

Mixed Solid Sorbents for CO₂ Capture Technologies: Theoretical Predictions and Experimental Validations

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I. Introduction

Carbon dioxide is one of the major combustion products which once released into the air can contribute to global climate change.¹⁻⁴ One approach to solve such environmental problems is to capture and sequester the CO₂. Current technologies for capturing CO₂ including solvent-based (amines) and CaO-based materials are still too energy intensive. Hence, there is critical need for development of new materials that can capture and release CO₂ reversibly with acceptable energy costs. In particular, solid oxide sorbent materials have been proposed for capturing CO₂ through a reversible chemical transformation leading primarily to formation of carbonate products. Solid sorbents containing alkali and alkaline earth metals have been reported in several previous studies to be promising candidates for CO₂ sorbent applications due to their high CO₂ absorption capacity at moderate working temperatures.⁵⁻⁸

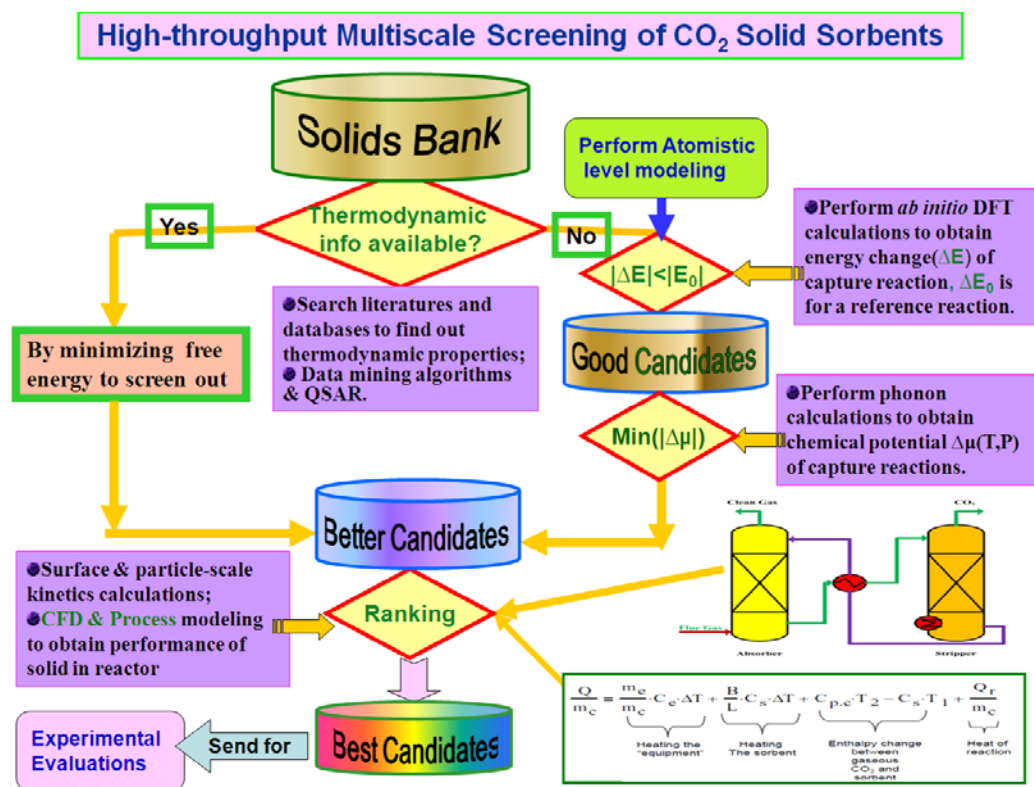


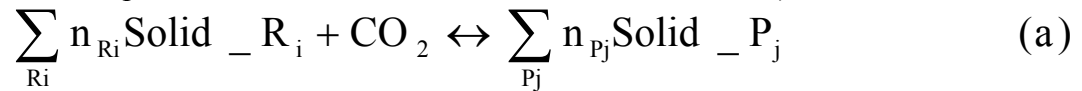
Fig. 1. Schematic of our screening methodology.

During past few years we developed a theoretical methodology to identify promising solid sorbent candidates for CO₂ capture by combining thermodynamic database searching with *ab initio* thermodynamics obtained based on first-principles density functional theory (DFT) and lattice phonon dynamics.^{5-7, 9-13} As shown in Fig.1, the primary outcome of our screening scheme is a list of promising CO₂ sorbents with optimal energy usage.

At a given CO₂ pressure, the turnover temperature (T_t) of an individual solid capture CO₂ reaction is fixed. Such T_t may be outside the operating temperature range (ΔT_o) for a particularly capture technology. In order to adjust T_t to fit the practical ΔT_o , in this study, we demonstrate that by mixing different types of solids it's possible to shift T_t to the range of practical operating conditions.

II. Calculation Methods for Mixed Solid Sorbents

The complete description of the computational methodology together with relevant applications can be found in our previous publications.^{5-7, 9-16} The CO₂ capture reactions of solids can be expressed generically in the form (for convenient description, we normalized the reaction to 1 mole of CO₂)



where n_{R_i} , n_{P_j} are the numbers of moles of reactants (R_i) and products (P_j) involved in the capture reactions. We treat the gas phase CO₂ as an ideal gas. By assuming that the difference between the chemical potentials ($\Delta\mu^0$) of the solid phases of reactants (R_i) and products (P_j) can be approximated by the difference in their total energies (ΔE^{DFT}), obtained directly from DFT calculations, and the vibrational free energy of the phonons and by ignoring the PV contribution terms for solids, the variation of the chemical potential ($\Delta\mu$) for reaction (a) with temperature and pressure can be written as^{5-7, 9-16}

$$\Delta\mu(T, P) = \Delta\mu^0(T) - RT \ln \frac{P_{\text{CO}_2}}{P_0} \quad (1)$$

where

$$\Delta\mu^0(T) \approx \Delta E^{\text{DFT}} + \Delta E_{\text{ZP}} + \Delta F^{\text{PH}}(T) - G_{\text{CO}_2}^0(T) \quad (2)$$

Here, ΔE^{DFT} is the DFT energy difference between the reactants and products of the reaction (a), ΔE_{ZP} is the zero point energy difference between the reactants and products and can be obtained directly from phonon calculations. ΔF^{PH} is the phonon free energy change excluding zero-point energy (which is already counted into the ΔE_{ZP} term) between the solids of products and reactants. P_{CO_2} is the partial pressure of CO₂ in the gas phase and P_0 is the standard state reference pressure taken to be 1 bar. The heat of reaction ($\Delta H^{\text{cal}}(T)$) can be evaluated through the following equation

$$\Delta H^{\text{cal}}(T) = \Delta\mu^0(T) + T[\Delta S_{\text{PH}}(T) - S_{\text{CO}_2}(T)] \quad (3)$$

where $\Delta S_{\text{PH}}(T)$ is the difference of entropies between product solids and reactant solids. The free energy of CO₂ ($G_{\text{CO}_2}^0$) can be obtained from standard statistical mechanics,^{6, 7, 13} and its entropy (S_{CO_2}) can be found in the empirical thermodynamic databases.¹⁷

III. Results and Discussions

When we mix two solids *A* and *B* to form a new sorbent *C*, the turnover temperature of the newly resulted system (T_C) is located between those of *A* and *B* (T_A , T_B). Here it was assumed that *A* is a strong

CO₂ sorbent while B is a weak CO₂ sorbent and $T_A > T_B$. Also, we assumed that the desired operating temperature T_O is between T_A and T_B ($T_A > T_O > T_B$). Now, depending on the properties of A and B , we have typically three scenarios to synthesize the mixing sorbent C :

3.1. $T_A \gg T_B$ and the A component is the key part to capture CO₂.

An example of this case is represented by Li₂O. This is a very strong CO₂ sorbent which forms Li₂CO₃. However, its regeneration from Li₂CO₃ only can occur at very high temperature (T_A). In order to move its T_A to lower temperatures, one can mix some weak CO₂ sorbents (such as SiO₂, ZrO₂). Fig. 2 shows the relationship of chemical potential, P_{CO_2} , and T of the CO₂ capture reactions by the mixed Li₂O/SiO₂ and Li₂O/ZrO₂ solids with different mixing ratios. Fig. 3 shows the turnover T and the CO₂ capture capacity of Li₂O/SiO₂ mixture versus the ratio of Li₂O/SiO₂.^{5-7, 9, 15, 16, 18, 19}

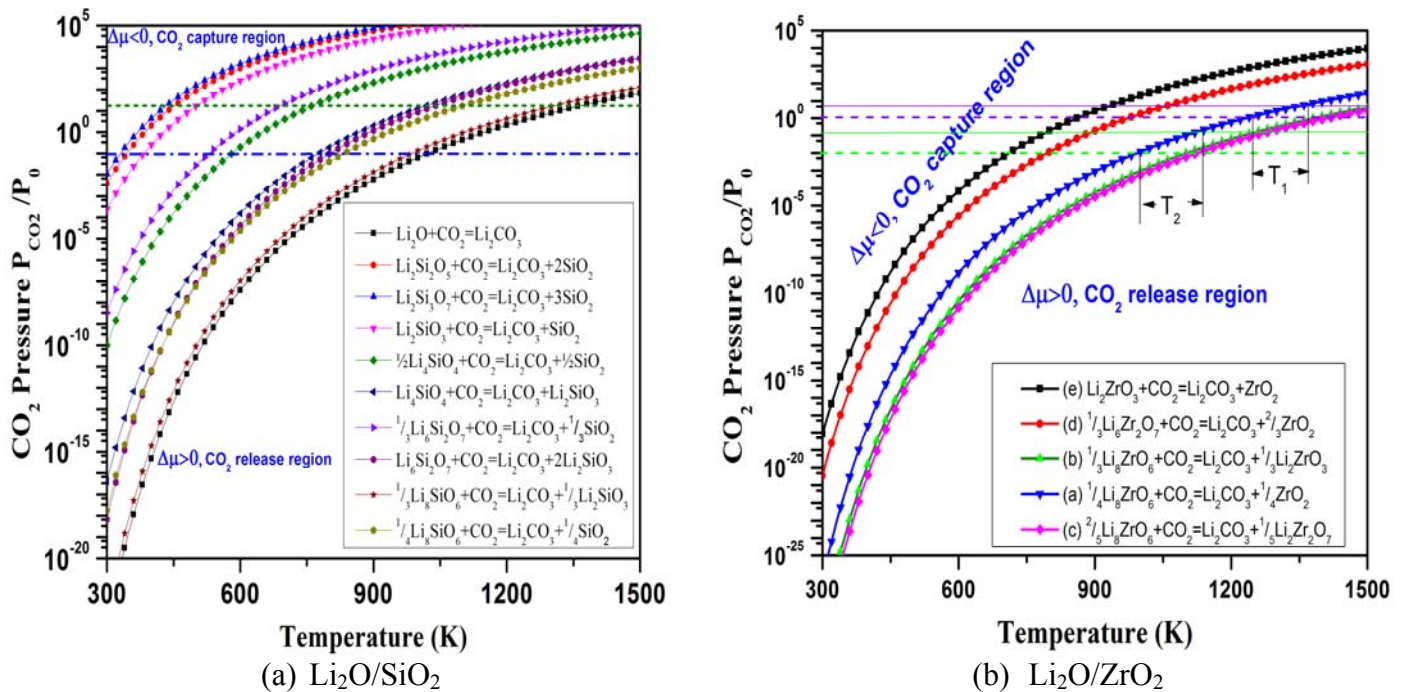


Fig. 2. Contour plots of the calculated chemical potential ($\Delta\mu$) versus temperature and the CO₂ pressure (P plotted in logarithmic scale) for the CO₂ capture reactions. Only $\Delta\mu=0$ curve is shown explicitly. For each reaction, above its $\Delta\mu=0$ curve, their $\Delta\mu<0$, which means the sorbents absorb CO₂ and the reaction goes forward, whereas below the $\Delta\mu=0$ curve, their $\Delta\mu>0$, which indicates CO₂ start to be released and reaction goes backward with regeneration of the sorbents.

