Instructions for Preparing Manuscripts for TechConnect World 2015

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ABSTRACT

These pages provide an example of the layout and style required for the preparation of four-page papers for the TechConnect World 2015 technical proceedings. Documents must be submitted in electronic (Adobe PDF file) format. Please study the enclosed materials before beginning the final preparation of your paper. Proofread your paper carefully before submitting (it will appear in the published volume in exactly the same form). Your PDF manuscript must be uploaded online by April 11th, 2015. You will receive no proofs. Begin your paper with an abstract of no more than 18 lines. Thoroughly summarize your article in this section since this text will be used for on-line listing and classification of the publication.

Keywords: provide up to five comma separated, keywords for indexing, don't capitalize

1 PAPER LAYOUT

Text should be produced within the dimensions shown on these pages; each column should be **85 mm** wide. The two columns should be separated by 10 mm and should be **right/left justified**. Use a **US-Letter** paper size (8-1/2x11"), and a print area no larger than **235 mm** (length) **x 180 mm** (width). On each page of the manuscript, position the print area **20 mm from the top** and **15 mm from the left** edge of the paper (see Fig. 1). Make use of the maximum stipulated length except for the following cases, (a) do not begin a new section at the bottom of a page, transfer the heading to the top of the next column, (b) you may exceed the text area by one line to complete a section of text or a paragraph.

2 TEXT FORMAT

The title should be in boldface letters centered across the top of the first page using 14-point type. First letter capitals only for the title. Insert a blank line after the title, followed by Author Name(s) and Affiliation(s), centered and in 12 point non-bold type. The paper begins with the abstract and keywords followed by the main text. It ends with a list of references.

2.1 Fonts and Spacing

Times or Times Roman is the recommended typeface for the main text using 10-point type. The smallest allowed type size for all text, figures, captions, references and within figures is 10-points. See Table 1 for a compete summary of Font formats. Single (1.0) line spacing is recommended for the main text.

2.2 Section and Sub-section Headings

Section headings should be 12-point boldface capital letters, centered in the column. Sub-section headings require initial capitals using boldface and left justification. Headings should appear on separate lines, using the Arabic numbering scheme. The abstract and reference section headings are not numbered.

2.3 Page Numbers, Footers and Headers

Do not put page numbers on page. Do not put running footers or headers on any page.

2.4 References

References should be collected at the end of your paper. They should be prepared according to a recognized style, e.g. the Harvard or sequential numeric system making sure that your accumulated list corresponds to the citations made in the main text and that all material mentioned is generally available to the readers. When referring to them in the text, type the corresponding reference number in square brackets as in this example [1].

3 EQUATIONS

Equations must be placed flush-left with the text margin and preceded and followed by a line of white space.

$$\frac{ih}{2\pi}\frac{\partial\psi}{\partial t} = -\frac{h^2}{8\pi^2 m}\Delta\psi + U(x,y,z,t)\psi \qquad (1)$$

Numbered equations should be numbered consecutively, with numbers in parentheses, flush right, and level with the last line of the equation.

4 TABLES AND ILLUSTRATIONS

Tables and illustrations can appear within columns or span both columns. If two column figures or tables are required, place them at the top or at the bottom a page. They should have a self-contained caption and be center justified. Figures must be 600 dpi resolution or equivalent. All lettering should be 10-point type or larger. Figures must not extend into the margins.

	Style	Size	Justified
Title	**Bold**	**14**	**Center**
Authors	Normal	12	Center
SECTION	**BOLD, ALL CAPS**	**12**	**CENTER**
Subsection	**Bold**	**12**	**Left**
Main Text	Normal	10	Left/Right
Captions	Normal	10	Center
Figure Text	Normal	10	N.A.

Table 1: Formatting summary for TechConnect World manuscripts.

Figures and Tables should be sequentially numbered. Captions should be centered and use the same type and size font as regular text.

