oxides, hydroxides, Salts)
Semiconductors
Composited Materials
Organic Compounds
Biological Materials
etc.

Experimental Testing

Cons:
- **Take long time. Impossible.**
- **Costly. Test all compounds.**

Promising candidates

Modeling pre-selection

Pros:
- **Faster, cheaper.**
- **Design new materials**

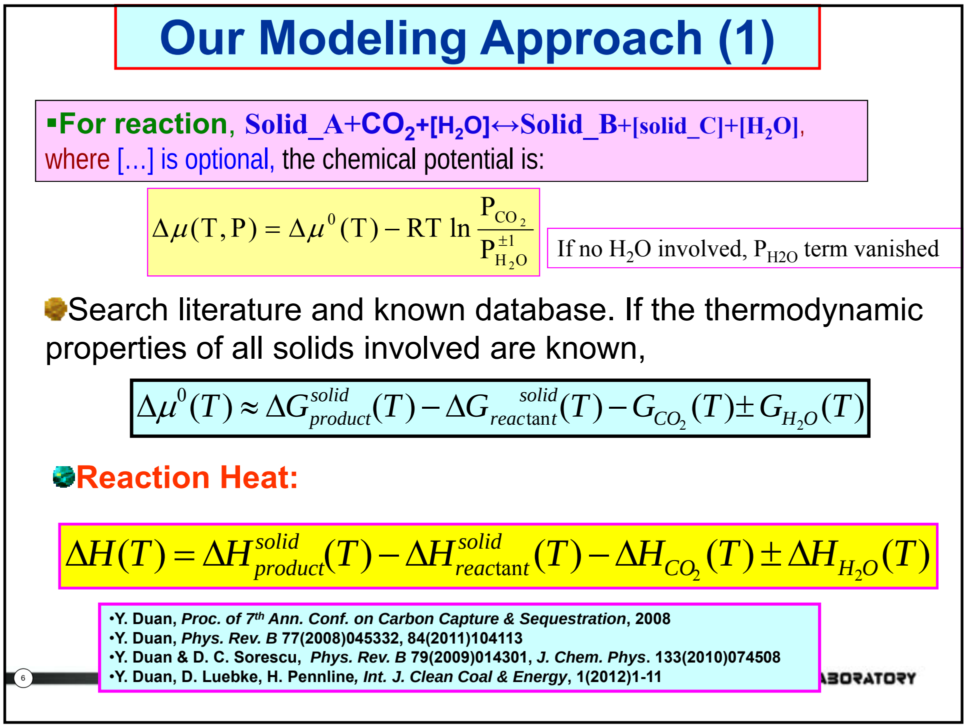
Best Candidates

Experimental Evaluations

Only testing on small # of compounds

Pre-combustion

Post-combustion



Our Modeling Approach (1)

- **For reaction, Solid_A+CO_2+[H_2O]↔Solid_B+[solid_C]+[H_2O],** where [...] is optional, the chemical potential is:

$$\Delta\mu(T,P) = \Delta\mu^0(T) - RT\ \ln\frac{P_{CO_2}}{P^{\pm1}_{H_2O}}$$

If no H_2O involved, P_{H2O} term vanished

Search literature and known database. If the thermodynamic properties of all solids involved are known,

$$\Delta\mu^0(T) \approx \Delta G^{solid}_{product}(T) - \Delta G^{solid}_{reactant}(T) - G_{CO_2}(T) \pm G_{H_2O}(T)$$

Reaction Heat:

$$\Delta H(T) = \Delta H^{solid}_{product}(T) - \Delta H^{solid}_{reactant}(T) - \Delta H_{CO_2}(T) \pm \Delta H_{H_2O}(T)$$

- **Y. Duan, *Proc. of 7th Ann. Conf. on Carbon Capture & Sequestration*, 2008**
- **Y. Duan, *Phys. Rev. B* 77(2008)045332, 84(2011)104113**
- **Y. Duan & D. C. Sorescu, *Phys. Rev. B* 79(2009)014301, *J. Chem. Phys.* 133(2010)074508**
- **Y. Duan, D. Luebke, H. Pennline, *Int. J. Clean Coal & Energy*, 1(2012)1-11**

Our Theoretical Approach (2)

▪For reaction, Solid_A+CO_2+[H_2O]↔Solid_B+[solid_C]+[H_2O], where [...] is optional, the chemical potential is:

If the thermodynamic data of solids are not available

$$\Delta\mu(T,P) = \Delta\mu^0(T) - RT\ln\frac{P_{CO_2}}{P_{H_2O}^{\pm 1}}$$

where

$$\Delta\mu^0(T) \approx \Delta E^{DFT} - G_{CO_2}(T) \pm G_{H_2O}(T) + \Delta E_{ZP} + \Delta F^{PH}(T)$$

VASP

Ideal gas
Statistics physics

For solids
Phonon dynamics

First approximation:
do DFT calculation only

Filter I

Filter II

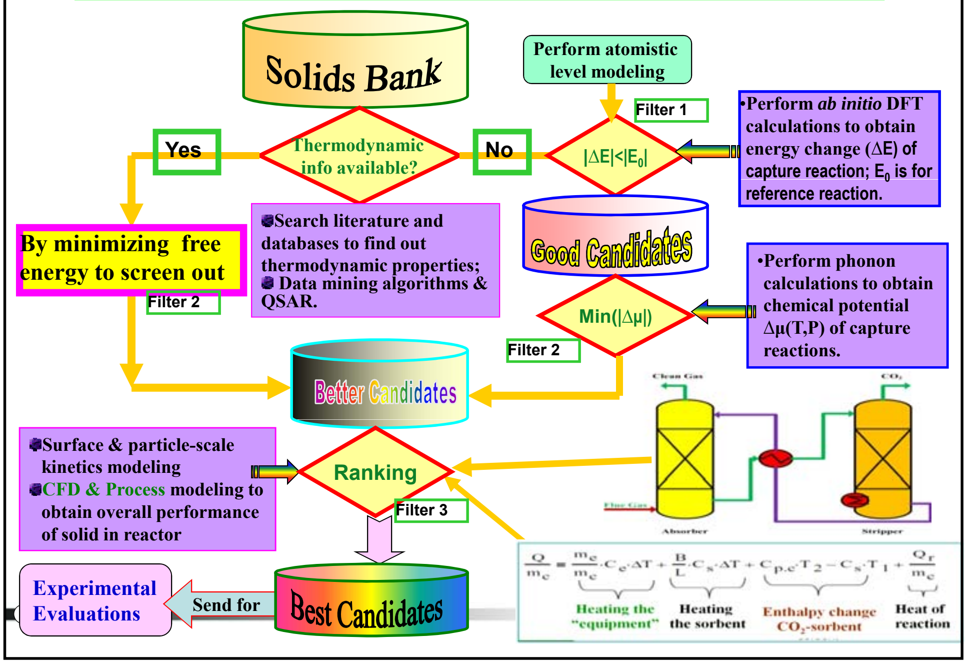
For these promised candidate selected by filter I based on a reference capture reaction, do phonon free energy and entropy calculations.