From Figs. 2 and 3, one can see that after mixing Li₂O and SiO₂ (or ZrO₂) with different Li₂O/SiO₂ (or Li₂O/ZrO₂) ratios, the T_C of the newly formed C compound (silicate or zirconate) is lower than T_A of pure Li₂O and could be close to the ΔT_O range to fit the practical needs.

From Figs. 2 and 3, one can see that during absorption of CO₂, the lithium silicates with Li₂O/SiO₂ ratio >1 (e.g. Li₈SiO₆, Li₆Si₂O₇, Li₄SiO₄) can be fully converted into SiO₂ and Li₂CO₃ because thermodynamically Li₂SiO₃ can further absorb CO₂ to gain energetic advantage. As shown in Fig. 12, for these Li₂O-rich lithium silicates, in order to obtain maximum CO₂ capture capacity, the operating temperatures during capture should be lower than the turnover temperatures (T_1 for pre-combustion capture or T_2 for post-combustion capture) of Li₂SiO₃. If the capture temperature is higher than that temperature for Li₂SiO₃, the reverse reaction ($Li_2CO_3 + SiO_2 = Li_2SiO_3 + CO_2$) will start and the products will be Li₂SiO₃ and

Li_2CO_3 . In this case, the CO_2 capture capacities of these Li_2O -rich lithium silicates could not reach their maxima. However, during regeneration, when Li_2CO_3 and Li_2SiO_3 (or SiO_2) react with each other to release CO_2 and regenerate the sorbent, the temperature is the key factor to ensure that the original lithium silicate being regenerated. Actually, from Fig. 12 one can see that from the “ CO_2 capture region” to the “ CO_2 release region” we can have different regenerating temperatures for different silicates.

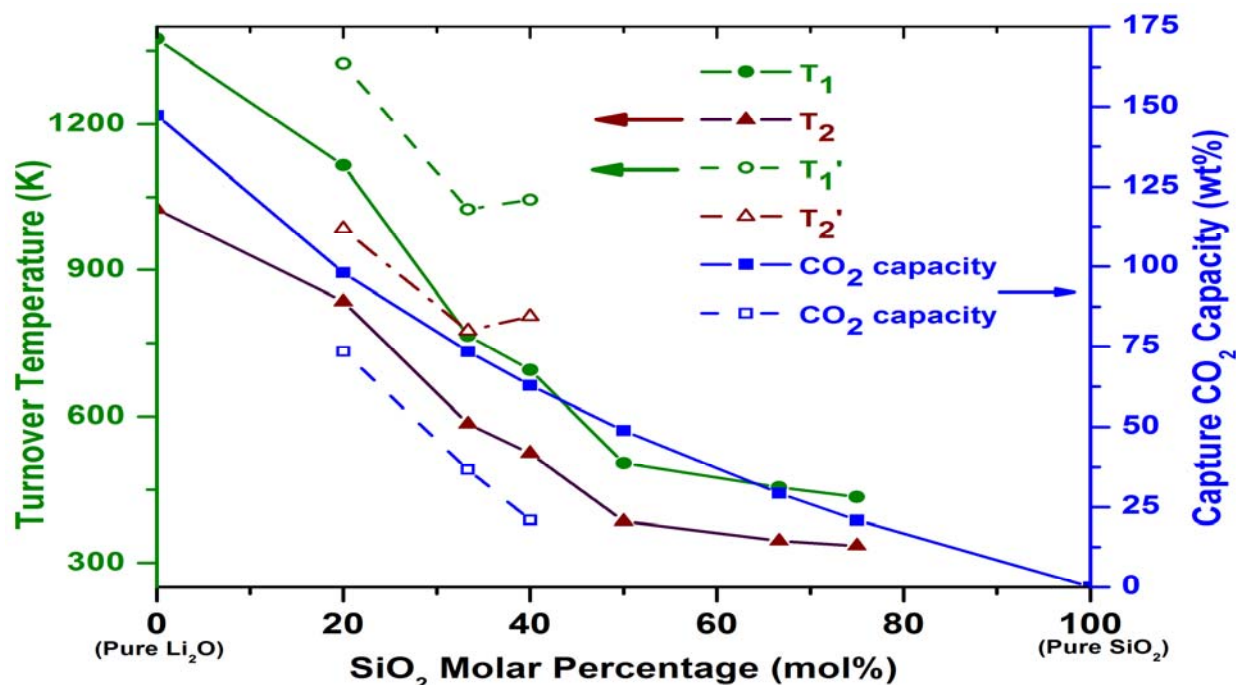


Fig. 3 The dependence of the turnover temperatures defined in the text and of CO_2 capture capacity on molar percentage of SiO_2 in the silicates for which calculations are reported here. T_1 and T_1' are the turnover temperatures under pre-combustion conditions with CO_2 partial pressure at 20 bars, while T_2 and T_2' are the turnover temperatures under post-combustion conditions with CO_2 partial pressure at 0.1 bar. The solid lines indicate to convert lithium silicates to SiO_2 and Li_2CO_3 (T_1 , T_2). For those Li_2O -rich lithium silicates (Li_8SiO_6 , Li_4SiO_4 , $\text{Li}_6\text{Si}_2\text{O}_7$) capturing CO_2 , the data shown in dash lines indicate convert them to Li_2SiO_3 and Li_2CO_3 (T_1' , T_2'). The corresponding CO_2 capture capacities are plotted with open blue squares.

Among these lithium silicates, Fig. 4 shows our dynamic TGA data on the CO_2 capture of these lithium silicates, in addition to the Li_2O . From these curves, it is clearly seen how the $\text{Li}_2\text{O}/\text{SiO}_2$ ratio modified the amount of CO_2 captured and the temperature range in which the process is performed. We note that these experiments are not quantitative, thus the weight increase analysis must be performed in other types of experiments presented below. From the temperature point of view, it is evident that all the silicates captured CO_2 in two different steps, as it was previously described. Analyzing the Li_2O , as example, the first CO_2 capture process occurred between 180 and 380 °C. The weight increase at this stage is associated with the CO_2 superficial reaction. Then, once the diffusion processes are activated, the second weight increment was produced between 580 and 710 °C. Here, the CO_2 capture is produced in the silicate bulk. A similar interpretation is possible for the other curves depicted as inset in Fig. 4, although the reaction process and the external shell composition may differ in each lithium silicate.

The maximum temperature, at which each lithium silicate is able to trap CO_2 , has the following trend: $\text{Li}_2\text{O} > \text{Li}_8\text{SiO}_6 > \text{Li}_4\text{SiO}_4 > \text{Li}_2\text{SiO}_3$, at which the CO_2 capture properties of Li_2SiO_3 can be considered as

negligible. These results are in good agreement with our theoretical results presented in Figs. 2 and 3. Therefore, based on these results, if the non-tested lithium silicates were evaluated as possible CO₂ capture sorbent, the Li₆Si₂O₇ (Li₂O/SiO₂ ratio higher than that of Li₂SiO₃) could present some interesting properties.

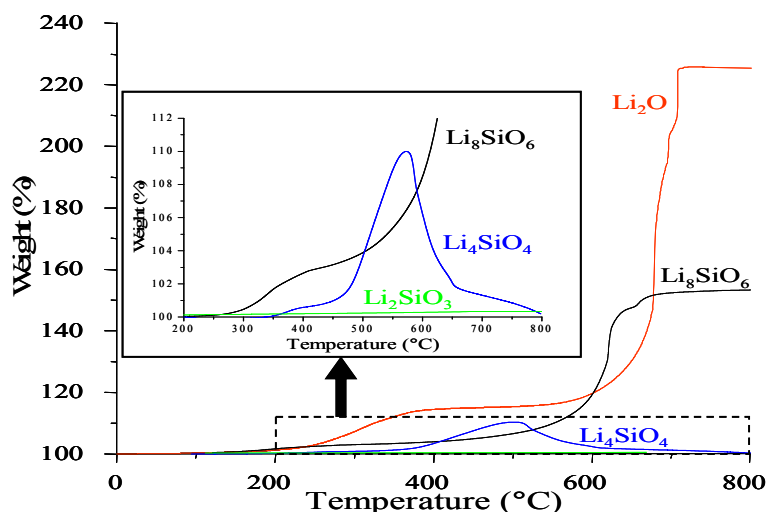


Fig.4. Dynamic thermogravimetric analyses of different lithium silicates (Li₂O, Li₈SiO₆, Li₄SiO₄ and Li₂SiO₃) into a CO₂ flux (60 mL/min).^{18, 19}

Fig. 5 shows the CO₂ isothermal weight gain due to CO₂ absorption as a function of time the same lithium silicates, at 600 °C. Qualitatively, at short times (~10min) the CO₂ capture rates for the lithium silicates are ordered as follows (fastest first): Li₂O > Li₈SiO₆ > Li₄SiO₄ > Li₂SiO₃, and the same trend is observed for long times (~80min). The only significant variation of this tendency was observed between Li₂O and Li₈SiO₆: At large values of weight increase (long times) the order inverted and Li₈SiO₆ started to absorb faster than Li₂O. This change was observed at a specific time, where the diffusion process must begin to control the reaction process. Therefore, different microstructural features may have induced this change. In addition, although none of the isothermal curves reached equilibrium, Li₂O is the one which possesses the highest CO₂ absorption capacity at 600 °C for a long time.

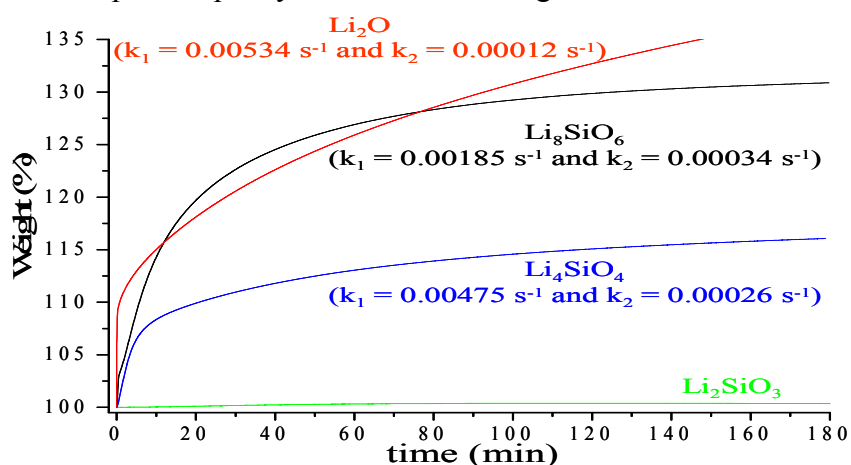
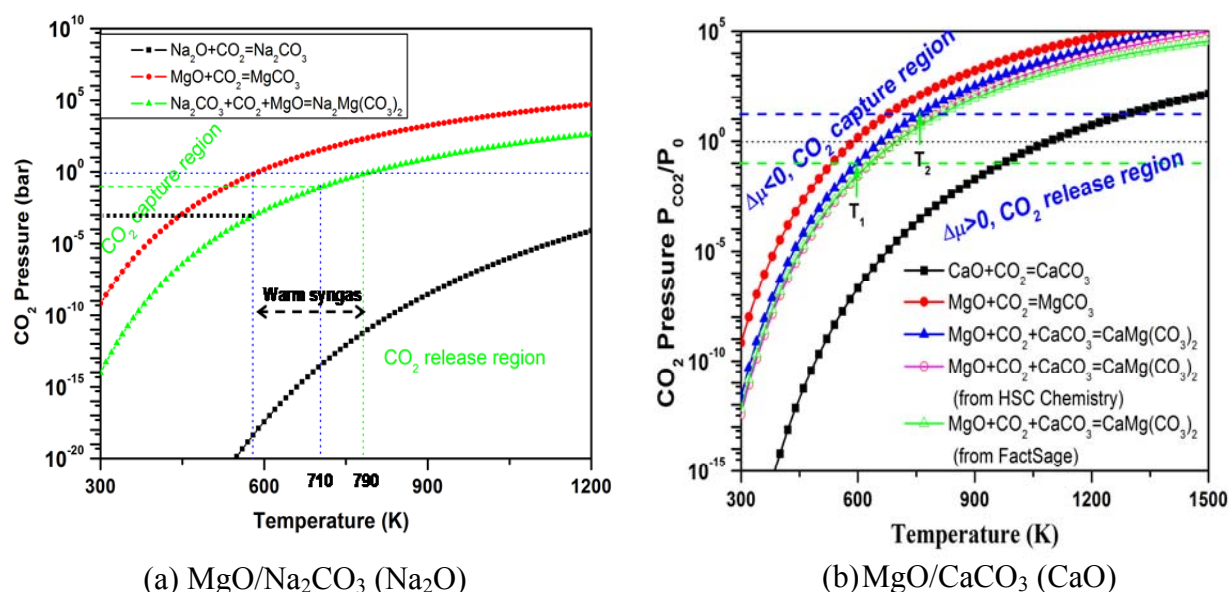


Fig.5. CO₂ isothermal experiments performed at 600 °C in the following lithium silicates Li₈SiO₆, Li₄SiO₄, Li₂SiO₃ and Li₂O. The k constants values reported correspond to the isothermal fitting to a double exponential model.