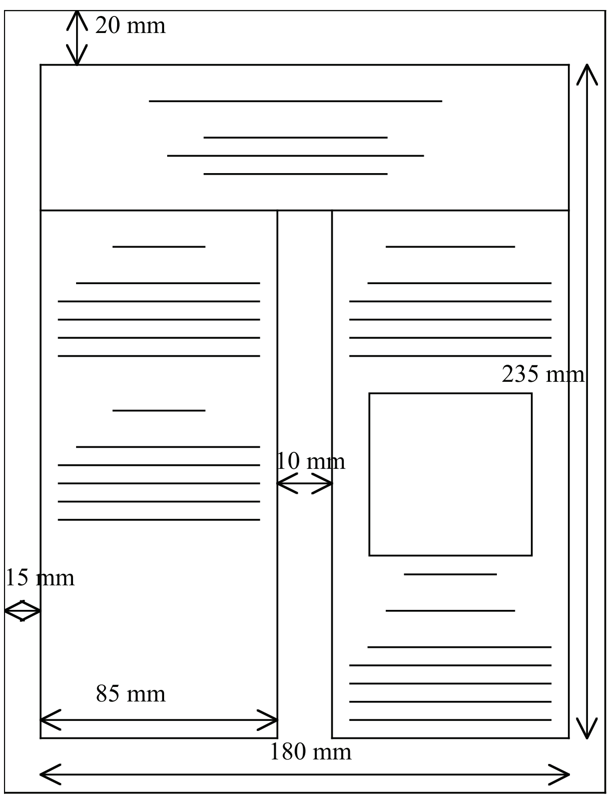

Figure 1: Formatting dimensions for manuscripts.

5 COLOR

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Manuscripts received after April 11th, 2015, not uploaded online, or without a signed copyright form will not be published[1].

REFERENCES

[1] Timoshenko and Woinowski-Krieger, "Theory of Plates and Shells," McGraw-Hill, 415-4215, 1959.

[2] D. Snow, M. Major and L. Green, Microelectronic Engr. 30, 969, 1996.

[3] Author, "Title (optional)," Journal, Volume, Pages, Year.

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Theoretical Synthesis of Mixed Materials for CO_2 Capture Applications

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TechConnect World Innovation Conf. & Expo

(11:20-11:40 am, Jun. 15, 2015)

(Gaylord National Resort & Convention Center Camellia 1)

Collaborators

•Drs. Dan C. Sorescu, David Luebke, H. W. Pennline, Bryan Morreale, Jonathan Lekse (NETL)

•Drs. Xianfeng Wang, Bingyun Li (WVU)

•Drs. Keling Zhang, Xiaohong S. Li, David King (PNNL)

•Drs. Jinling Chi, Lifeng Zhao, Yunhan Xiao (CAS)

•Drs. Heriberto Pfeiffer, Brenda Alcantar-Vazquez (NAUM)

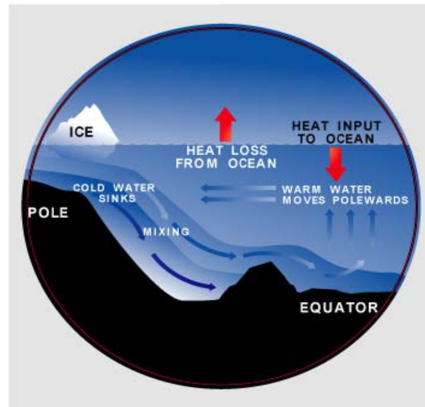
•Drs. Bo Zhang, J. Karl Johnson (Pitt)

•Prof. K. Parlinski (IFJ, Poland)

•Prof. J. Woods Halley (UMN)

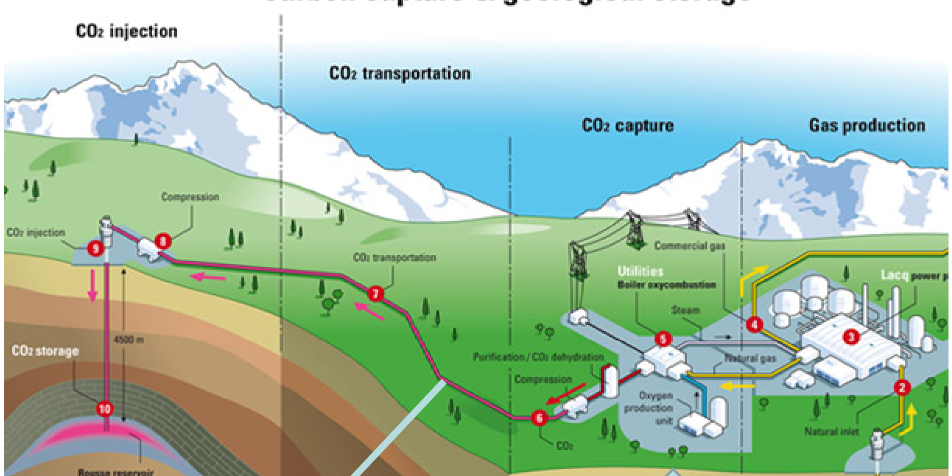
Motivation

- CO_2 emission causes Global Warming.