Reaction Heat:

$$\Delta H^{cal}(T) = \Delta\mu^0(T) + T*(-S_{CO_2} \pm S_{H_2O} + \Delta S_{harm})$$

- **Y. Duan, *Proc. of 7th Ann. Conf. on Carbon Capture & Sequestration*, 2008**
- **Y. Duan & D. C. Sorescu, *Phys. Rev. B* 79(2009)014301, *J. Chem. Phys.* 133(2010)074508**
- **Y. Duan, D. Luebke, H. Pennline, *Int. J. Clean Coal & Energy*, 1(2012)1-11**

High-throughput Multiscale Screening of CO_2 Solid Sorbents



- Perform *ab initio* DFT calculations to obtain energy change (ΔE) of capture reaction; E_0 is for reference reaction.
- Search literature and databases to find out thermodynamic properties;
- Data mining algorithms & QSAR.
- Perform phonon calculations to obtain chemical potential Δμ(T,P) of capture reactions.
- Surface & particle-scale kinetics modeling
- CFD & Process modeling to obtain overall performance of solid in reactor

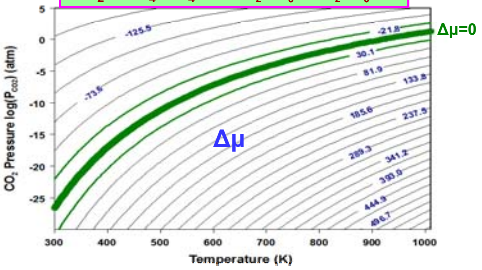
$$\frac{Q}{m_c} = \underbrace{\frac{m_e}{m_c}\cdot C_e\cdot\Delta T}_{\text{Heating the "equipment"}} + \underbrace{\frac{B}{L}\cdot C_s\cdot\Delta T}_{\text{Heating the sorbent}} + \underbrace{C_{p,c}T_2 - C_s\cdot T_1}_{\text{Enthalpy change } CO_2\text{-sorbent}} + \underbrace{\frac{Q_r}{m_c}}_{\text{Heat of reaction}}$$

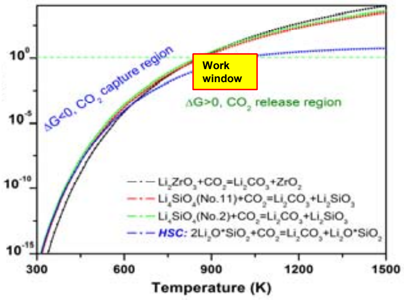
What Info. Can We Obtain?

A. Thermodynamic Properties of Capture Reaction: ΔH(T), ΔG(T), ΔS(T), etc.

B. Chemical Potential (Δμ(T, P)) , T, P_{CO2} Relationship to Identify Suitable Sorbent Materials

CO_2 + Li_4SiO_4 ↔ Li_2SiO_3 + Li_2CO_3



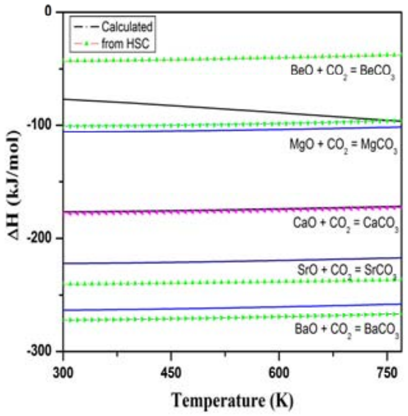


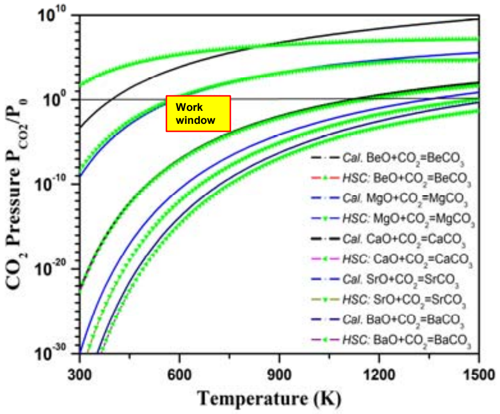
- For each solid, provide its working conditions (T, P_{gas})
- At given work window, select suitable solid materials.