3.2 $T_A \gg T_B$ and B component is the key part to capture CO_2

In this case, since T_B is lower than T_O , by mixing A into B will increase the turnover temperature T_C of the C solid to values closer to T_O . For example, pure MgO has a very high theoretical CO_2 capture capacity. However, its turnover temperature (250°C) is lower than the required temperature range of $300\text{--}470^\circ\text{C}$ used in warm gas clean up technology and its practical CO_2 capacity is very low, and therefore, it cannot be used directly as a CO_2 sorbent in this technology.^{20, 21}

As shown in Fig. 6, by mixing alkali metal oxides M_2O ($\text{M}=\text{Na}, \text{K}, \text{Cs}, \text{Ca}$) or carbonates (M_2CO_3) into MgO , the corresponding newly formed mixing systems have higher turnover temperatures making them useful as CO_2 sorbents through the reaction $\text{MgO} + \text{CO}_2 + \text{M}_2\text{CO}_3 = \text{M}_2\text{Mg}(\text{CO}_3)_2$.^{20, 22}



(a) $\text{MgO}/\text{Na}_2\text{CO}_3$ (Na_2O) (b) MgO/CaCO_3 (CaO)
Fig. 6. Plots of the calculated chemical potentials versus CO_2 pressures and temperatures for the CO_2 capture reaction by MgO to form double salts.

Fig.7 shows the TSA and PSA test results comparison test of Na-promoted MgO sorbent. As one can see the CO_2 capture capacity is kept constant after first couple cycles.

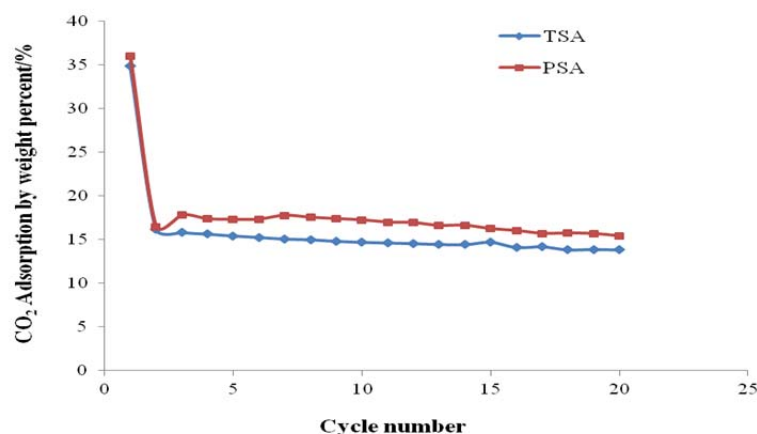


Fig.7. Na-promoted MgO sorbent 20-cycle TSA and PSA test results.

Fig.8 shows the x-ray diffraction pattern of Na-promoted MgO sorbent after loaded with CO₂. Clearly to see, there is double salt Na₂Mg(CO₃)₂ formed.^{20, 21}

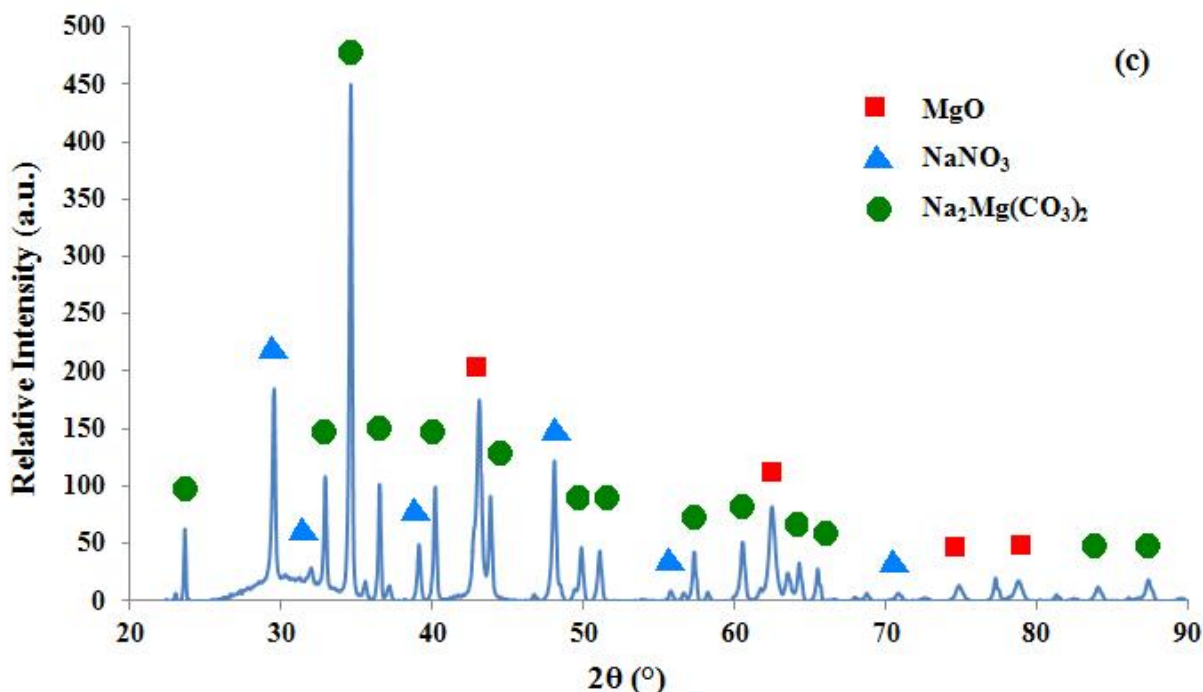


Fig.8. Na-promoted MgO sorbent after test, loaded with CO₂ x-ray diffraction patterns

Table 1. The weight percentage of CO₂ capture, the calculated energy change ΔE^{DFT} , the zero-point energy changes ΔE^{ZP} and the thermodynamic properties (ΔH , ΔG) of the CO₂ capture reactions. (unit: kJ/mol). The turnover temperatures (T_1 and T_2) of the reactions of CO₂ capture by solids under the conditions of pre-combustion ($P_{\text{CO}_2}=20$ bar) and post-combustion ($P_{\text{CO}_2}=0.1$ bar) are also listed.

reaction	absorbing CO ₂ Wt%	ΔE^{DFT}	ΔE^{ZP}	ΔH (T=300K)	ΔG (T=300K)	Turnover T (K)	
						T_1	T_2
$\text{Li}_2\text{ZrO}_3 + \text{CO}_2 \leftrightarrow \text{Li}_2\text{CO}_3 + \text{ZrO}_2^{\text{a}}$	28.75	-146.648	11.311	-158.562	-103.845	1000	780
$\text{LiNaZrO}_3 \text{ A} + \text{CO}_2 \leftrightarrow \frac{1}{2}(\text{Li}_2\text{CO}_3 + \text{Na}_2\text{CO}_3) + \text{ZrO}_2$	26.01	-152.936	7.069	-176.666	-110.892	805	685
$\text{LiNaZrO}_3 \text{ B} + \text{CO}_2 \leftrightarrow \frac{1}{2}(\text{Li}_2\text{CO}_3 + \text{Na}_2\text{CO}_3) + \text{ZrO}_2$	26.01	-167.872	6.934	-191.526	-126.477	865	745
$\text{LiKZrO}_3 \text{ A} + \text{CO}_2 \leftrightarrow \frac{1}{2}(\text{Li}_2\text{CO}_3 + \text{K}_2\text{CO}_3) + \text{ZrO}_2$	23.75	-264.115	6.006	-287.513	-225.611	1275	1095
$\text{LiKZrO}_3 \text{ B} + \text{CO}_2 \leftrightarrow \frac{1}{2}(\text{Li}_2\text{CO}_3 + \text{K}_2\text{CO}_3) + \text{ZrO}_2$	23.75	-311.604	7.080	-332.612	-272.410	hT ^b	1285
$\text{Na}_2\text{ZrO}_3 + \text{CO}_2 \leftrightarrow \text{Na}_2\text{CO}_3 + \text{ZrO}_2^{\text{a}}$	23.76	-140.862	2.236	-158.327	-114.121	1275	925
$\text{K}_2\text{ZrO}_3 + \text{CO}_2 \leftrightarrow \text{K}_2\text{CO}_3 + \text{ZrO}_2^{\text{a}}$	20.24	-223.158	5.813	-238.490	-187.884	hT ^b	1285

^a from Refs.^{15, 18, 23}

^b hT means the temperature is higher than our temperature range (1500K)

3.3 T_A and T_B are close to each other and both A and B are active to capture CO₂

In this case, both A and B components are active to capture CO₂, and the CO₂ capacity of the mixture is the summation of those of A and B . As we know another potential advantage of mixing solids is to increase

the surface area of the solids in order to have faster reaction rates. Such a mixing scenario doesn't show too much advantage in shifting the capture temperature, but may enhance the kinetics of the capture process and eventually make the mixtures more efficient. Although there is no such report in literature, we think such an attempt is worthwhile and are working on several doped systems.

Currently, we are working on doping systems. Here we presented the results of LiMZrO_3 ($M=\text{Na}, \text{K}$) capturing CO_2 . In this case, we substituted half of Li in Li_2ZrO_3 with Na or K. The calculated results are shown in Figure 9 and Table 1.²⁴ Obviously, such doping system also can be treated as mixing three oxides, Li_2O , ZrO_2 , M_2O , $M=\text{Na}, \text{K}$. The doping level/mixing ratios could change their thermodynamic properties to fit the industrial needs.