- To solve such environmental issue, instead of emitting into atmosphere, the CO_2 must be captured and sequestrated.

Carbon capture & geological storage

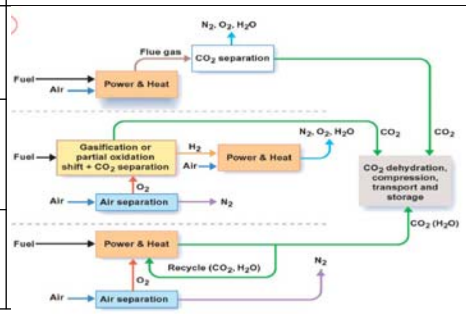


Utilization: (only can use very small portion <5%)
- Enhanced oil recovery;
- Chemical resource, *etc*.

Capture technologies are developed.

Current CO_2 Capture Technology

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	**Solvent**: Selexsol **Solid**: salts, oxides **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.

- J. D. Figueroa *et al*, **Int. J. Greenhous Contr. 2**(2008)9-20
- **Applied Energy**, 102(2013)1439-47

Objectives

- To capture CO_2, we need materials with optimal performance and low costs;
- We are establishing ***a theoretical procedure*** *to* identify most potential candidates of CO_2 solid sorbents from a large solid material databank*;*
- Computational synthesis new materials to fit industrial needs;
- To explore the optimal working conditions for the promised CO_2 solid sorbents, especially from room to warm T ranges with optimal energy usage.

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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:

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

If no H_2O involved, P_{H2O} term vanished

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

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

Reaction Heat:

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

- ***Proc. of 7th Ann. Conf. on Carbon Capture & Sequestration***, 2008
- ***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, 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

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

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

Reaction Heat:

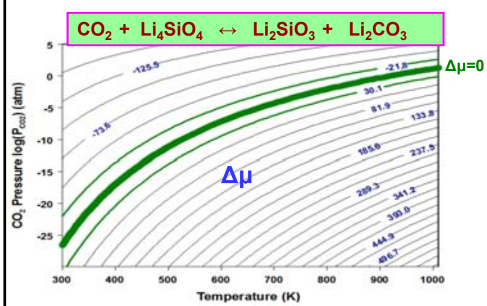
$$\Delta H^{cal}(T)=\Delta\mu^0(T)+T*(-S_{CO_2}\pm S_{H_2O}+\Delta S_{harm})$$

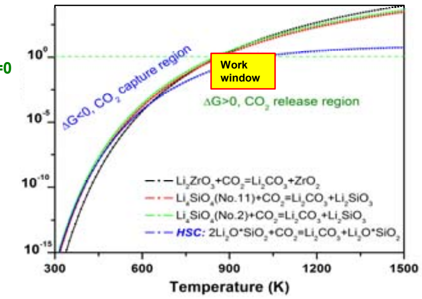
- ***Proc. of 7th Ann. Conf. on Carbon Capture & Sequestration***, 2008
- ***PRB* 79**(2009)014301, ***J. Chem. Phys.* 133**(2010)074508; ***Int. J. Clean Coal & Energy*, 1**(2012)1-11

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



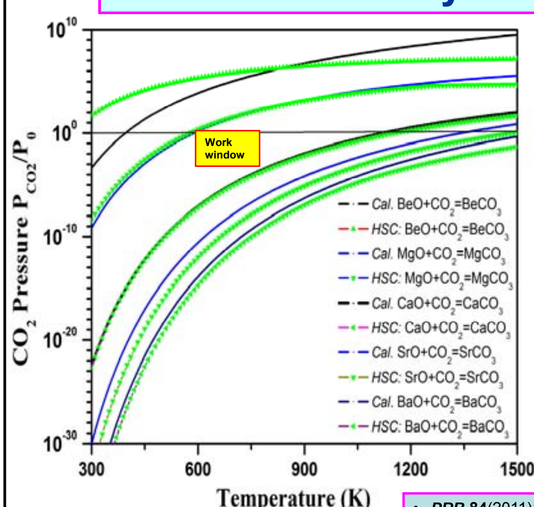


- For each solid, provide its working conditions (T, P_{gas})
- At given work window, select suitable solid materials.

