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Kinetics of CO₂ Absorption Into Aqueous Potassium Carbonate Solution Promoted by Carbonic Anhydrase Enzyme

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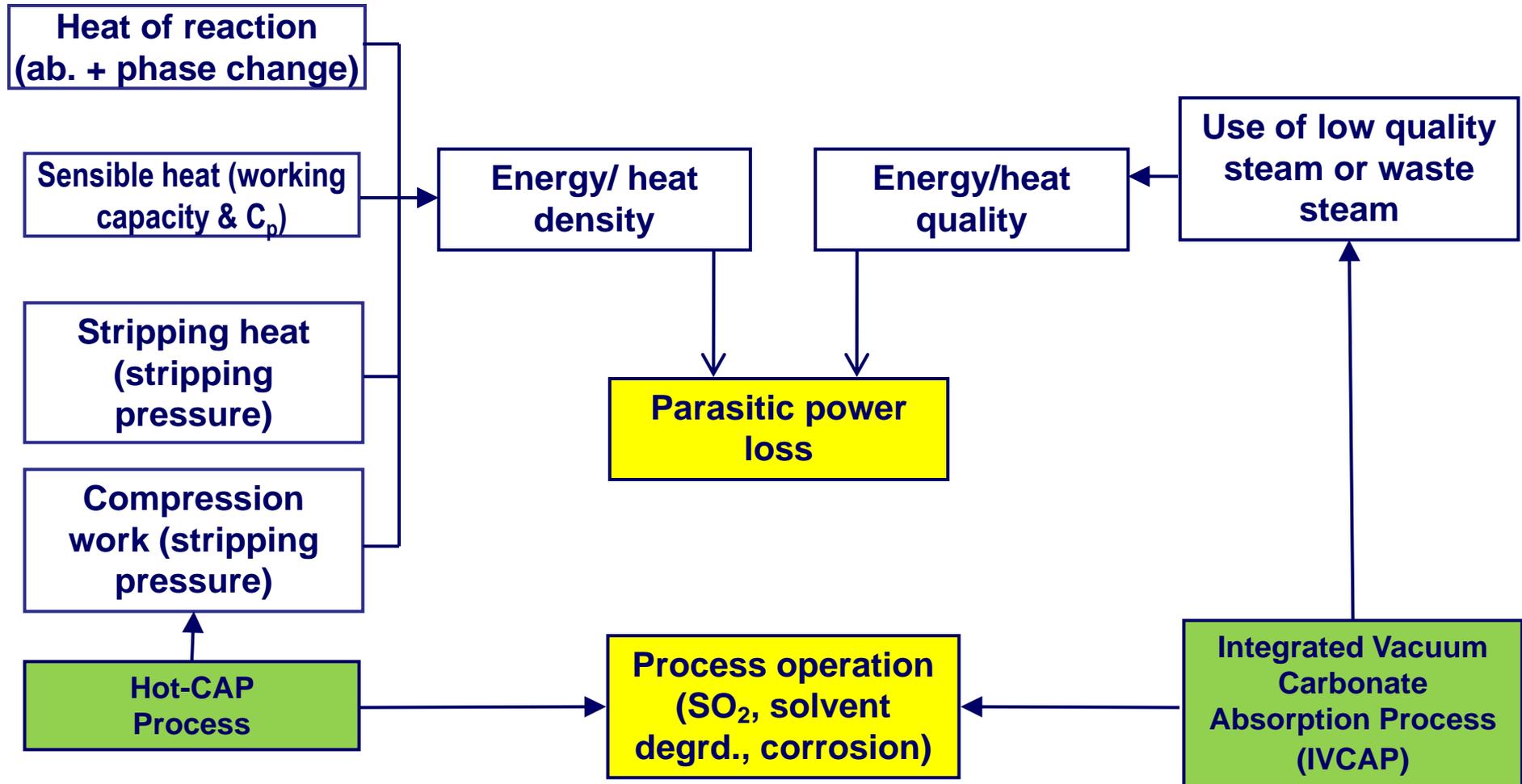
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2011 AIChE Annual Meeting, Minneapolis, MN