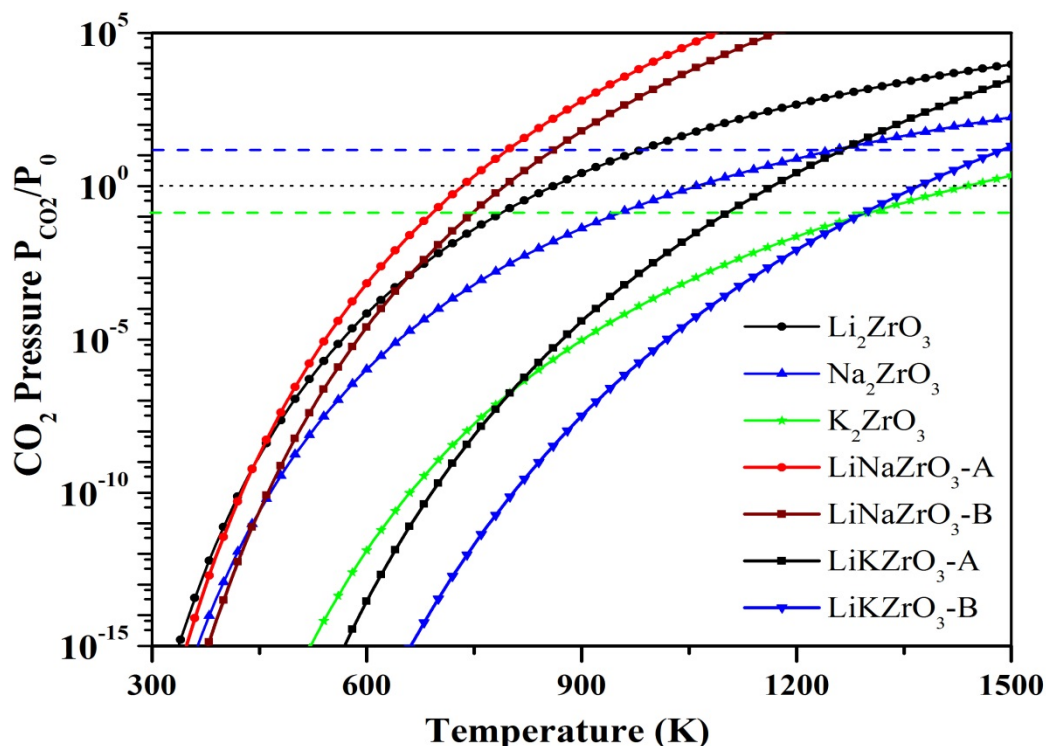


Fig. 9. The contour plotting of calculated chemical potentials versus CO_2 pressures and temperatures of the CO_2 capture reactions by LiMZrO_3 and M_2ZrO_3 . Y-axis plotted in logarithm scale. Only the $\Delta\mu=0$ curve is shown explicitly. For each reaction, above its $\Delta\mu=0$ curve, their $\Delta\mu<0$, which means the solids absorb CO_2 and the reaction goes forward, whereas below the $\Delta\mu=0$ curve, their $\Delta\mu>0$, which means the CO_2 start to release and the reaction goes backward to regenerate the sorbents.

As one can see from Fig. 9 and Table 1, our results showed that by doping Na into Li_2ZrO_3 , the obtained new solid LiNaZrO_3 has better performance as a CO_2 sorbent for post-combustion capture technologies. For K doping into Li_2ZrO_3 , our calculated thermodynamic results showed that the new solid LiKZrO_3 does not gain improvement on its CO_2 capture performance because its regeneration temperature is much higher than Li_2ZrO_3 . Further detailed analyzes with different ratios of doping/mixing are under the way.

IV. Conclusions

The obtained results showed that by changing the mixing ratio of solid *A* and solid *B* to form mixed solid *C* it's possible to shift the turnover T_t of the newly formed solid *C* to fit the practical CO₂ capture technologies. When mixing SiO₂ or ZrO₂ into the strong Li₂O sorbent, one can obtain a series of lithium silicates (or zirconates) with T_t lower than that of pure Li₂O. By mixing oxides (Na₂O, K₂O, CaO) or their corresponding carbonates into MgO, the obtained mixtures exhibit different thermodynamic behaviors and their T_t are higher than that of pure MgO. Such results can be used to provide insights for designing new CO₂ sorbents. Therefore, although one single material taken in isolation might not be an optimal CO₂ sorbent to fit the particular needs to operate at specific temperature and pressure conditions, by mixing or doping two or more materials to form a new material, our results showed that it is possible to synthesize new CO₂ sorbent formulations which can fit the industrial needs. Our results also show that computational modeling can play a decisive role for identifying materials with optimal performance.

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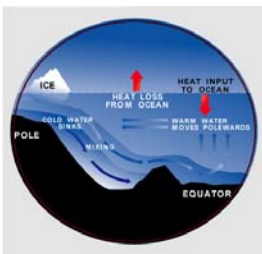
31st Pittsburgh Coal Conference
(03:45-04:05 pm, Oct. 08, 2014, Pittsburgh, PA)

Collaborators

- Drs. Dan C. Sorescu, David Luebke, Bryan Morreale (NETL)
- Drs. Xianfeng Wang, Bingyun Li (WVU)
- Drs. Keling Zhang, Xiaohong S. Li, David King (PNNL)
- Drs. Jinling Chi, Lifeng Zhao, Yunhan Xiao (CAS)

Motivation

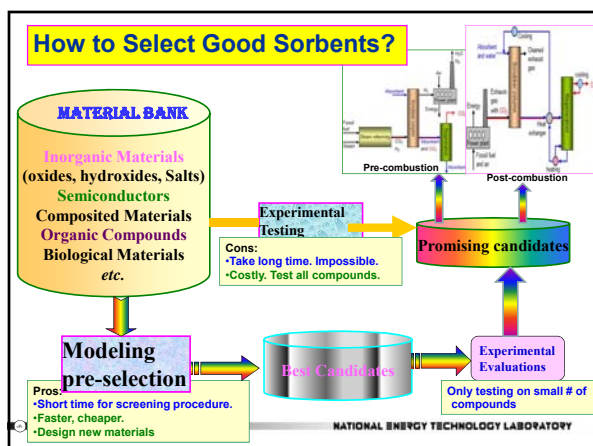
- CO₂ emission causes Global Warming.

- To solve such environmental issue, instead of emitting into atmosphere, the CO₂ must be captured and sequestered.

Objectives

- To capture CO₂, we need materials with optimal performance and low costs;
- We established *a theoretical procedure* to identify most potential candidates of CO₂ solid sorbents from a large solid material databank;
- By computational modeling to guide synthesis new solid sorbents.
- To explore the optimal working conditions for the promised CO₂ solid sorbents used for both pre- and post-combustion capture technologies.



Our Modeling Approach (1)

• For reaction, $\text{Solid}_A + \text{CO}_2 + [\text{H}_2\text{O}] \leftrightarrow \text{Solid}_B + [\text{Solid}_C] + [\text{H}_2\text{O}]$, where [...] is optional, the chemical potential is:

$$\Delta\mu(T, P) = \Delta\mu^0(T) - RT \ln \frac{P_{\text{CO}_2}}{P_{\text{H}_2\text{O}}^{\pm 1}}$$

If no H₂O involved, P_{H₂O} term vanished

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

$$\Delta\mu^0(T) \approx \Delta G_{\text{product}}^{\text{solid}}(T) - \Delta G_{\text{reactant}}^{\text{solid}}(T) - G_{\text{CO}_2}(T) \pm G_{\text{H}_2\text{O}}(T)$$

- Reaction Heat:

$$\Delta H(T) = \Delta H_{\text{product}}^{\text{solid}}(T) - \Delta H_{\text{reactant}}^{\text{solid}}(T) - \Delta H_{\text{CO}_2}(T) \pm \Delta H_{\text{H}_2\text{O}}(T)$$

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• Phys. Rev. B 77(2008)045332, 84(2011)104113, 79(2009)014301
• J. Chem. Phys. 133(2010)074508, 136(2012)064516; Int. J. Clean Coal & Energy, 1(2012)1-11

Our Theoretical Approach (2)

For reaction, $\text{Solid}_A + \text{CO}_2 + [\text{H}_2\text{O}] \leftrightarrow \text{Solid}_B + [\text{solid}_C] + [\text{H}_2\text{O}]$, where [...] is optional, the chemical potential is:

If the thermodynamic data of solids are not available

$$\Delta\mu(T, P) = \Delta\mu^0(T) - RT \ln \frac{P_{\text{CO}_2}}{P_{\text{H}_2\text{O}}}$$

where

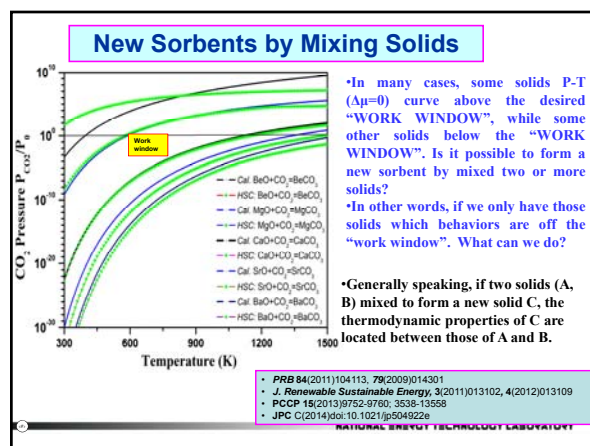
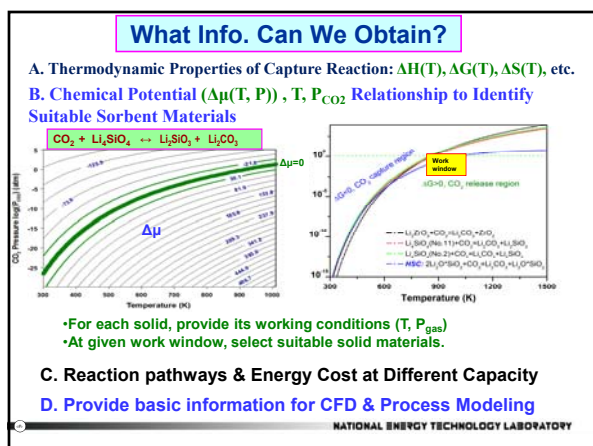
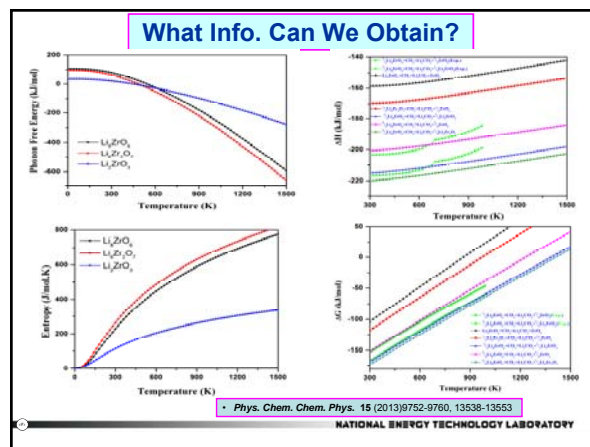
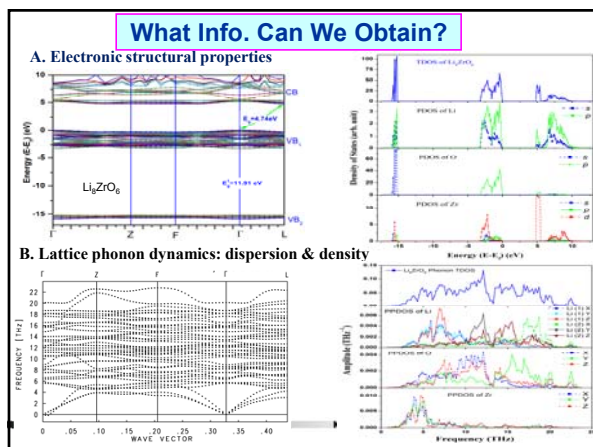
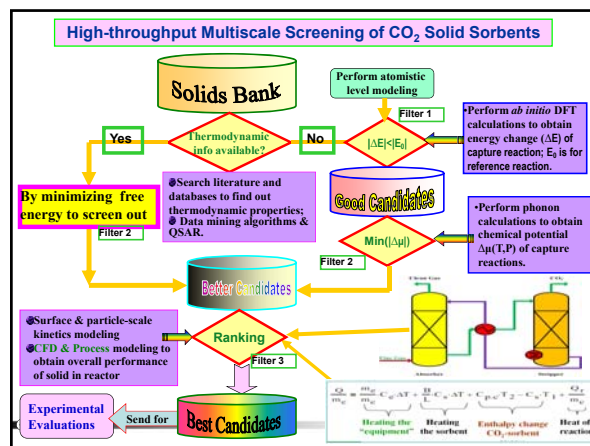
$$\Delta\mu^0(T) \approx \Delta E^{\text{DFT}} - G_{\text{CO}_2}(T) \pm G_{\text{H}_2\text{O}}(T) + \Delta E_{\text{ZP}} + \Delta F^{\text{PH}}(T)$$