D. Reaction pathways & Energy Cost at Different Capacity

E. Provide basic information for CFD & Process Modeling

Calculated Results of Alkaline Oxides

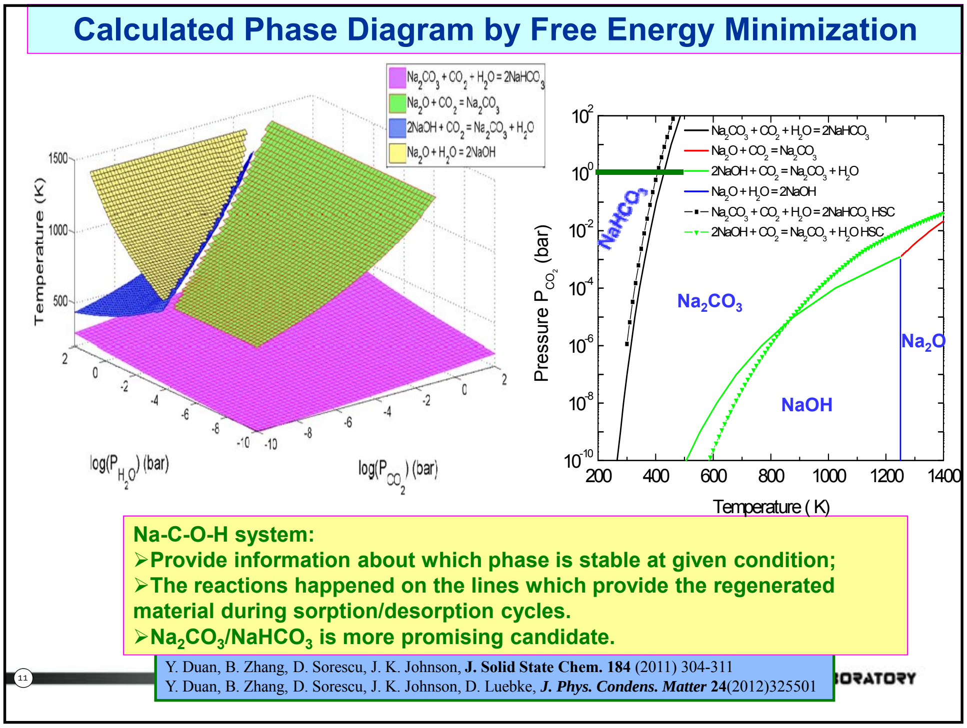




From them, at given capture conditions (T,P), the suitable sorbents can be identified.

Except for BeO and $Be(OH)_2$ systems, (Reason: *$BeCO_3$ structure unknown*), our DFT+Phonon calculated results are in good agreement with experimental measurements.

Y. Duan, D. C. Sorescu, ***J. Chem. Phys.*** 133(2010)074508

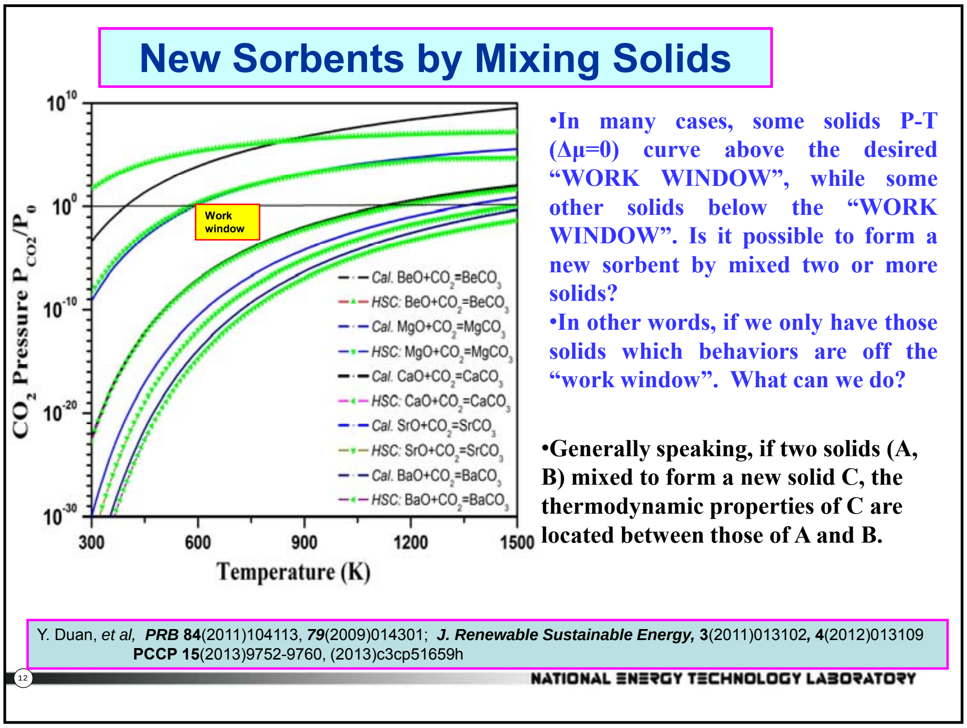


Calculated Phase Diagram by Free Energy Minimization

Na-C-O-H system:

- ➢Provide information about which phase is stable at given condition;
- ➢The reactions happened on the lines which provide the regenerated material during sorption/desorption cycles.
- ➢$Na_2CO_3/NaHCO_3$ is more promising candidate.

Y. Duan, B. Zhang, D. Sorescu, J. K. Johnson, **J. Solid State Chem. 184** (2011) 304-311
Y. Duan, B. Zhang, D. Sorescu, J. K. Johnson, D. Luebke, ***J. Phys. Condens. Matter* 24**(2012)325501



New Sorbents by Mixing Solids

•In many cases, some solids P-T ($\Delta\mu=0$) curve above the desired "WORK WINDOW", while some other solids below the "WORK WINDOW". Is it possible to form a new sorbent by mixed two or more solids?

•In other words, if we only have those solids which behaviors are off the "work window". What can we do?

•Generally speaking, if two solids (A, B) mixed to form a new solid C, the thermodynamic properties of C are located between those of A and B.

Y. Duan, *et al*, ***PRB* 84**(2011)104113, ***79***(2009)014301; ***J. Renewable Sustainable Energy,* 3**(2011)013102**, 4**(2012)013109
PCCP 15(2013)9752-9760, (2013)c3cp51659h

Mixture Sorbents

- Single material may not work at desired conditions.
- By mixing two (A and B) or more solids to form a new sorbent may fit our needs.