October 19, 2011



Background: Hot-CAP & IVCAP processes based on K_2CO_3 solution as solvent for post-combustion CO_2 capture



Outline

- ❑ Introduction
 - *Carbonic Anhydrase (CA)* enzyme applied as a biocatalyst in the Integrated Vacuum Carbonate Absorption Process (IVCAP)
- ❑ Kinetics of CO₂ absorption into K₂CO₃ (PC) solutions promoted by CA enzyme
 - Determination of reaction rate constant
 - Catalytic activity and enhancement factor
- ❑ Long-term thermal stability
- ❑ Summary

CA enzyme is applied as a biocatalyst to promote CO₂ absorption into PC solutions in IVCAP

- ❑ K₂CO₃ (PC) solvent (20-30 wt%)
 - Low absorption heat (600 kJ/kg)
 - High CO₂ capacity
- ❑ Typical operational conditions
 - Absorption at 40-60°C, 1 atm
 - Regeneration by pressure swing (50-70°C, 2-8 psia) to use low quality steam from the power plant
 - CO₂ loading of PC solutions equivalent to carbonate to bicarbonate (CTB) conversion rate ranging between 20% (top) and 50% (bottom)
- ❑ CA enzyme biocatalyst
 - Most efficient catalyst ever known
 - Other catalysts/additives (sodium arsenate, NaClO, formaldehyde, etc.) have some drawbacks, e.g., low activity, toxicity, or instability
 - Mixing with amines or other solvents increases absorption heat

CA enzyme promotes CO₂ absorption into PC solutions

Overall reaction



Reactions are slow in PC solutions without a catalyst (low [OH⁻])



CA enzyme significantly promotes Rx(1)



$$r = -\frac{d[\text{CO}_2]}{dt} = (k_{\text{H}_2\text{O}} + k_{\text{OH}^-}[\text{OH}^-] + k_{\text{CA}}[\text{CA}]) \times [\text{CO}_2]$$

Cents A.H.G., Brillman D.W.F., Versteeg G.F. Chem. Eng. Sci. 2001, 56:1075-1083.

Pandey A., Webb C., Soccol C. R., Larroche C. (Eds), Enzyme Technology, New York: Springer Science, 2006.



Kinetics: classic theory for gas absorption

- Classic Danckwerts theory for gas absorption with chemical reaction

$$R = k_L \sqrt{\left(1 + \frac{Dk_{ov}}{k_L^2}\right)} \times (C^* - C^b)$$

$$C^* = \frac{P_i}{H e_i} \quad E = \sqrt{\left(1 + \frac{Dk_{ov}}{k_L^2}\right)} \quad (\text{Enhancement factor})$$

$$k_{ov} = k_{H_2O} + k_{OH} [OH^-] + k_{CA} [CA]$$

Criterion for pseudo-first order reaction

$$C^* \left(\frac{1}{a} + \frac{2}{b} \right) \left[\sqrt{\left(1 + \frac{Dk_{ov}}{k_L^2}\right)} - 1 \right] < 0.1$$

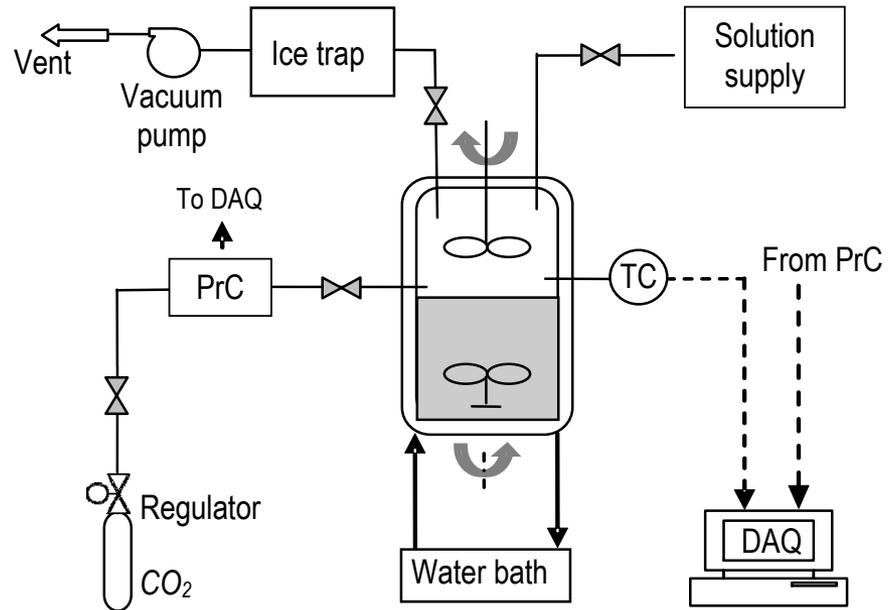
Kinetics: determination of k_{CA} using a stirred cell reactor