C. Reaction pathways & Energy Cost at Different Capacity

D. Provide basic information for CFD & Process Modeling

New Sorbents by Mixing Solids



- **In many cases, some solids P-T (Δμ=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.

- *PRB* **84**(2011)104113, *79*(2009)014301
- *J. Renewable Sustainable Energy*, **3**(2011)013102, **4**(2012)013109
- Phys. Chem. Chem. Phys. **15**(2013)9752-9760; 13538-13558
- J. Phys. Chem. C**118**(2014)19822-32; **116**(2012)14461-70
- RSC Advances, **5**(2015)34157-65

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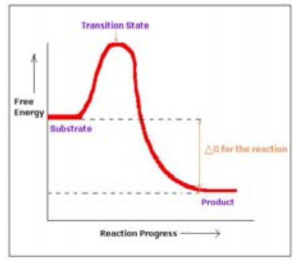
Mixing Scheme

- For a promising sorbents, its CO_2 capture turnover temperature T_t is fixed. In order to use them in different CO_2 capture technologies under specific working conditions, we need to adjust their T_t.



Reactant + CO_2 = Product-CO_2

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

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

Goal on T_t	$\Delta\mu^0(T)$	$\Delta\mu_{product}^{0}(T)$	$\Delta\mu_{reactant}^{0}(T)$
Decrease	Less negative	↑, destablize	↓, stablize
Increase	More negative	↓, stable, lower energy level	↑, destablize, increase energy level

- We proposed a mixing scheme to shift T_t.

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

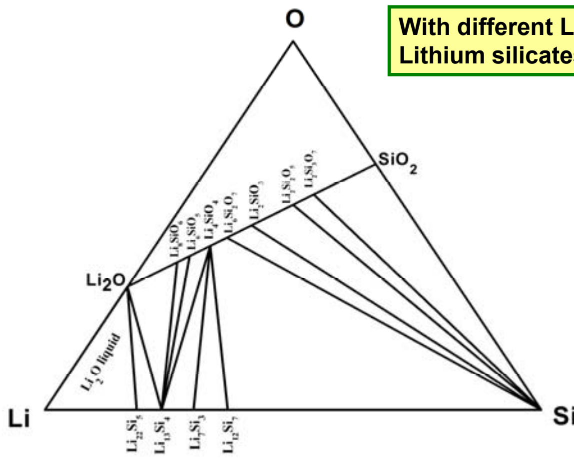
B. $T_A>T_B$, using B component to capture CO_2. In this way, to increase T_B to T_C since $T_C>T_B$. N_2O (N=Na, K, Cs), CaO-promoted MgO

C. 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
- **Phys. Rev. Applied** 3(2015)044013

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.

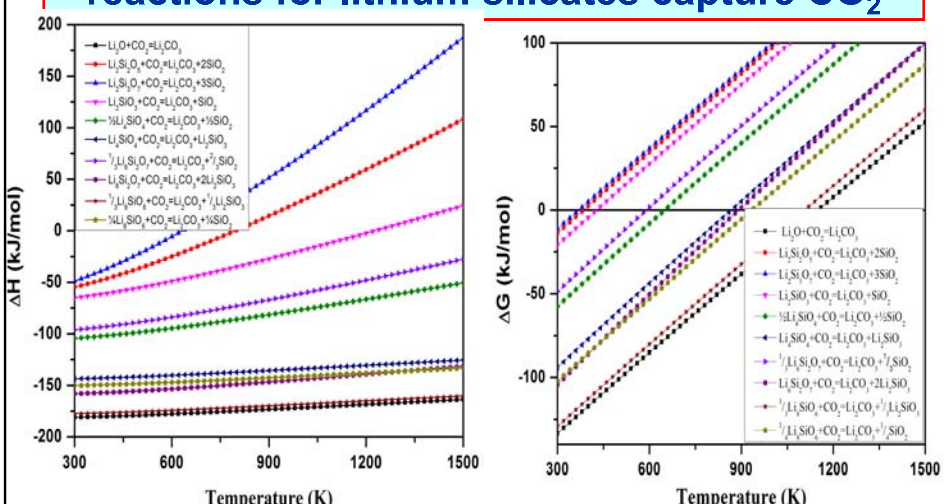


With different Li_2O/SiO_2 ratios, a series of Lithium silicates can be formed.