First approximation: do DFT calculation only

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

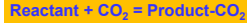
Reaction Heat: $\Delta H^{\text{cal}}(T) = \Delta\mu^0(T) + T * (-S_{\text{CO}_2} \pm S_{\text{H}_2\text{O}} + \Delta S_{\text{harm}})$

• Proc. of 7th Ann. Conf. on Carbon Capture & Sequestration, 2008
• PRB 79(2009)014301, J. Chem. Phys. 133(2010)074508; Int. J. Clean Coal & Energy, 1(2012)1-11



Mixing Scheme

- For a promising sorbent, its CO₂ capture turnover temperature T₁ is fixed. In order to use them in different CO₂ capture technologies under specific working conditions, we need to adjust their



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

$$\Delta\mu^0(T) = \Delta\mu_{product}^0(T) - \Delta\mu_{reactant}^0(T)$$



Goal on T ₁	Δμ ⁰ (T)	Δμ _{product} ⁰ (T)	Δμ _{reactant} ⁰ (T)
Decrease	Less negative	↑, destabilize	↓, stabilize
Increase	More negative	↓, stabilize, lower energy level	↑, destabilize, increase energy level

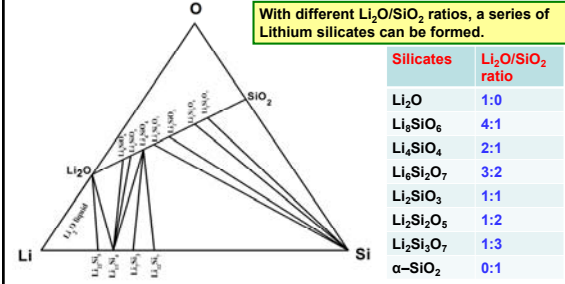
- We proposed a mixing scheme to shift T₁.

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

- A: Li₂O: strong CO₂ adsorbent
- B: SiO₂: does not absorb CO₂.

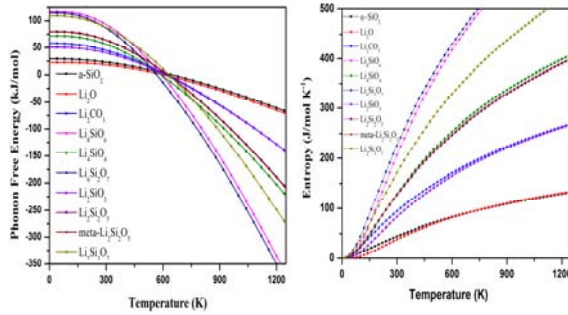
With different Li₂O/SiO₂ ratios, a series of Lithium silicates can be formed.



PRB 84(2011)104113, 79(2009)014301, Phys. Chem. Chem. Phys. 15(2013)13538-13558

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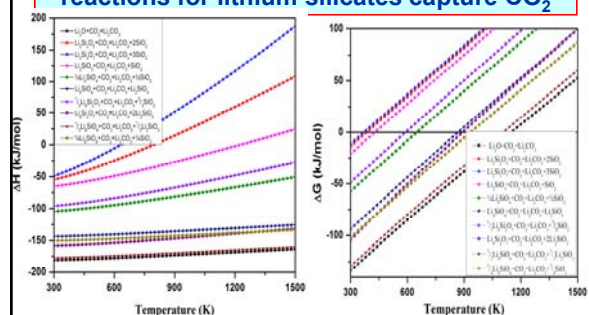
Calculated phonon free energy & entropy



Phys. Rev. B 84(2011)104113, 79(2009)014301, PCCP 15 (2013)9752-9760, 13538-13553

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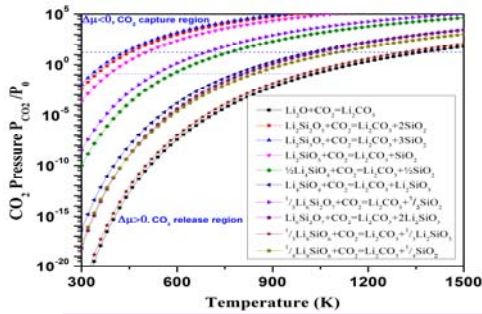
Calculated thermodynamic properties of the reactions for lithium silicates capture CO₂



Phys. Rev. B 84(2011)104113, 79(2009)014301, PCCP 15 (2013)9752-9760, 13538-13553

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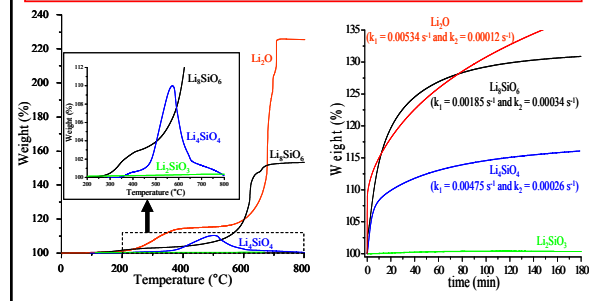
Relationship of chemical potential, temperature, and CO₂ pressure



Phys. Rev. B 84(2011)104113, 79(2009)014301, PCCP 15 (2013)9752-9760, 13538-13553

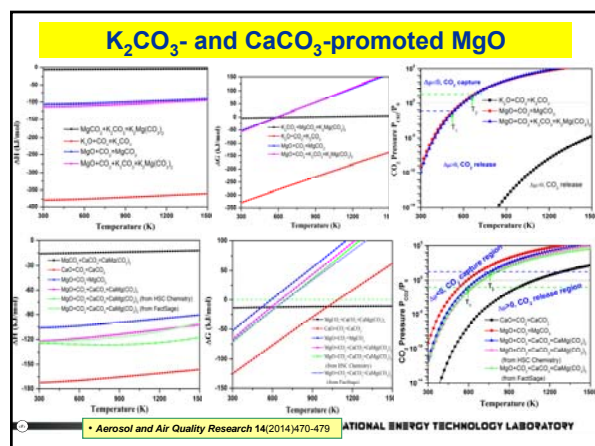
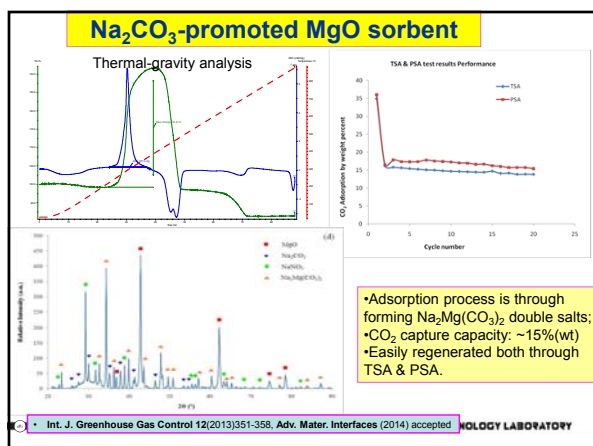
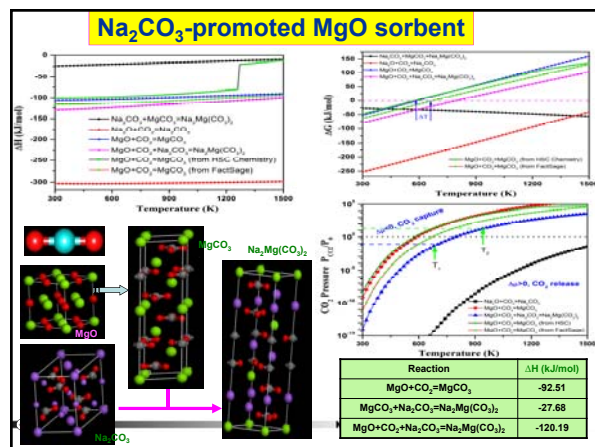
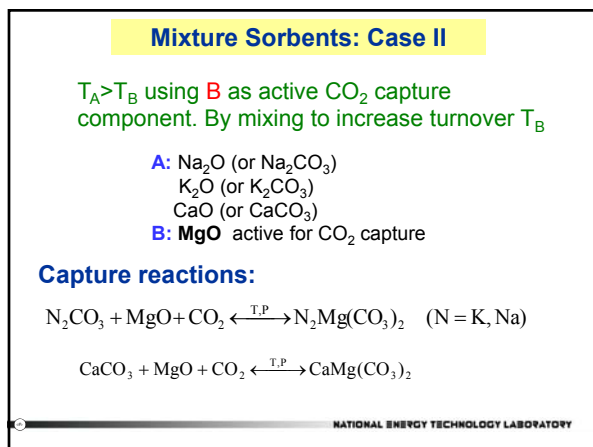
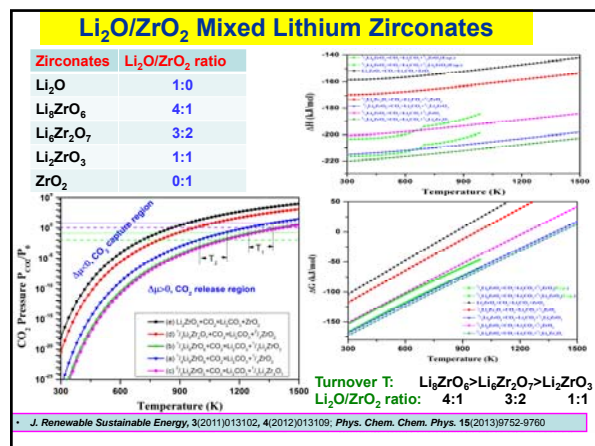
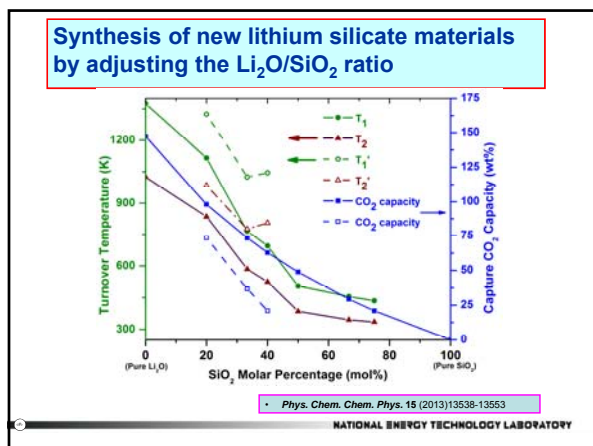
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Experimental measured dynamic TGA and CO₂ isotherms of different lithium silicates (Li₂O, Li₈SiO₆, Li₄SiO₄ and Li₂SiO₃) into a CO₂ flux (60 mL/min).



Phys. Chem. Chem. Phys. 15 (2013)9752-9760, 13538-13553

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

The turnover temperature (T_1) at $P_{CO_2}=1$ bar, the highest temperatures for sorbents capturing CO_2 at post-combustion (T_2) condition with $P_{CO_2}=0.1$ bar and pre-combustion (T_3) condition with $P_{CO_2}=10$ bar

Reactions	T_1 (K)	Post-combustion T_2 (K)	Pre-combustion T_3 (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

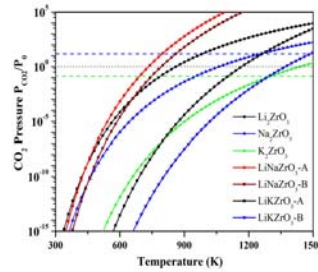
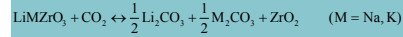
^b Calculated by the FactSage package

^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;
- With process modeling by assuming their CO_2 capacities are half of their theoretical value, the overall performance of Na_2CO_3 - MgO is better than CaO .

