Understanding the enhancement effect of high-temperature steam on the carbonation reaction of CaO with CO₂

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Steam is always present in flue gases.

Steam can enhance the carbonation, indirect and direct sulphation, and can decrease the oxidation of NH$_3$ on the CaO.


Background

The steam-enhanced carbonation reaction of CaO with CO$_2$ is a widely observed phenomenon, but its mechanism is unclear.

Manovic et al. and Arias et al. suggested that steam does not affect the initial reaction rate in the kinetically controlled stage but enhances the diffusion in the product layer.

Hu et al. concluded that the promoting effect is due to the enhanced ion mobility in the presence of steam.

Wang et al. postulated that the existence of Ca(OH)$_2$ contributes to the carbonation process and that the carbonation of Ca(OH)$_2$ is much faster than that of CaO.

However, Yang and Xiao found that Ca(OH)$_2$ formation may not be the main reason for the significant carbonation enhancement.

This research aimed to
(1) apply the theories of defect chemistry and ion diffusion to analyze the steam enhancement,
(2) discuss the effects of steam fraction and temperature on carbonation.
The interaction of $\text{H}_2\text{O}$ molecule with oxygen vacancy

Dissociative adsorption of $\text{H}_2\text{O}$ occurs on the $\text{CaO}$ and $\text{CaCO}_3$ surface.

Oxygen vacancies are shown to dissociate $\text{H}_2\text{O}$ molecules by transferring one proton to nearby oxygen atoms and forming two hydroxyl groups for every vacancy.

\[
\text{H}_2\text{O} \ (g) + v_0^* + O_0 = 2\text{OH}^* 
\]

(I) Oxygen vacancy  
(II) bridging hydroxyl group  
(III) terminal hydroxyl group  
(IV) water molecule.

Red atoms: $\text{O}$

The interaction of H$_2$O molecule with oxygen vacancy

\[ \text{H}_2\text{O} (g) + \text{v}_{\text{O}}^{\bullet\bullet} + \text{O} = 2\text{OH}^{\bullet} \]

**Defect equilibrium**

\[ K = \exp(\Delta S^0 / R) \exp(-\Delta H^0 / RT) = [\text{OH}^{\bullet}]^2 / ([\text{v}_{\text{O}}^{\bullet\bullet}][\text{O}] \rho_{\text{H}_2\text{O}}) \]

**The electroneutrality condition**

\[ 2[\text{v}_{\text{O}}^{\bullet\bullet}] + [\text{OH}^{\bullet}] = [\text{A}] \]

**The lattice structure balance**

\[ [\text{O}] + [\text{v}_{\text{O}}^{\bullet\bullet}] + [\text{OH}^{\bullet}] = [\text{O}] \]

**The fraction of proton defect**

\[ y_{\text{OH}^{\bullet}} = \frac{[\text{OH}^{\bullet}]}{[\text{A}]} = \frac{Kp_{\text{H}_2\text{O}}(1 - \sqrt{1 - \frac{2[A]}{[O]} + \frac{8[A]}{[O]}Kp_{\text{H}_2\text{O}} + \frac{[A]^2}{[O]^2} - \frac{4[A]^2}{[O]^2} Kp_{\text{H}_2\text{O}}})}{(Kp_{\text{H}_2\text{O}} - 4) \frac{[A]}{[O]}} \]

The relationship of proton defect $y_{\text{OH}^{\bullet}}$ with steam $\rho_{\text{H}_2\text{O}}$ is built.
Solid product nucleation and growth

Solid product grows with the morphology of the island shape

A part of solid reactant surface is covered by the product islands

the fraction of reactant surface covered by product: $1 - \alpha$

The other part of solid reactant surface remains in contact with gas

the fraction of fresh reactant surface: $\alpha$
Solid product nucleation and growth

CO$_2$ is in contact with CaO and CaCO$_3$ surface.