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

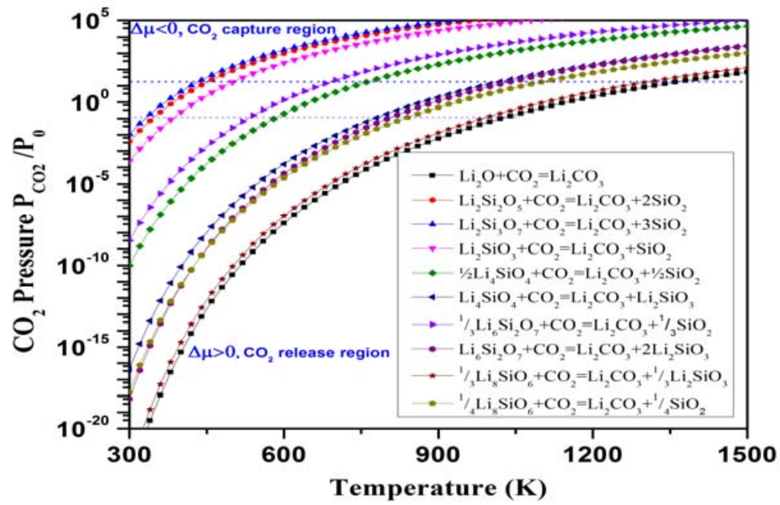
PRB **84**(2011)104113, *79*(2009)014301; *Phys. Chem. Chem. Phys.* *15*(2013)13538-13558

Calculated thermodynamic properties of the reactions for lithium silicates capture CO_2



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

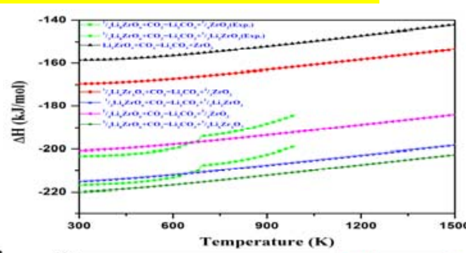
Relationship of chemical potential, temperature, and CO_2 pressure

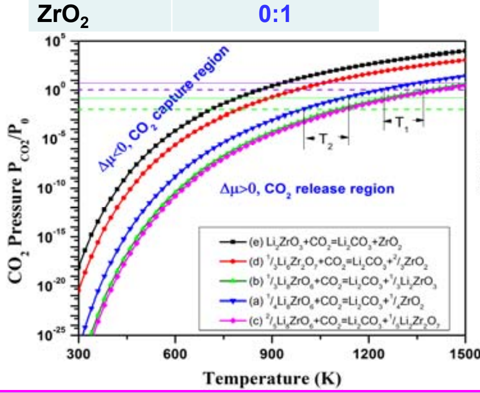


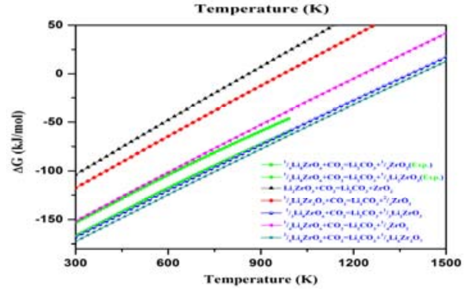
- ***Phys. Rev. B* 84**(2011)104113, *79*(2009)014301; ***PCCP.* 15** (2013)9752-9760, 13538-13553

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



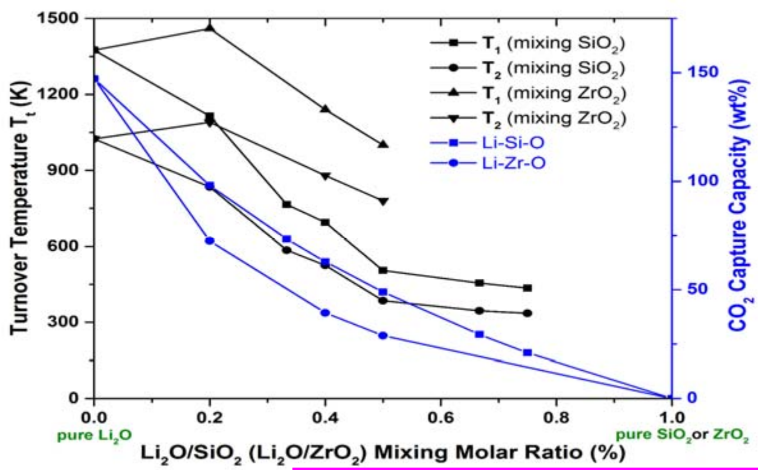




Turnover T: $Li_8ZrO_6 > Li_6Zr_2O_7 > Li_2ZrO_3$
Li_2O/ZrO_2 ratio: 4:1 3:2 1:1

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

Synthesis of new lithium silicate materials by adjusting the Li_2O/SiO_2 or Li_2O/ZrO_2 ratio