$$R = -\frac{V_G}{A \times R_{gas} T} \frac{dP_i}{dt}$$

$$= k_L \sqrt{\left(1 + \frac{Dk_{ov}}{k_L^2}\right)} \times \left(\frac{P_i}{He_i} - C^b\right)$$

When $C^b \ll C^*$

$$\ln\left(\frac{P_{i,0}}{P_i}\right) = \sqrt{k_L^2 + Dk_{ov}} \frac{R_{gas} T A}{V_G He_i} \Delta t$$



(PrC: Pressure controller; TC: Thermal couple; DAQ: Data acquisition)

Advantages of a stirred cell reactor

- ❑ Only gas pressure change profile used for calculation of CO_2 absorption rates
- ❑ A relatively constant gas-liquid interface area
- ❑ Negligible impact of gas phase mass transfer resistance (pure CO_2 gas used)
- ❑ Easy operation (batch mode)

Kinetics: determination of k_{CA} using a stirred cell reactor (contd.)

□ Designing experiments under conditions that satisfy

- Criterion for pseudo first order reaction
- Negligible C^b ($C^b \ll C^*$)

$$\ln\left(\frac{P_{i,0}}{P_i}\right) = \sqrt{k_L^2 + Dk_{ov}} \frac{R_{gas}TA}{V_G He_i} \Delta t$$

Slope of the lines: $m_{CA} = \sqrt{k_L^2 + D(k_{H_2O} + k_{OH}[OH^-] + k_{CA}[CA])}$ (Containing CA)