☐Assume A is a strong CO_2 sorbent with turnover temperature T_A, B is a week CO_2 sorbent with turnover temperature T_B. Obviously, $T_A > T_B$;
☐For mixing A and B to form sorbent C with turnover temperature T_C, $T_A > T_C > T_B$. We have typically three scenarios:

A. $T_A > T_B$, using A component to capture CO_2. In this way, to reduce T_A to T_C since $T_C < T_A$. For example, Li_2O/SiO_2, Li_2O/ZrO_2

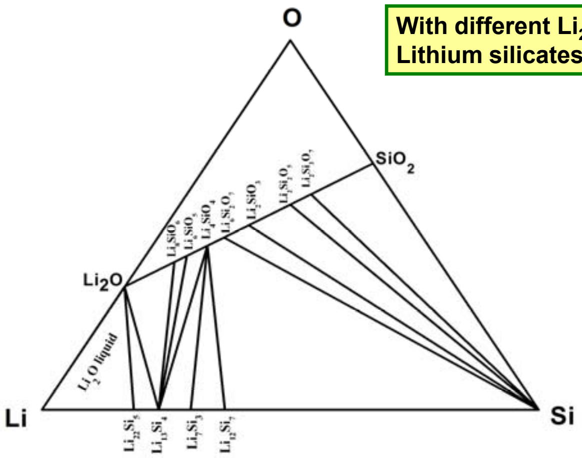
B. $T_A > T_B$, using B component to capture CO_2. In this way, to increase T_B to T_C since $T_C > T_B$. N_2O (N=Na, K, Cs), CaO-promoted MgO

C. $T_A \approx T_B$, using both A and B components to capture CO_2. In this way, the turnover T_C does not change much as $T_A \approx T_C \approx T_B$, the capacity does not decrease.

Y. Duan, *et al*, ***PRB* 84**(2011)104113, ***79***(2009)014301; ***J. Renewable Sustainable Energy,* 3**(2011)013102**, 4**(2012)013109
PCCP 15(2013)9752-9760, (2013)c3cp51659h

Mixture A/B Sorbents (I): $T_A > T_B$ using A

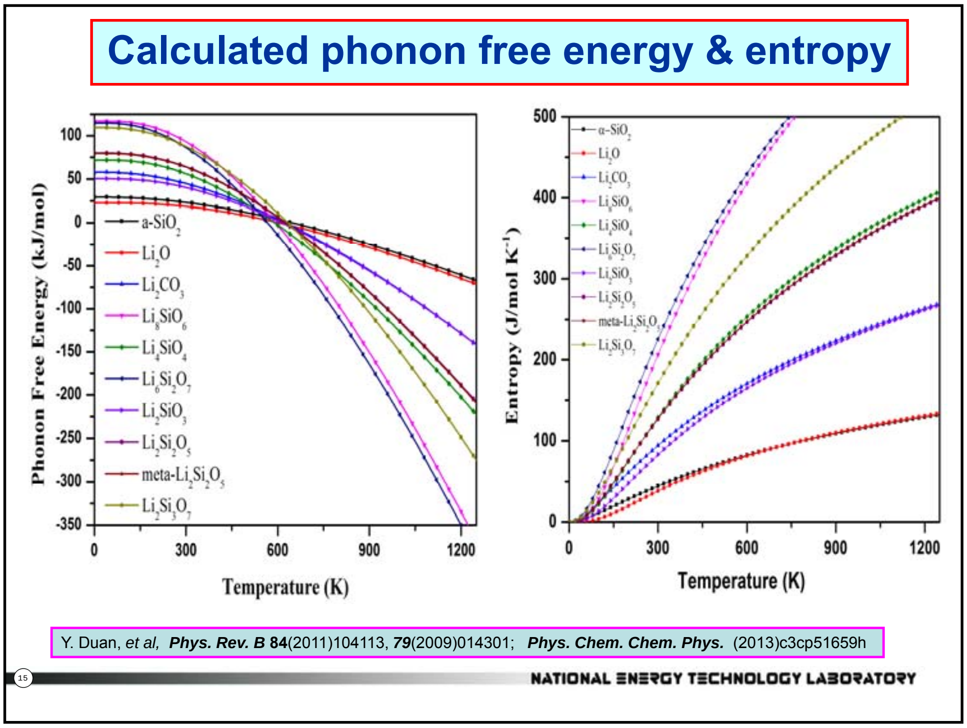
A: Li_2O: strong CO_2 adsorbent
B: SiO_2: does not absorb CO_2.



With different Li_2O/SiO_2 ratios, a series of Lithium silicates can be formed.

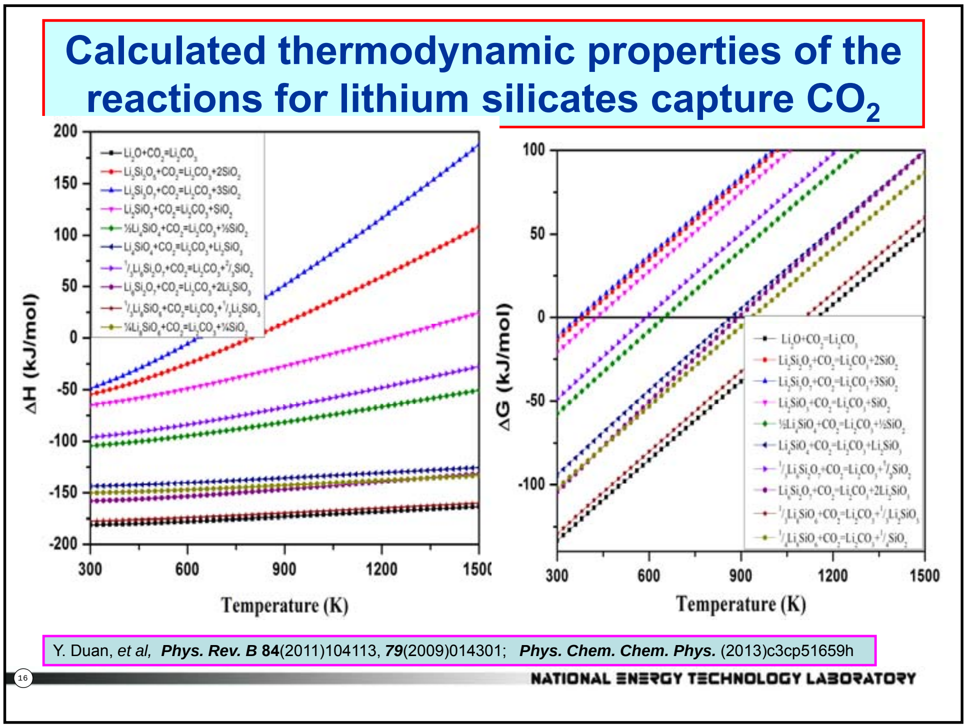
Silicates	Li_2O/SiO_2 ratio
Li_2O	1:0
Li_8SiO_6	4:1
Li_4SiO_4	2:1
$Li_6Si_2O_7$	3:2
Li_2SiO_3	1:1
$Li_2Si_2O_5$	1:2
$Li_2Si_3O_7$	1:3
α–SiO_2	0:1