- ***Phys. Chem. Chem. Phys.* 15** (2013)9752-9760; 13538-13553
- ***J. Renew. Sustain. Energy*, 3**(2011)013102, **4**(2012)013109
- ***Phys. Rev. B* 84**(2011)104113; ***Phys. Rev. Applied*, 3**(2015)044013

Mixture Sorbents: Case II

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

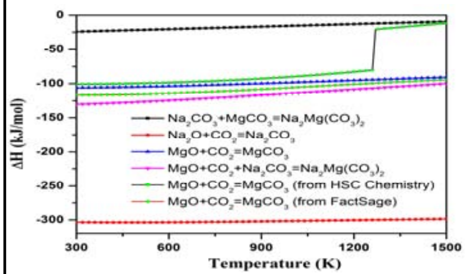
A: Na_2O (or Na_2CO_3)
K_2O (or K_2CO_3)
CaO (or $CaCO_3$)
B: **MgO** active for CO_2 capture

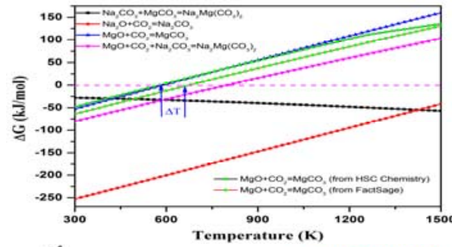
Capture reactions:

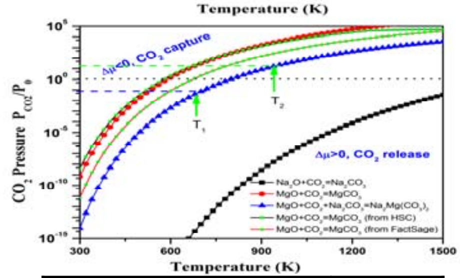
$$N_2CO_3 + MgO + CO_2 \xleftrightarrow{T,P} N_2Mg(CO_3)_2 \quad (N = K, Na)$$

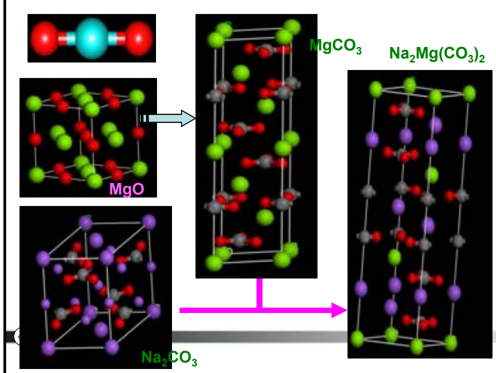
$$CaCO_3 + MgO + CO_2 \xleftrightarrow{T,P} CaMg(CO_3)_2$$