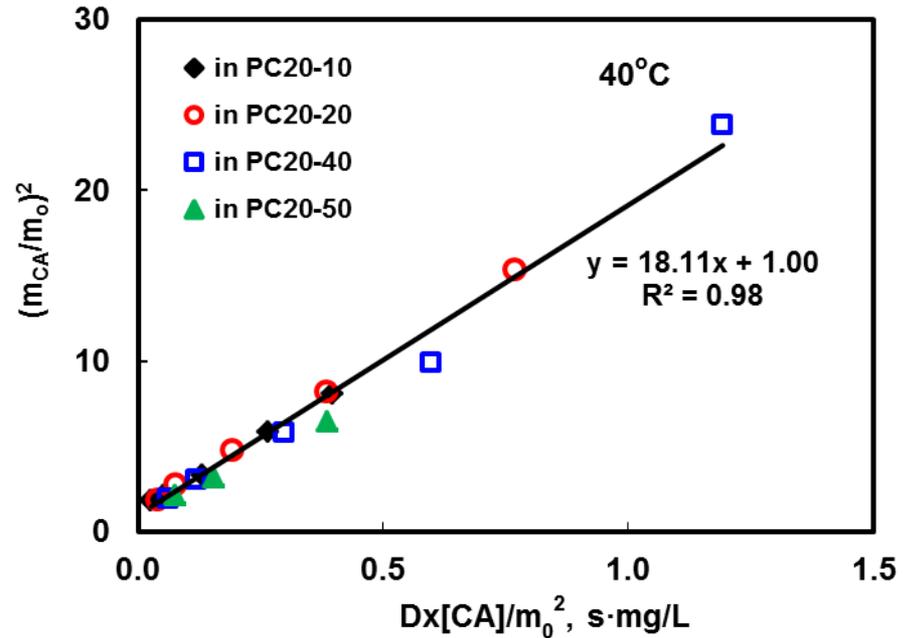
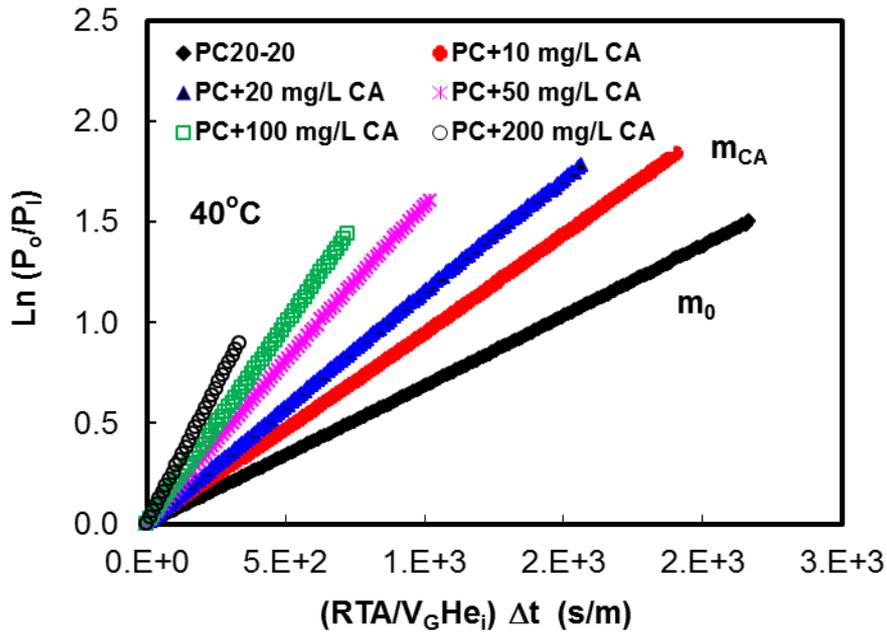
$$m_0 = \sqrt{k_L^2 + D(k_{H_2O} + k_{OH}[OH^-])}$$
 (Without CA)

$$\left(\frac{m_{CA}}{m_0}\right)^2 = 1 + \frac{k_{CA}D[CA]}{m_0^2}$$

- k_{CA} can be experimentally determined by measuring the rates of CO_2 absorption into PC solutions w/o and w/ CA enzymes.
- Errors of k_{CA} values associated with calculation/estimation of physical properties can be minimized.