Y. Duan, *et al*, ***PRB* 84**(2011)104113, ***79***(2009)014301; ***Phys. Chem. Chem. Phys.*** (2013)c3cp51659h



Calculated phonon free energy & entropy

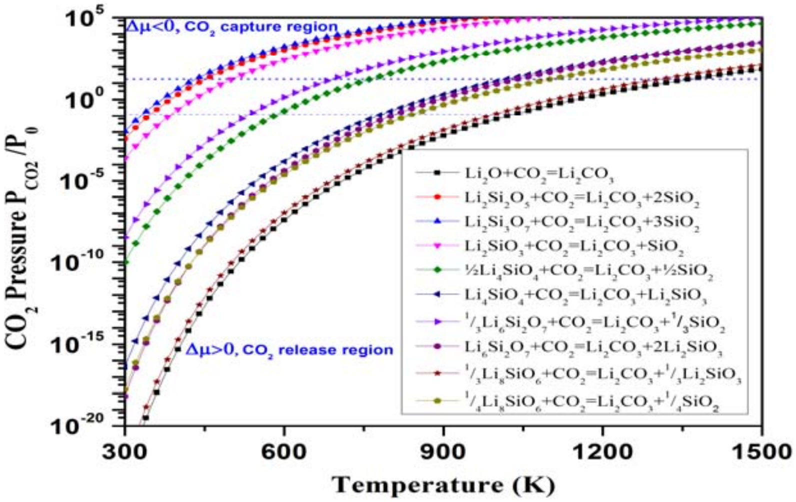
Y. Duan, *et al*, ***Phys. Rev. B*** **84**(2011)104113, ***79***(2009)014301; ***Phys. Chem. Chem. Phys.*** (2013)c3cp51659h



Calculated thermodynamic properties of the reactions for lithium silicates capture CO_2

Y. Duan, *et al*, ***Phys. Rev. B*** **84**(2011)104113, ***79***(2009)014301; ***Phys. Chem. Chem. Phys.*** (2013)c3cp51659h

Relationship of chemical potential, temperature, and CO_2 pressure



Y. Duan, *et al*, ***Phys. Rev. B* 84**(2011)104113, ***79***(2009)014301; ***Phys. Chem. Chem. Phys.*** (2013)c3cp51659h

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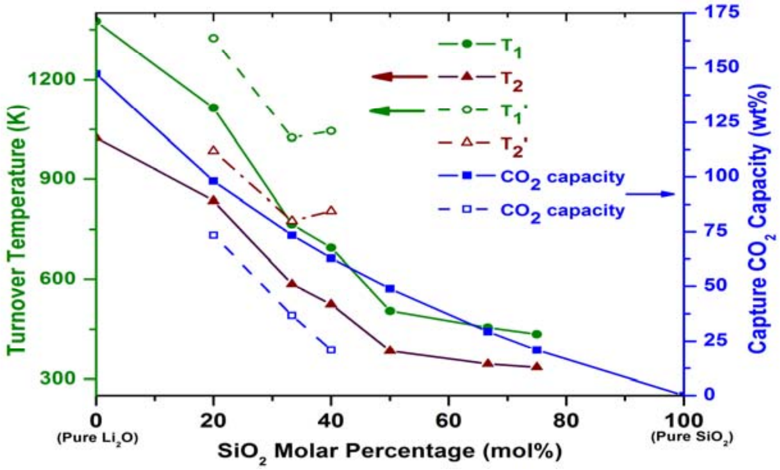
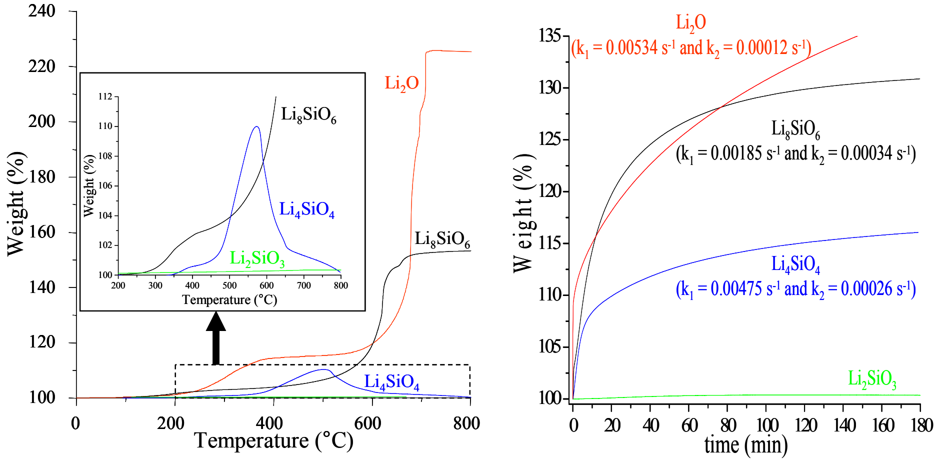
Synthesis of new lithium silicate materials by adjusting the Li_2O/SiO_2 ratio



By adjusting Li_2O/SiO_2 to form a lithium silicate, it's possible to fit the given operating condition.

Y. Duan, *et al*, ***Phys. Chem. Chem. Phys.*** (2013)c3cp51659h

Experimental measured dynamic TGA and CO_2 isotherms of different lithium silicates (Li_2O, Li_8SiO_6, Li_4SiO_4 and Li_2SiO_3) into a CO_2 flux (60 mL/min).