Na_2CO_3-promoted MgO sorbent





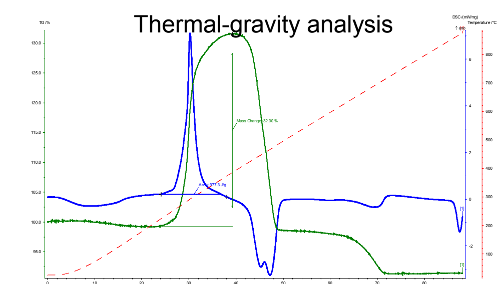


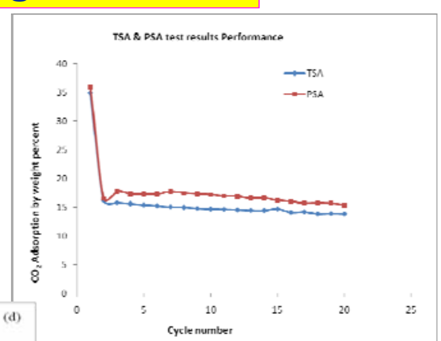


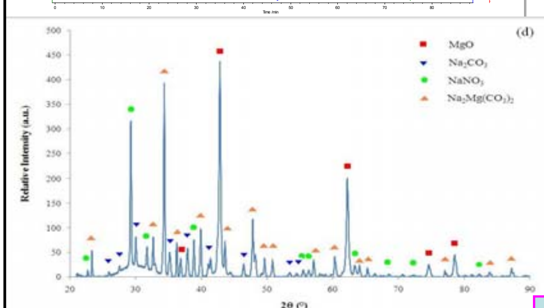
Reaction	ΔH (kJ/mol)
$MgO+CO_2=MgCO_3$	-92.51
$MgCO_3+Na_2CO_3=Na_2Mg(CO_3)_2$	-27.68
$MgO+CO_2+Na_2CO_3=Na_2Mg(CO_3)_2$	-120.19

Na_2CO_3-promoted MgO sorbent

Thermal-gravity analysis



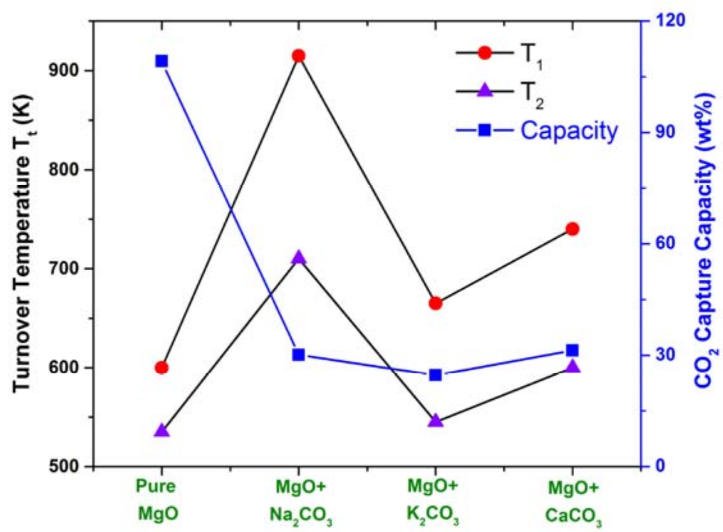




- Adsorption process is through forming $Na_2Mg(CO_3)_2$ double salts;
- CO_2 capture capacity: ~15%(wt)
- Easily regenerated both through TSA & PSA.

- **Int. J. Greenhouse Gas Control 12**(2013)351-358,
- **Adv. Mater. Interfaces 1**(2014)1400030

Turnover T for salt-promoted MgO sorbents



Mixture Sorbents: Case III

Using both A and B as CO_2 capture components

Doped systems: Li_2ZrO_3 doping with M=Na, K to form $Li_{2-x}M_xZrO_3$
Na_2ZrO_3 doping with M=Li, K to form $Na_{2-x}M_xZrO_3$
Li_2MeSiO_4: Me=transitional metal

Such doped system can be treated as mixing of 3 or more oxides:

- $Li_{2-x}M_xZrO_3 \leftrightarrow (2-x)Li_2O+(x)M_2O+ZrO_2$
- $Na_{2-x}M_xZrO_3 \leftrightarrow (2-x)Na_2O+(x)M_2O+ZrO_2$
- $Li_{2-x}M_xMeSiO_4 \leftrightarrow (2-x)Li_2O+(x)M_2O+MeO+SiO_2$

Capture CO_2 reactions:

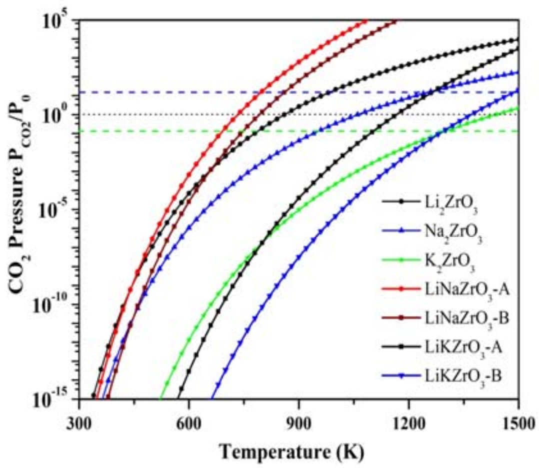
$$LiMZrO_3 + CO_2 \leftrightarrow \frac{1}{2}Li_2CO_3 + \frac{1}{2}M_2CO_3 + ZrO_2 \qquad (M = Na, K)$$