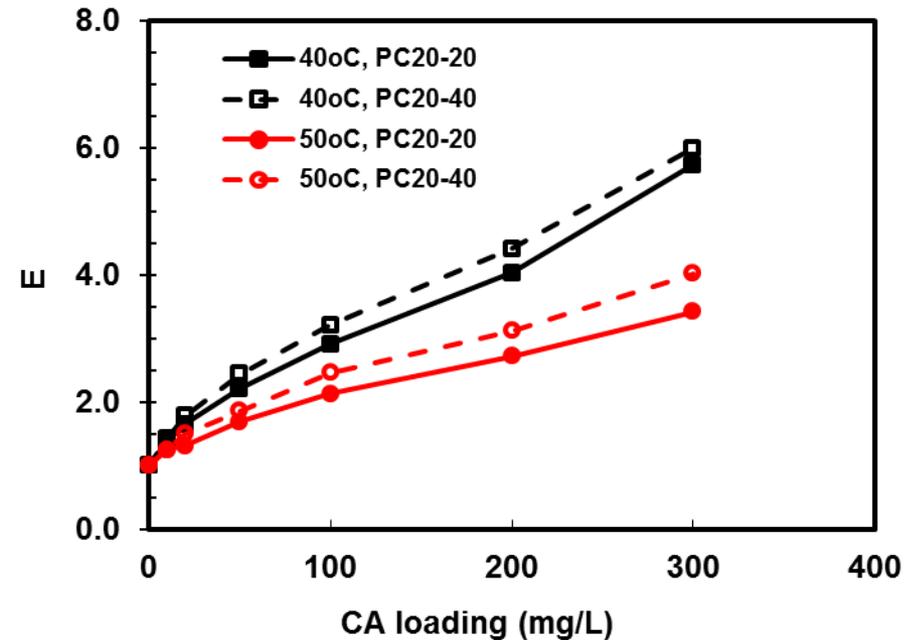
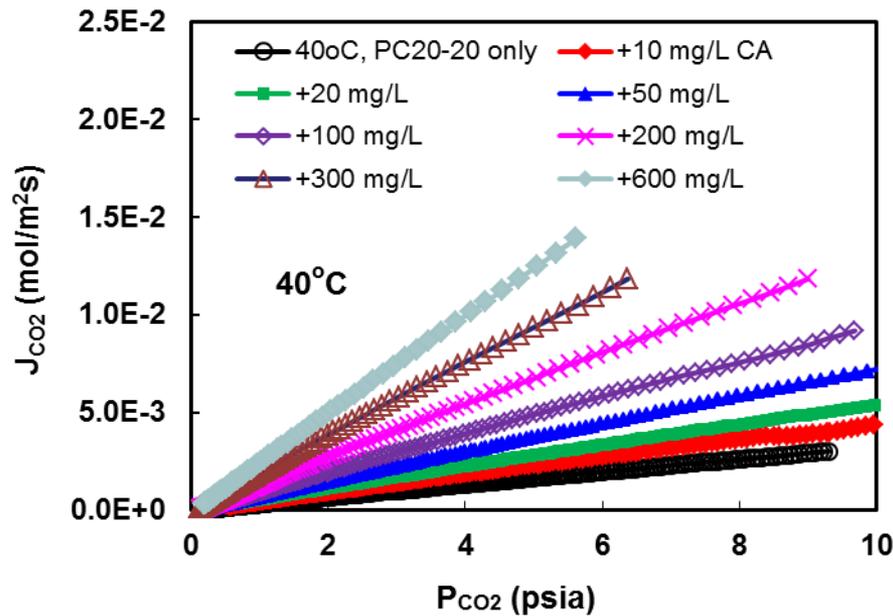
Kinetics: determination of k_{CA} from experimental data (contd.)



- Good linear relationships were obtained from the experimental data:
 - CA enzyme dosage (10 to 200 mg/L);
 - Temperature (25~50°C);
 - CO₂ loading (10%~50% CTB).