• *Aerosol and Air Quality Research* 14(2014)470-479
• *Int. J. Hydrogen Energy* 39(2014)6479-6491

Mixture Sorbents: Case III



Doped system.

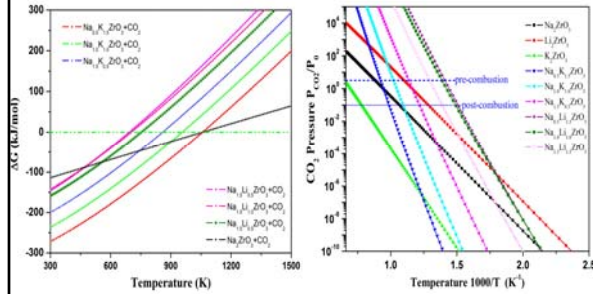
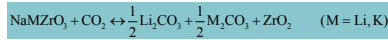
- Such doped system can be treated as mixing 3 oxides: $LiMzrO_3 \leftrightarrow Li_2O + M_2O + ZrO_2$
- Using Li_2O & M_2O as CO_2 capture components.
- Here the ratio is $Li_2O:M_2O:ZrO_2=1:1:2$
- Other mixing ratios are under investigation.

Using both A and B as CO_2 capture components

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Mixture Sorbents: Case III



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Mixture Sorbents: Case III

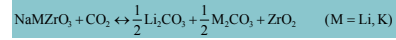


Table III. The weight percentage of CO_2 capture, the ratios of $Na_2O:M_2O:ZrO_2$ (M=Li, K), the calculated energy change ΔE^{991} , the zero-point energy changes ΔE^{992} and the thermodynamic properties (ΔH , ΔG) of the CO_2 capture reactions (unit: kJ/mol). The turnover temperatures (T_1 and T_2) of the reactions of CO_2 capture by solids under the conditions of pre-combustion ($P_{CO_2}=20$ bar) and post-combustion ($P_{CO_2}=0.1$ bar) are also listed.

reaction	absorbing CO_2 Wt%	$Na_2O:M_2O:ZrO_2$ ratio	ΔE^{991}	ΔE^{992}	ΔH (T=300K)	ΔG (T=300K)	Turnover T (K) T_1 T_2
$Na_2ZrO_3 + CO_2 \leftrightarrow Na_2CO_3 + ZrO_2$	23.76	1:0:1	-140.862	2.236	-158.562	-114.121	1275 925
$Na_{0.5}Li_{0.5}ZrO_3 + CO_2 \leftrightarrow \frac{1}{2}Na_2CO_3 + \frac{1}{2}Li_2CO_3 + ZrO_2$	26.01	$1/2 Li_2O$	-170.881	4.607	-242.009	-139.144	805 715
$Na_{0.5}Li_{0.5}ZrO_3 + CO_2 \leftrightarrow \frac{1}{2}Na_2CO_3 + \frac{1}{2}Li_2CO_3 + ZrO_2$	26.01	$1/2 Li_2O$	-157.839	6.400	-228.381	-142.555	745 675
$Na_{0.5}Li_{0.5}ZrO_3 + CO_2 \leftrightarrow \frac{1}{2}Na_2CO_3 + \frac{1}{2}Li_2CO_3 + ZrO_2$	27.31	$1/2 Li_2O$	-169.827	9.652	-237.765	-146.230	735 665
$Na_{0.5}K_{0.5}ZrO_3 + CO_2 \leftrightarrow \frac{1}{2}Na_2CO_3 + \frac{1}{2}K_2CO_3 + ZrO_2$	22.77	$1/2 K_2O$	-210.081	2.466	-281.253	-199.996	915 825
$Na_{0.5}K_{0.5}ZrO_3 + CO_2 \leftrightarrow \frac{1}{2}Na_2CO_3 + \frac{1}{2}K_2CO_3 + ZrO_2$	21.86	$1/2 K_2O$	-245.436	2.658	-316.756	-236.789	1015 915
$Na_{0.5}K_{0.5}ZrO_3 + CO_2 \leftrightarrow \frac{1}{2}Na_2CO_3 + \frac{1}{2}K_2CO_3 + ZrO_2$	21.82	$1/2 K_2O$	-278.147	1.519	-349.877	-272.038	1125 1015
$Li_2ZrO_3 + CO_2 \leftrightarrow Li_2CO_3 + ZrO_2$	28.75	0:1:1	-146.648	11.311	-158.562	-103.845	1000 780
$K_2ZrO_3 + CO_2 \leftrightarrow K_2CO_3 + ZrO_2$	20.24	0:1:1	-223.158	5.813	-238.490	-187.884	927 1285

⁹⁹¹ From Ref. [1]
⁹⁹² From Ref. [2]
⁹⁹³ hT means the temperature is higher than 1500K.

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Mixture Sorbents: Case III

The weight percentage of CO_2 capture, the calculated energy change ΔE^{991} , the zero-point energy changes ΔE^{992} and the thermodynamic properties (ΔH , ΔG) of the CO_2 capture reactions (unit: kJ/mol). The turnover temperatures (T_1 and T_2) of the reactions of CO_2 capture by solids under the conditions of pre-combustion ($P_{CO_2}=20$ bar) and post-combustion ($P_{CO_2}=0.1$ bar) are also listed.

reaction	absorbing CO_2 Wt%	ΔE^{991}	ΔE^{992}	ΔH (T=300K)	ΔG (T=300K)	Turnover T (K) T_1 T_2
$Li_2ZrO_3 + CO_2 \leftrightarrow Li_2CO_3 + ZrO_2$	28.75	-146.648	11.311	-158.562	-103.845	1000 780
$LiNaZrO_3 + CO_2 \leftrightarrow \frac{1}{2}Li_2CO_3 + \frac{1}{2}Na_2CO_3 + ZrO_2$	26.01	-152.936	7.069	-176.666	-110.892	805 685
$LiNaZrO_3 + CO_2 \leftrightarrow \frac{1}{2}Li_2CO_3 + \frac{1}{2}Na_2CO_3 + ZrO_2$	26.01	-167.872	6.934	-191.526	-126.477	865 745
$LiKZrO_3 + CO_2 \leftrightarrow \frac{1}{2}Li_2CO_3 + \frac{1}{2}K_2CO_3 + ZrO_2$	23.75	-264.115	6.006	-287.513	-225.611	1275 1095
$LiKZrO_3 + CO_2 \leftrightarrow \frac{1}{2}Li_2CO_3 + \frac{1}{2}K_2CO_3 + ZrO_2$	23.75	-311.604	7.080	-332.612	-272.410	1285 1285
$Na_2ZrO_3 + CO_2 \leftrightarrow Na_2CO_3 + ZrO_2$	23.76	-140.862	2.236	-158.562	-114.121	1275 925
$K_2ZrO_3 + CO_2 \leftrightarrow K_2CO_3 + ZrO_2$	20.24	-223.158	5.813	-238.490	-187.884	927 1285

Results:

- To be CO_2 sorbent the performance of $LiNaZrO_3$ is better than that of Li_2ZrO_3 , but the performance of $LiKZrO_3$ is much worse as its regeneration T is higher.
- By doping with Na into Li_2ZrO_3 , the obtained new solid $LiNaZrO_3$ is a better CO_2 sorbent applying to post-combustion capture technology;
- By doping K into Li_2ZrO_3 to form new solid $LiKZrO_3$, from the thermodynamic point of view, our calculated results showed that the $LiKZrO_3$ didn't gain any improvements over Li_2ZrO_3 on its overall CO_2 capture performance.

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Conclusions

- Our methodology can predict thermodynamic properties of solid materials and their CO_2 capture reactions, which can be used to identify good candidates from vast of material databank.
- Single solid may not satisfy the industrial operating conditions as a CO_2 sorbent, however, by mixing two or more solids, the new formed solid may satisfy the industrial needs by shifting the turnover T into practical operation range.
- These results provide guidelines to synthesize sorbent materials by mixing different solids with different ratio.

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Thank You!

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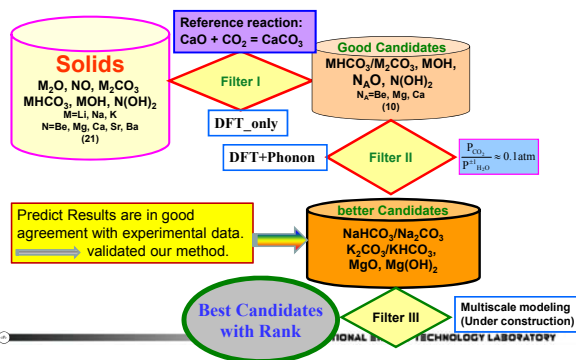
Acknowledgement

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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- Dr. Y. H. Xiao (CAS)
- Dr. J. Lekse (URS)
- Dr. J. Fisher (URS)

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In the Case of Alkali & Alkaline Metal Oxides, Hydroxides, Bicarbonates



The calculated thermodynamic properties of reactions of CO_2 captured by anhydrous and dehydrated potassium carbonates. T_1 refers Pre-combustion while T_2 refers Post-combustion.

Reactions	CO_2 wt%	ΔE_{DFT} (kJ/mol)	ΔE_{ZP} (kJ/mol)	ΔH (T=300K) (kJ/mol)	ΔG (T=300K) (kJ/mol)	T_1 (K)	T_2 (K)	T_{10} (K)
$K_2CO_3 \cdot 1.5H_2O + CO_2 = 2KHCO_3 + 0.5H_2O(g) +$	26.88	-40.47	-0.74	-40.68	-12.82	580 ^b 665 ^c 510 ^d	370 ^b 395 ^c 335 ^d	445 ^b 395 ^c 515 ^d
$K_2CO_3 + CO_2 + H_2O(g) = 2KHCO_3$	31.84	-154.43	18.29	-141.73 -142.85 ^a	-46.28 -44.72 ^a	490 ^b 455 ^c 515 ^d	420 ^b 395 ^c 445 ^d	

^a Calculated by Chemistry package¹⁶
^b when $P_{CO_2} = 1 \text{ bar}$
^c when $P_{CO_2} = 0.1 \text{ bar}$
^d when $P_{CO_2} = 10 \text{ bar}$