$$Na_{2-\alpha}M_\alpha ZrO_3 + CO_2 \leftrightarrow \frac{2-\alpha}{2}Na_2CO_3 + \frac{\alpha}{2}M_2CO_3 + ZrO_2 \quad (M = Li, K; \alpha = 0, 0.5, 1.0, 1.5, 2.0)$$

$$M_xN_{2-x}MeSiO_4 + CO_2 \leftrightarrow \frac{x}{2}M_2CO_3 + \frac{2-x}{2}N_2CO_3 + MeSiO_3 \quad (M, N = Li, Na, K; Me: \text{transition metal})$$

Mixture Sorbents: Case III

$$LiMZrO_3 + CO_2 \leftrightarrow \frac{1}{2}Li_2CO_3 + \frac{1}{2}M_2CO_3 + ZrO_2 \qquad (M = Na, K)$$



Doped system.

- Such doped system can be treated as mixing 3 oxides:

$LiMZrO_3$←→ 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

Using both Li_2O and M_2O as CO_2 capture components

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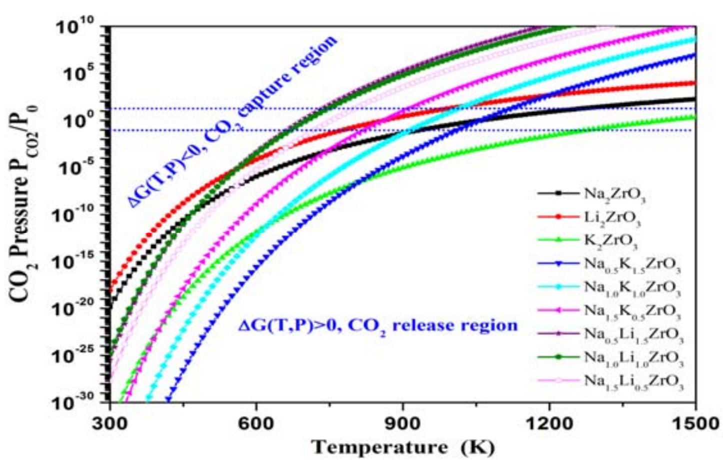
Na_2O+M_2O+ZrO_2 Mixing sorbents

$$Na_{2-\alpha}M_\alpha ZrO_3 + CO_2 \leftrightarrow \frac{2-\alpha}{2}Na_2CO_3 + \frac{\alpha}{2}M_2CO_3 + ZrO_2 \qquad (M = Li, K; \alpha = 0, 0.5, 1.0, 1.5, 2.0)$$



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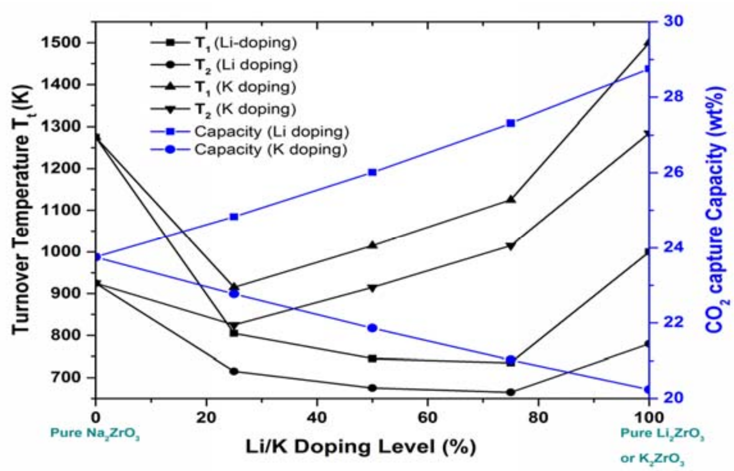
Doping level versus Turnover T



Doping Li into Na_2ZrO_3, T_t decrease with doping level
Doping K into Na_2ZrO_3, T_t first decrease then increase with increasing K-level

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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.
- Depending on the needs of specific capture technology, by different mixing schemes, it's possible to move turnover T of newly formed sorbent to the desired operating T range.
- These results provide guidelines to synthesize sorbent materials by mixing different solids with different ratio.

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