•H. Pfeiffer, **O3-12** (#60) (This Afternoon); **O3-2** (#61) (6/25/2013)

Y. Duan, *et al*, ***Phys. Chem. Chem. Phys.*** (2013)c3cp51659h

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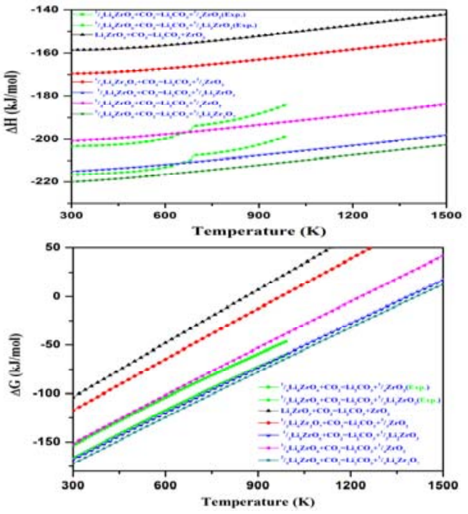
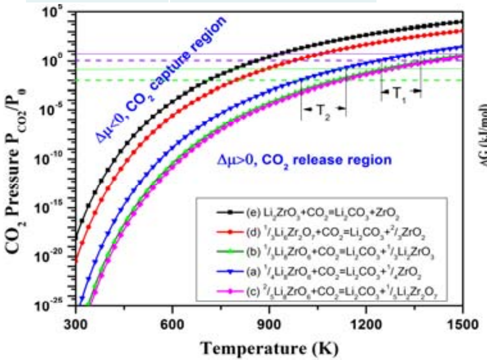
Li_2O/ZrO_2 Mixed Lithium Zirconates

Zirconates	Li_2O/ZrO_2 ratio
Li_2O	1:0
Li_8ZrO_6	4:1
$Li_6Zr_2O_7$	3:2
Li_2ZrO_3	1:1
ZrO_2	0:1





Turnover T:	**Li_8ZrO_6>**	**$Li_6Zr_2O_7$>**	**Li_2ZrO_3**
Li_2O/ZrO_2 ratio:	**4:1**	**3:2**	**1:1**

Y. Duan, ***J. Renewable Sustainable Energy,* 3**(2011)013102, **4**(2012)013109; **Phys. Chem. Chem. Phys. 15**(2013)9752-9760

Mixture Sorbents: Case II

$T_A > T_B$ using B as active CO_2 capture component. By mixing to increase turnover T_B

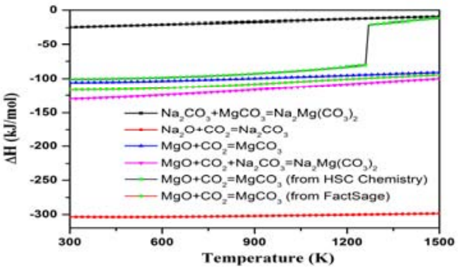
A: Na_2O (or Na_2CO_3)
K_2O (or K_2CO_3)
CaO (or $CaCO_3$)
B: **MgO** active for CO_2 capture

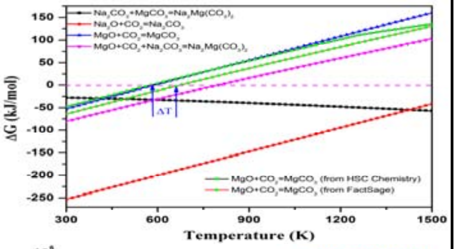
Capture reactions:

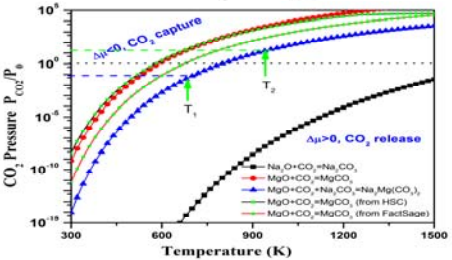
$$N_2CO_3 + MgO + CO_2 \xleftrightarrow{T,P} N_2Mg(CO_3)_2 \quad (N = K, Na)$$

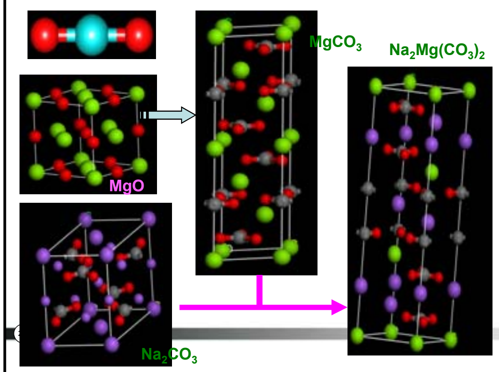
$$CaCO_3 + MgO + CO_2 \xleftrightarrow{T,P} CaMg(CO_3)_2$$