J. Phys. Chem. C 116(2012)14461-14470

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Summary of the Methodology

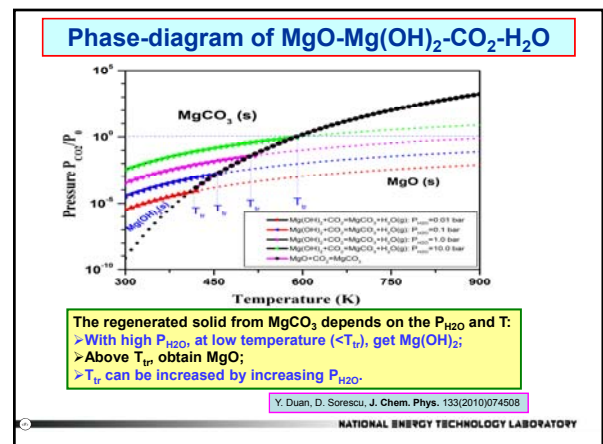
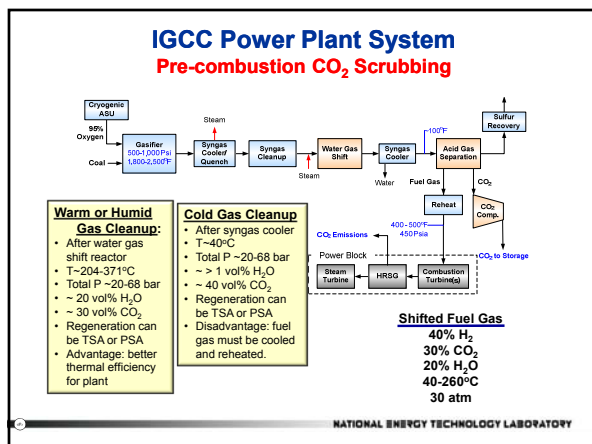
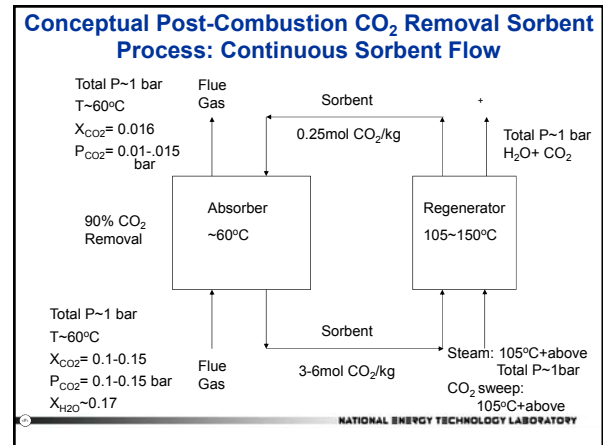
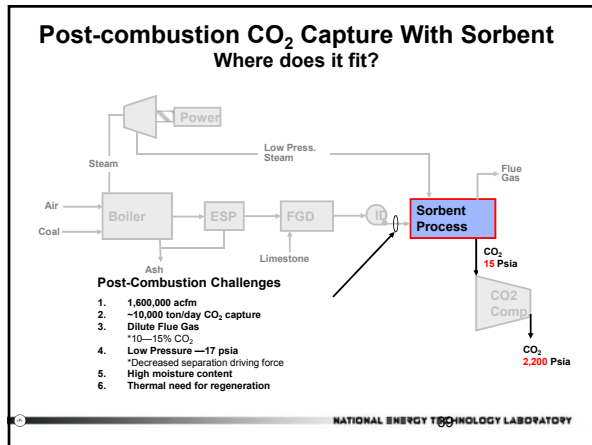
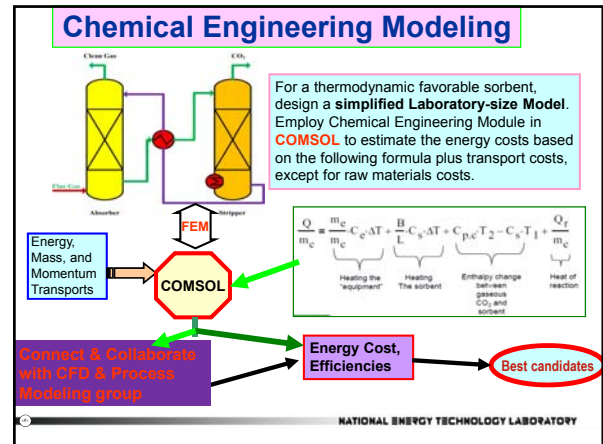
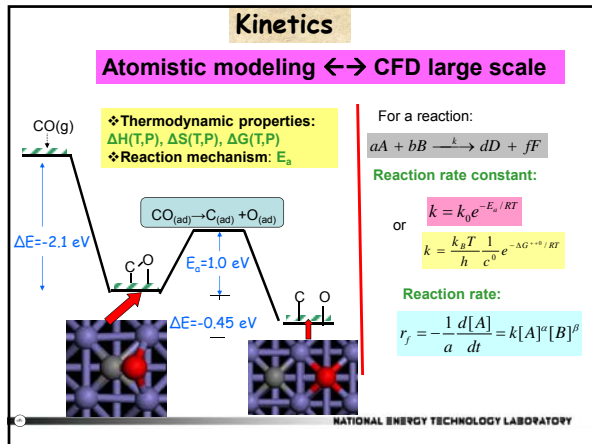
- **Pros:**
 - **Performance:** the methodology can be used to search for solid materials with improved CO_2 capture performances;
 - **Reliability:** For a given dataset, the promised candidates are always in the final short list and are not screened out;
 - **Economics:** Only promised candidates are needed for experimental tests, which can speed up the searching process and save money;
 - **Forward predictions:**
 - Exploring new materials with unknown thermodynamic properties;
 - Provide guidelines for future experimental work.
 - Generally, this methodology can be expanded to other classes of solid compounds as well as solutions (*ab initio* + MD).
- **Cons:**
 - Need to know the structures of materials with phase transitions;
 - High accurate thermodynamic data (<10 kJ/mol) is not achievable;
 - High computational demand for complicated systems.

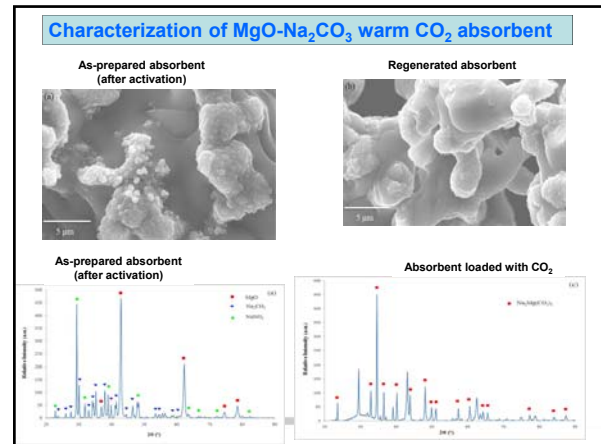
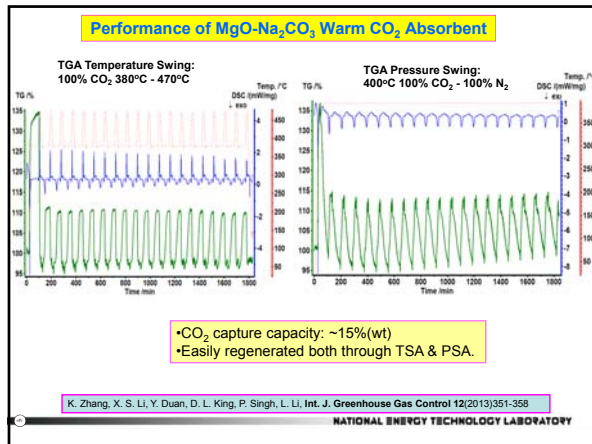
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Further Work

- Using our computational screening methodology continue to explore different classes of oxides, multi-component salts, mixed/substituted/doped solids, etc.
- Exploring the kinetics of the capture process to obtain the activation energy and reaction rates;
- Collaborate with CFD and Process modeling group, establish multi-scale modeling on capture process. (Atomistic-kinetic-CFD-process modeling).
- Based on screening results, experimental measurements will be conducted on those promising candidates;
- Build a database of solid sorbents to satisfy industrial requirements.

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- ### Conclusions
- Our methodology can predict thermodynamic properties of solid materials and their CO₂ capture reactions.
 - By exploring series of lithium silicates with different Li₂O/SiO₂ ratio, we found that with decreasing Li₂O/SiO₂ ratio the corresponding silicate has a lower turnover temperature, and vice versa.
 - Compared to pure MgO, the Na₂CO₃, K₂CO₃ and CaCO₃ promoted MgO sorbent has a higher turnover T.
 - These results provide guidelines to synthesize sorbent materials by mixing different solids with different ratio.
 - Single solid may not satisfy the industrial operating conditions as CO₂ sorbent, however, by mixing two or more solids, the new formed solid may satisfy the industrial needs.
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- ### Further Work
- ✦ Using our computational screening methodology continue to explore different classes of oxides, multi-component salts, *mixed/substituted/doped* solids, *etc.*
 - ✦ Exploring the kinetics of the capture process to obtain the activation energy and reaction rates;
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 - ✦ Based on screening results, experimental measurements will be conducted on those promising candidates;
 - ✦ Build a database of solid sorbents to satisfy industrial requirements.
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Results of Alkali and Alkaline earth metal oxides and Hydroxides

NETL Experimental group developed several oxides/hydroxides sorbents:

- NaOH/CaO: capture: 315°C regeneration: 700°C
- Mg(OH)₂: 200-315°C, 375°C

Siriwardane *et al.*, *Energy & Fuels*, (2007); *Ind. Eng. Chem. Res.* (2009)

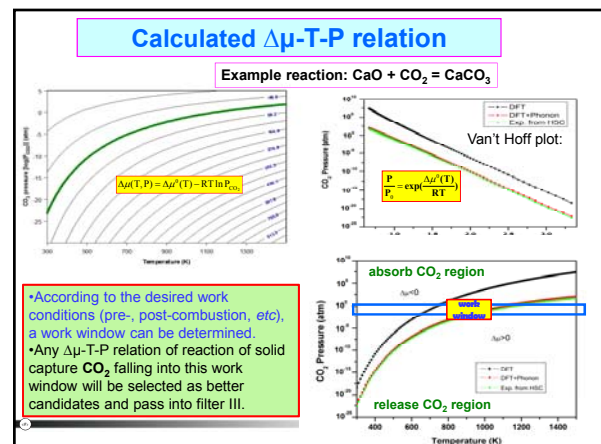
•Applying our methodology to systematically investigate the CO₂ capture properties of all alkali and alkaline earth metal oxides and hydroxides

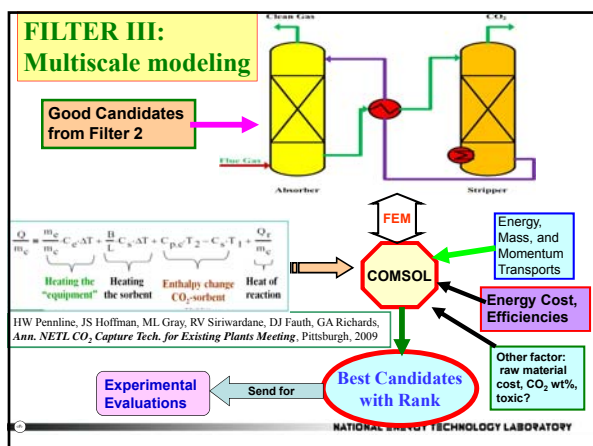
Oxides: M₂O, NO, M=Li, Na, K; N= Be, Mg, Ca, Sr, Ba
Hydroxides: MOH, N(OH)₂

Our goals:

- (1) Validating our screening methodology and verifying the experimental findings;
- (2) Based on CaO, to search better oxides and hydroxides;
- (3) Based on the results of individual oxide or hydroxide, explore the mixture of solid sorbents, such as NaOH/CaO, Mg(OH)₂/Al₂O₃, *etc.*

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Current Working on Large Data Sets

Experimental evidences show that the behaviors of substituted or doped solid materials have better CO₂ capture performances comparing with the pure substances. e.g.

- (1) Li_{1-2x}M_xZrO₃, (M=Na, K, 0<x<2) better than Li₂ZrO₃ and Na₂ZrO₃;
- (2) Doped CaO with Zr (Zr/Ca=3:10) better than CaO;

Using our computational screening methodology, we are exploring different classes of oxides, multi-component salts, semiconductors and substituted and doped sorbents. We are focusing on exploring the trends of substitutions and dopants in the periodic Table. The optimal amounts of substituted and doped atoms will be investigated.