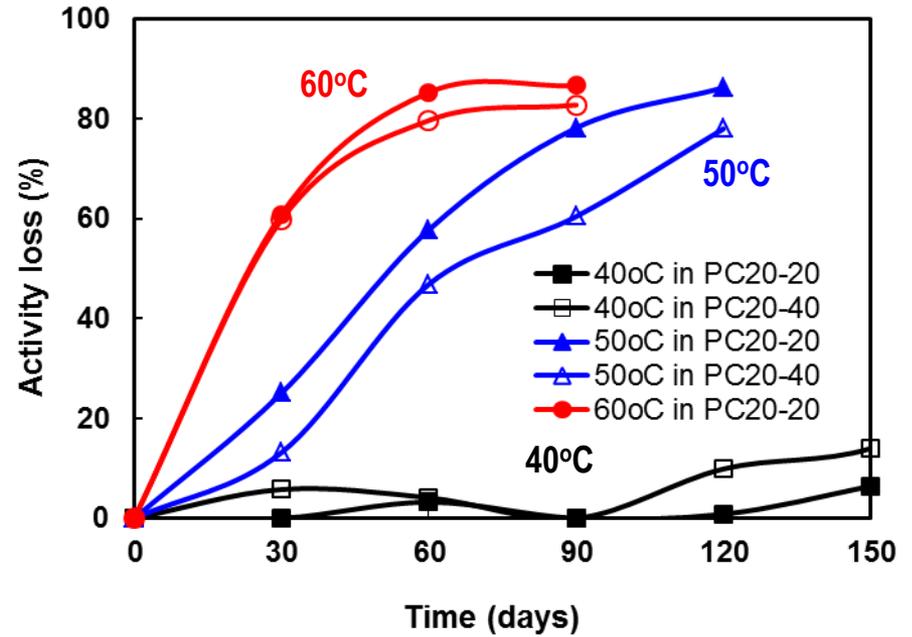
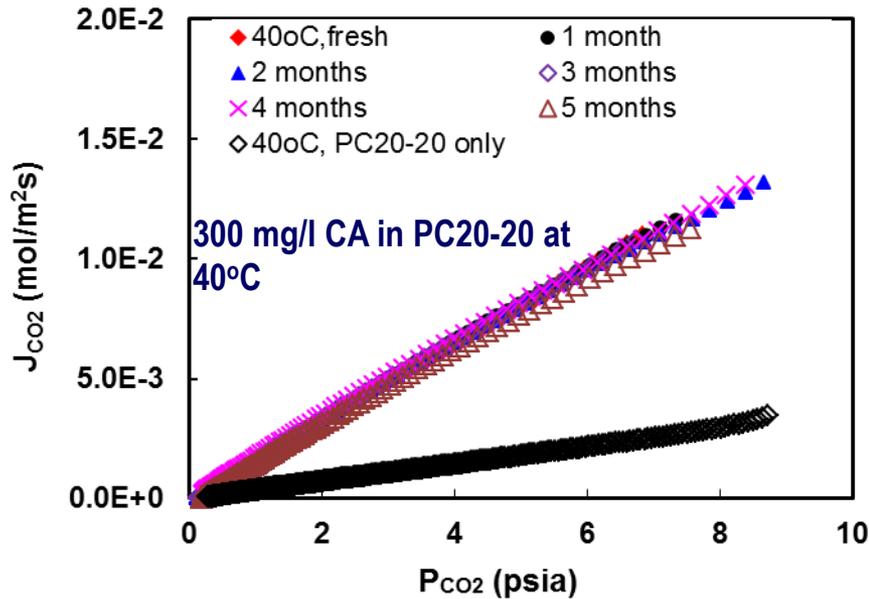
Temperature (°C)	k_{CA} (L/mg·s)	k_{CA} (M ⁻¹ ·s ⁻¹)
25	15.2	4.6x10 ⁸
40	18.1	5.4x10 ⁸
50	15.8	4.7x10 ⁸

Catalytic activity and E of CA enzyme to promote CO₂ absorption



- ❑ Rates increased with increasing CA dosage (but may level off at high dosages due to ion diffusion limit)
- ❑ Rates with 300 mg/l CA increased by ca. 6 and 3.5 times at 40°C and 50°C, respectively.
- ❑ E values were higher in PC solutions with higher CTB conversion rates such that the actual CO₂ absorption rates promoted by CA are comparable along an absorption column (data not shown).

Long term thermal stability of CA enzyme



$$\text{Activity loss} = \frac{E_{CA,0} - E_{CA,t}}{E_{CA,0} - 1.0} \times 100\%$$

- About 10% activity loss at 40°C in 5 months
- About 50% activity loss at 50°C in 2 months
- About 60% activity loss at 60°C in 1 month
- Temperature is a critical factor for long-term stability



Summary

- ❑ The values of k_{CA} were experimentally determined to be relatively a constant of $5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 25~50°C in PC solutions with 10~50% CTB conversion rates.
- ❑ Rates of CO_2 absorption increased with increasing CA dosage (but may level off at high loadings due to ion diffusion limitation). Rates promoted by 300 mg/l CA increased by ca. 6 and 3.5 times at 40°C and 50°C, respectively.
- ❑ Temperature is a critical factor for the stability of CA enzyme. The investigated CA enzyme demonstrated good thermal stability: about 10% activity loss at 40°C in 5 months and 50% activity loss at 50°C in 2 months.

Acknowledgements

- ❑ U.S. Department of Energy/ National Energy Technology Laboratory under Agreement No. DE-FC26-08NT0005498
- ❑ Illinois Department of Commerce and Economic Opportunity through the Office of Coal Development and the Illinois Clean Coal Institute under Project No. 08-1/1.1B-3