Na_2CO_3-promoted MgO sorbent

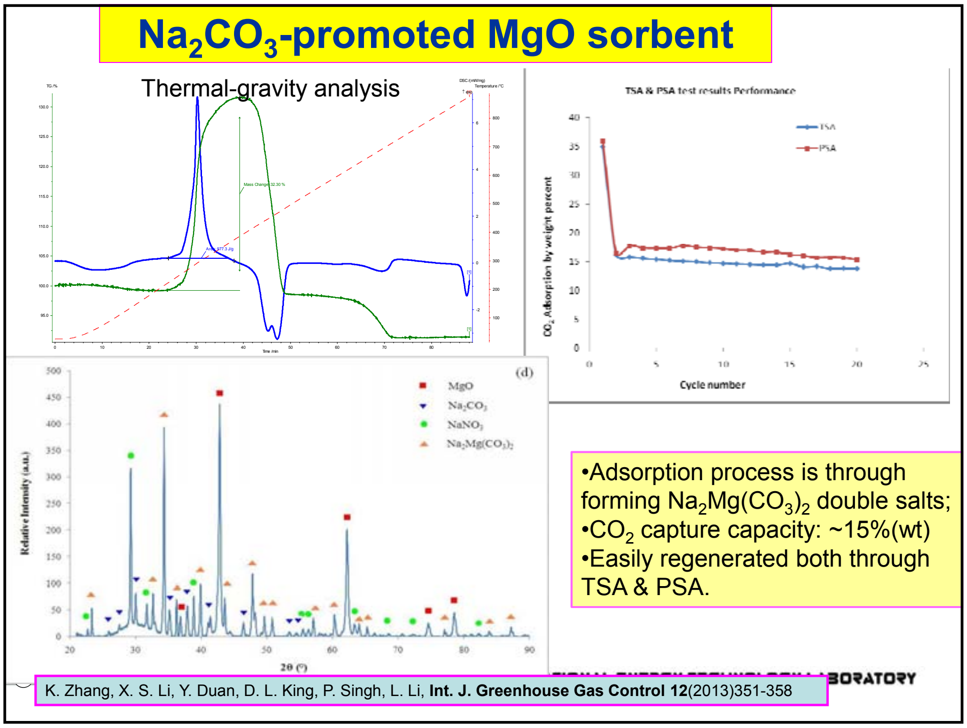








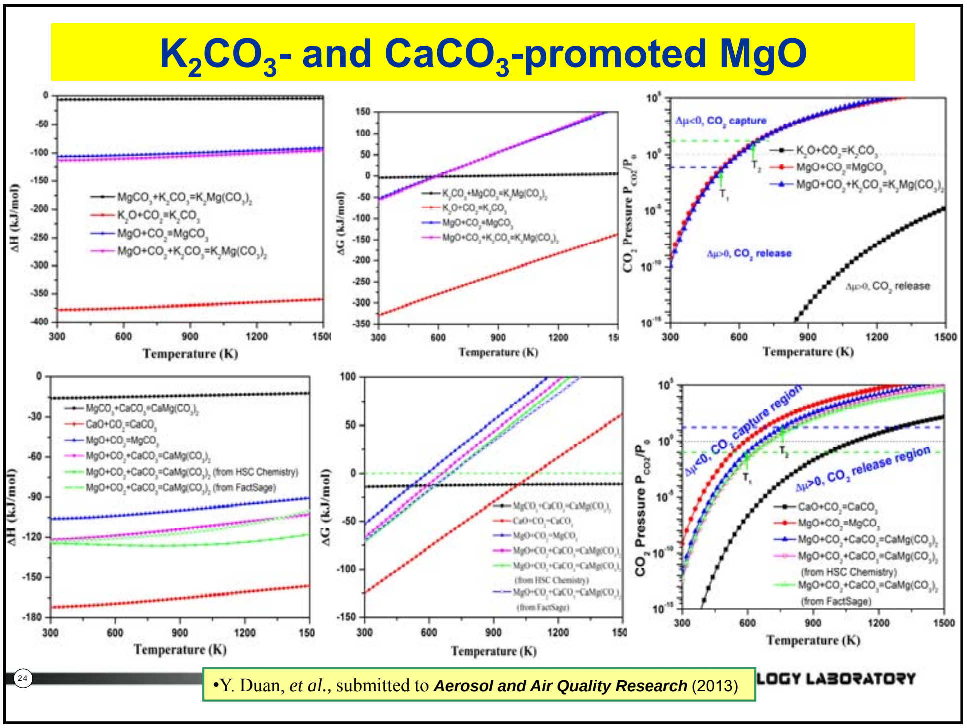
Reaction	ΔH (kJ/mol)
$MgO+CO_2=MgCO_3$	-92.51
$MgCO_3+Na_2CO_3=Na_2Mg(CO_3)_2$	-27.68
$MgO+CO_2+Na_2CO_3=Na_2Mg(CO_3)_2$	-120.19



Na_2CO_3-promoted MgO sorbent

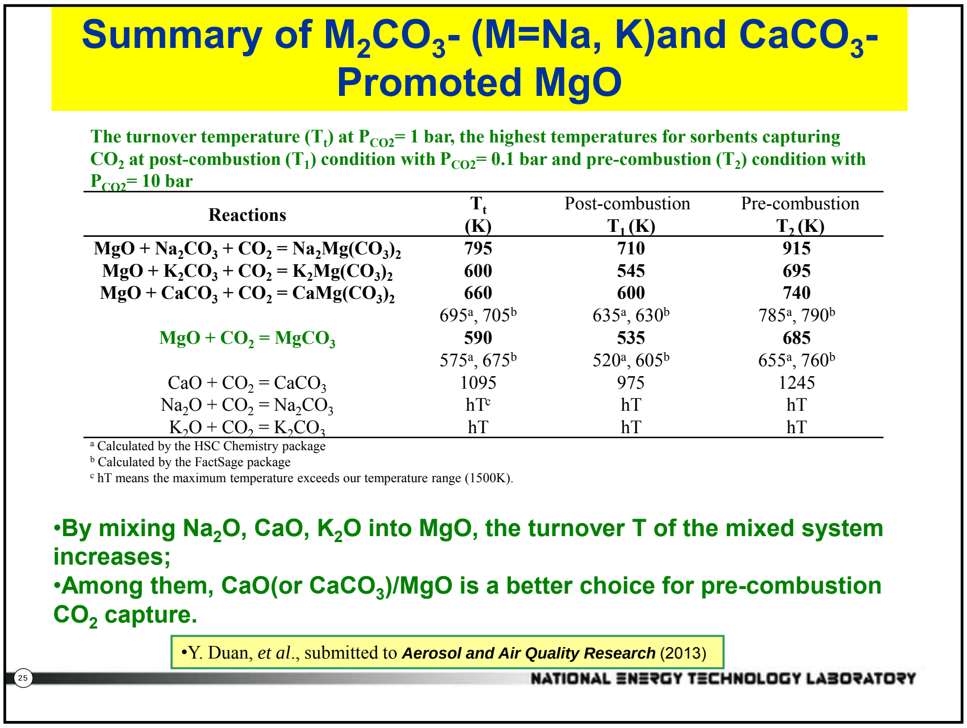
- Adsorption process is through forming $Na_2Mg(CO_3)_2$ double salts;
- CO_2 capture capacity: ~15%(wt)
- Easily regenerated both through TSA & PSA.