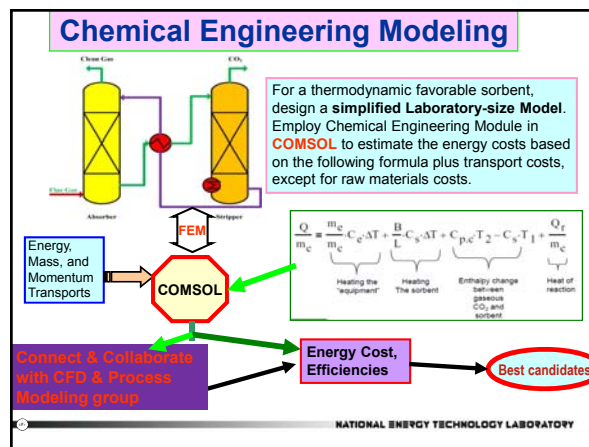
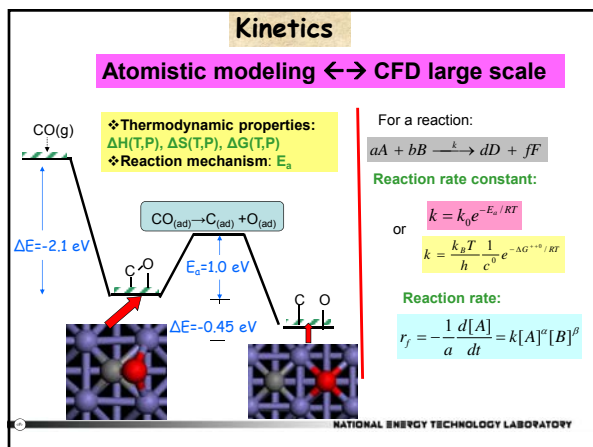
X-Y-O systems: X=Li, Na, K, Ca, Mg, Y=Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sn, Zr, etc

- > Li_{2-x}M_xZrO₃, Li_{2-x}M_xCO₃, Na_{2-x}M_xCO₃, (M=Li, Na, K);
- > Ca_{1-x}M_xO, (M= Si, Ti, Cr, Co, Zr, Ce);
- > Li_xMSiO₄, M=Ca, Mg, Mn, Fe, Co, Zn, Cd, Al, etc;

Biological and organic systems.

DFT performed on Several hundreds of solids. Several good candidates are identified. Further calculations are undergoing.

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No practical regenerable absorbents for CO₂ removal from warm syngas (300 – 500 °C).

Absorbent	Reactions for CO ₂ capture	ΔH° , K J/mol. CO ₂	T, °C for CO ₂ capture	T, °C for CO ₂ release	Capacity, mmol CO ₂ /g
MEA	2MEA + CO ₂ ↔ MEACOO + MEAH ⁺	-167	40-65	100-150	8.2
K ₂ CO ₃	K ₂ CO ₃ + CO ₂ + H ₂ O ↔ 2KHCO ₃	-143	~50	350-400	7.2
Na ₂ CO ₃	Na ₂ CO ₃ + CO ₂ + H ₂ O ↔ 2NaHCO ₃	-136	60-70	100-200	9.4
Li ₂ SiO ₃	Li ₂ SiO ₃ + CO ₂ ↔ Li ₂ CO ₃ + Li ₂ SiO ₃	-142	600	850	8.3
CaO	CaO + CO ₂ ↔ CaCO ₃	-178	600-700	800-900	17.9

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Property dominating factor: the mixing temperature

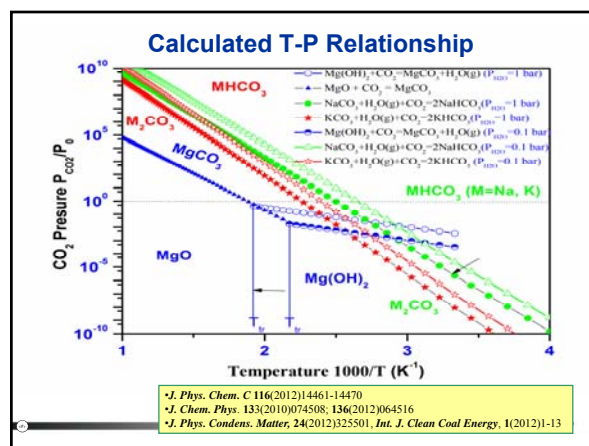
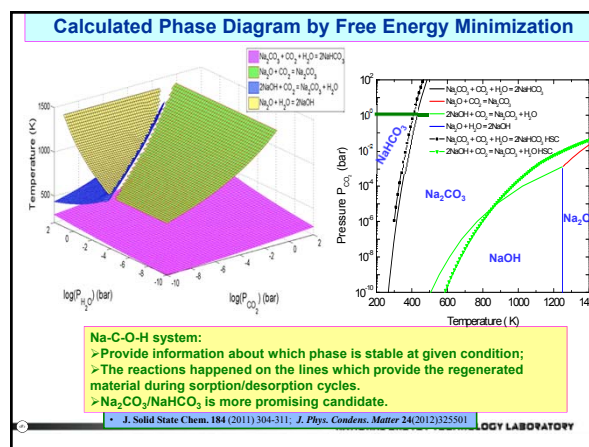
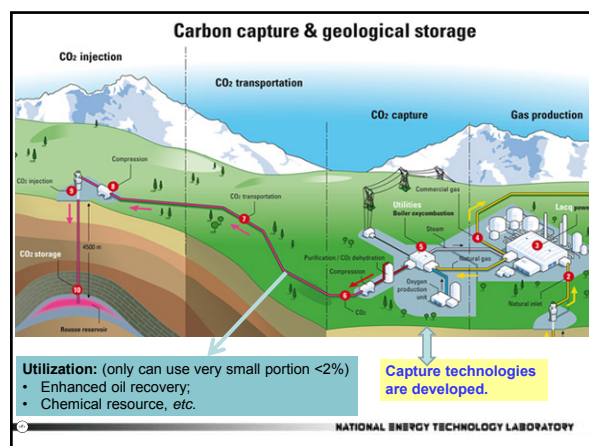
Materials	BET surface area m ² /g	TGA Performance CO ₂ wt%	
		Initial	10 Cycles.
Nano MgO	702	3.1	NA
5C synthesized	19.9	49.7	2.0
17C synthesized	16.8	50.6	5.2
24C synthesized	15.6	40.1	14.7
30C synthesized	9.3	42.5	15.1
37C synthesized	2.9	24.0	12.2

Test condition: CO₂ pressure swing at 400°C. (100% CO₂ ~100% N₂)

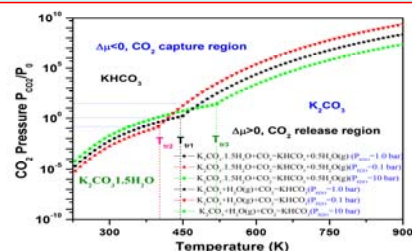
How to Prepare Stable MgO-Na₂CO₃ Double Salt Absorbents ?

1. Slowly mix Na₂CO₃ solution and Mg(NO₃)₂ solution at ~30 °C. White slurry forms.
2. Settle the slurry overnight at room temperature (~25°C).
3. Filtration under vacuum.
4. Dry the solid product at 70-120 °C.
5. Activate the powder at 400°C for 3 hr.

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Phase-diagram of K_2CO_3 - CO_2 - H_2O



The regenerated solid from $KHCO_3$ depends on the P_{H_2O} and T :
 > With high P_{H_2O} , at low temperature ($<T_{tr}$), get $K_2CO_3 \cdot (H_2O)_{1.5}$;
 > Above T_{tr} , obtain anhydrous K_2CO_3 ;
 > T_{tr} can be increased by increasing P_{H_2O} .
 > Korean scientists did find when CO_2/H_2O ratio=2:3, the sorbent has better performance. Further experimental study is conducted by Dr. Jonathan Lekse

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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 weak 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:

- $T_A > T_B$, 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
- $T_A > T_B$, 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
- $T_A \approx T_B$, 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.

PCCP 15(2013)13538-13558

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Summary of the Capture Reactions

reaction	Wt%	ΔE_{DFT} (kJ/mol)	ΔE_{ZP} (kJ/mol)	ΔH (kJ/mol)	ΔG (kJ/mol)	T_1 (K)	T_2 (K)
$Li_2O + CO_2 \rightarrow Li_2CO_3$	147.28	-203.96	4.52	-180.89	-133.42	1375	1025
$\frac{1}{2}Li_2SiO_3 + CO_2 \rightarrow Li_2CO_3 + \frac{1}{2}Li_2SiO_3$	73.51	-181.97	5.16	-177.37	-129.11	1325	985
$\frac{1}{2}Li_4SiO_4 + CO_2 \rightarrow Li_2CO_3 + \frac{1}{2}Li_4SiO_4$	98.01	-154.99	5.42	-150.13	-102.04	1115	835
$Li_2SiO_3 + CO_2 \rightarrow Li_2CO_3 + Li_2SiO_3$	36.72	-148.78	5.97	-143.55	-94.05	1025	775
$\frac{1}{2}Li_4SiO_4 + CO_2 \rightarrow Li_2CO_3 + \frac{1}{2}Li_4SiO_4$	73.44	-111.42	6.07	-104.36	-57.44	765	585
$Li_2Si_2O_5 + CO_2 \rightarrow Li_2CO_3 + 2Li_2SiO_3$	20.98	-169.26	13.09	-158.09	-104.38	1045	805
$\frac{1}{2}Li_4Si_2O_7 + CO_2 \rightarrow Li_2CO_3 + \frac{1}{2}Li_4Si_2O_7$	62.93	-105.79	8.48	-96.08	-48.68	695	525
$Li_2SiO_3 + CO_2 \rightarrow Li_2CO_3 + SiO_2$	48.92	-74.06	6.18	-65.08	-20.83	505	385
$Li_2Si_2O_5 + CO_2 \rightarrow Li_2CO_3 + 2SiO_2$	29.33	-66.75	5.90	-54.06	-13.87	455	345
$Li_2Si_3O_8 + CO_2 \rightarrow Li_2CO_3 + 3SiO_2$	20.94	-63.83	5.52	-48.60	-11.26	435	335

Phys. Rev. B 84(2011)104113, 79(2009)014301; PCCP 15 (2013)9752-9760, 13538-13553

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Summary of Li_2O/ZrO_2 Mixtures

The weight percentage of CO_2 capture, the calculated energy change (ΔE^{DFT}), the zero-point energy change (ΔE^{ZP}) and the thermodynamic properties (ΔH , ΔG) of the CO_2 capture reactions. (unit: kJ/mol). The turnover temperatures (T_1 and T_2) of the reactions of CO_2 capture by solids under the conditions of pre-combustion ($P_{CO_2}=0.1$ bar) and post-combustion ($P_{CO_2}=0.1$ bar) are also listed.

Li_2O/ZrO_2 ratio	reaction	absorbing CO_2 Wt%	ΔE^{DFT}	ΔE^{ZP}	ΔH (T=300K)	ΔG (T=300K)	Turnover T (K) T_1 T_2
Li_2ZrO_6	$\frac{1}{2}Li_4ZrO_7 + CO_2 \rightarrow Li_2CO_3 + \frac{1}{2}ZrO_2$	72.50	-185.495	5.681	-200.762	-151.694	1460 1090
4:1	$\frac{1}{2}Li_4ZrO_7 + CO_2 \rightarrow Li_2CO_3 + \frac{1}{2}Li_4ZrO_3$	54.38	-206.945	3.804	-215.156	-167.851	>1500 1220
	$\frac{1}{2}Li_4ZrO_7 + CO_2 \rightarrow Li_2CO_3 + \frac{1}{2}Li_4ZrO_6$	45.31	-203.751	3.914	-220.043	-172.551	>1500 1250
$Li_2Zr_2O_7$ 3:2	$\frac{1}{2}Li_4Zr_2O_7 + CO_2 \rightarrow Li_2CO_3 + \frac{1}{2}ZrO_2$	39.28	-155.942	8.624	-169.500	-117.564	1140 880
Li_2ZrO_3 1:1	$Li_2ZrO_3 + CO_2 \rightarrow Li_2CO_3 + ZrO_2$	28.75	-146.648	11.311	-158.562	-103.845	1000 780

Turnover T: $Li_2ZrO_6 > Li_2Zr_2O_7 > Li_2ZrO_3$
 Li_2O/ZrO_2 ratio: 4:1 3:2 1:1

Question: Can Li_2ZrO_6 & $Li_2Zr_2O_7$ be fully regenerated?
 Dr. Jonathan Lekse is currently working on it.

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

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