K. Zhang, X. S. Li, Y. Duan, D. L. King, P. Singh, L. Li, **Int. J. Greenhouse Gas Control 12**(2013)351-358



K_2CO_3- and $CaCO_3$-promoted MgO

- Y. Duan, *et al.*, submitted to ***Aerosol and Air Quality Research*** (2013)



Summary of M_2CO_3- (M=Na, K)and $CaCO_3$-Promoted MgO

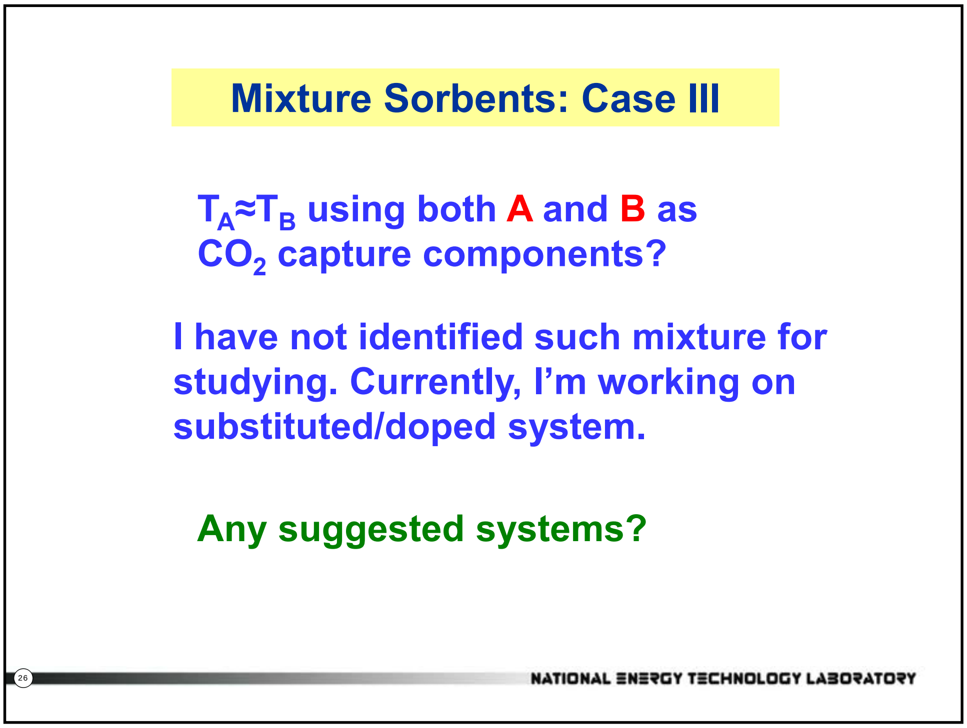
The turnover temperature (T_t) at P_{CO2}= 1 bar, the highest temperatures for sorbents capturing CO_2 at post-combustion (T_1) condition with P_{CO2}= 0.1 bar and pre-combustion (T_2) condition with P_{CO2}= 10 bar

Reactions	T_t (K)	Post-combustion T_1 (K)	Pre-combustion T_2 (K)
$MgO + Na_2CO_3 + CO_2 = Na_2Mg(CO_3)_2$	**795**	**710**	**915**
$MgO + K_2CO_3 + CO_2 = K_2Mg(CO_3)_2$	**600**	**545**	**695**
$MgO + CaCO_3 + CO_2 = CaMg(CO_3)_2$	**660**	**600**	**740**
	695[a], 705[b]	635[a], 630[b]	785[a], 790[b]
$MgO + CO_2 = MgCO_3$	**590**	**535**	**685**
	575[a], 675[b]	520[a], 605[b]	655[a], 760[b]
$CaO + CO_2 = CaCO_3$	1095	975	1245
$Na_2O + CO_2 = Na_2CO_3$	hT[c]	hT	hT
$K_2O + CO_2 = K_2CO_3$	hT	hT	hT

[a] Calculated by the HSC Chemistry package
[b] Calculated by the FactSage package
[c] hT means the maximum temperature exceeds our temperature range (1500K).

- **By mixing Na_2O, CaO, K_2O into MgO, the turnover T of the mixed system increases;**
- **Among them, CaO(or $CaCO_3$)/MgO is a better choice for pre-combustion CO_2 capture.**

•Y. Duan, *et al*., submitted to ***Aerosol and Air Quality Research*** (2013)



Mixture Sorbents: Case III

T_A≈T_B using both A and B as CO_2 capture components?

I have not identified such mixture for studying. Currently, I'm working on substituted/doped system.

Any suggested systems?

Conclusions

- Our methodology can predict thermodynamic properties of solid materials and their CO_2 capture reactions.
- Single solid may not satisfy the industrial operating conditions as CO_2 sorbent, however, by mixing two or more solids, the new formed solid may satisfy the industrial needs.
- By exploring series of lithium silicates with different Li_2O/SiO_2 ratio, we found that with decreasing Li_2O/SiO_2 ratio the corresponding silicate has a lower turnover temperature, and vice versa.
- Compared to pure MgO, the Na_2CO_3, K_2CO_3 and $CaCO_3$ promoted MgO sorbent has a higher turnover T.
- These results provide guidelines to synthesize sorbent materials by mixing different solids with different ratio.

Acknowledgement

I would like to express my gratitude for the following colleagues and collaborators for their fruitful discussions, helps and supports in many aspects.

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- **D. Fauth (NETL)**
- **Dr. M. Syamlal (NETL)**
- **Dr. R. Siriwardane (NETL)**
- **Dr. G. Richards (NETL)**
- **Dr. C. Taylor (NETL)**
- **Dr. H. P. Loh (NETL)**
- **Dr. Y. Soong (NETL)**
- **Dr. C. Matranga (NETL)**
- **R. Anderson (NETL)**
- **Prof. Karl Johnson (U of Pitt)**
- **Dr. Bo Zhang (U of Pitt)**
- **Prof. J. W. Halley (UMN)**
- **Prof. K. Parlinski (IFJ, Poland)**
- **Dr. H. Pfeiffer (Mexico)**
- **Prof. Bingyun Li (WVU)**
- **Keling Zhang (PNNL)**
- **Dr. David King(PNNL)**
- **Dr. Lifeng Zhao (CAS)**
- **Dr. Yunhan Xiao(CAS)**
- **Dr. Jonathan Lekse(URS)**

Thank You!