*When CO$_2$ makes contact with CaO surface, the carbonation reaction can directly occur on the CaO surface;*
*while for the CaCO$_3$ surface, the diffusion of ions through the CaCO$_3$ product layer is the controlled step.*

CaO conversion

$$X = (X_I + X_{II})(1 - \alpha)$$

- The fraction of CaO surface: $\alpha = \exp[-k_s(C_{CO_2} - C_{CO_2,e})t]$  
- CaO conversion during the product diffusion controlled stage  
- The critical CaO conversion (critical thickness of product layer)
Product layer diffusion

Proposed by Bhatia and Perlmutter and recently validated by Fan et al.:

- $\text{CO}_3^{2-}$ diffuses inward from the CaCO$_3$/gas interface to the CaCO$_3$/CaO interface
- $\text{O}_2^-$ diffuses outward from the CaCO$_3}$/CaO interface to the CaCO$_3$/gas interface
- $\text{CO}_3^{2-}$ and H$^+$ diffuse inward
- $\text{O}_2^-$ and OH$^-$ diffuse outward

With steam present

\[ J_{H^+} + J_{OH^-} + 2J_{O^2-} = 2J_{\text{CO}_3^{2-}} \]

\[ J_{\text{OH}^-} + J_{O^2-} = J_{\text{CO}_3^{2-}} \]
Product layer diffusion

- $\text{CO}_3^{2-}$ and $\text{H}^+$ diffuse inward while $\text{O}_2^-$ and $\text{OH}^-$ diffuse outward

\[
\text{J}_{\text{OH}^-} + \text{J}_{\text{O}_2^-} = \text{J}_{\text{CO}_3^{2-}}
\]

\[
\frac{dX_{\text{II}}}{dt} = D_{v_0}^* \left[0.5(1 - y_{\text{OH}_0^*}) + \frac{D_{\text{OH}_0^*}^*}{D_{v_0}^*} y_{\text{OH}_0^*} \right] \left(1 - \frac{X_{\text{II}}}{X_{\mu} - X_I}\right)
\]

$\text{OH}_0^*_{v_0}$ diffuses faster than $v_0^*$

$D_{\text{OH}_0^*}^*$ is bigger than $D_{v_0}^*$

\[
y_{\text{OH}_0^*} = \frac{Kp_{\text{H}_2\text{O}} (1 - \sqrt{1 - \frac{2[A]}{[O]} + \frac{8[A]}{[O]} Kp_{\text{H}_2\text{O}} + \frac{[A]^2}{[O]^2} - \frac{4[A]^2}{[O]^2} Kp_{\text{H}_2\text{O}}})}{(Kp_{\text{H}_2\text{O}} - 4) \frac{[A]}{[O]}}
\]

CaO $\rightarrow$ $\text{CaCO}_3$

CaO solid conversion

Fick diffusion

CaO $\rightarrow$ $\text{CaCO}_3$

CaO solid conversion

$\text{CO}_2$

$\text{O}_2^-$ $\text{OH}^-$ $\text{H}^+$ $\text{CO}_3^{2-}$

CaCO$_3$

$h$

$h_p$

$h_0$
Validation of OH formation

Water gas shift reaction (WGS)

\[ \text{CO} \rightleftharpoons \text{Co}_{\text{ad}} \]
\[ \text{OH} + \text{CO}_{\text{ad}} \rightleftharpoons \text{COOH}_{\text{ad}} \]
\[ \text{COOH}_{\text{ad}} \rightleftharpoons \text{CO}_2 + \text{H}_{\text{ad}} \]
\[ 2\text{H}_{\text{ad}} \rightleftharpoons \text{H}_2 \]

OH⁻ is required for WGS because OH⁻ reacts with CO to form COOH. COOH finally generates CO₂ and H₂. Hydroxyl groups are formed; otherwise, WGS reaction cannot occur.

500 °C in bubbling fluidized bed reactor, 50g CaO
Validation

\[
\frac{dX_{\text{II}}}{dt} = D_{v_{O}}^{\ast} [0.5(1 - y_{OH_{O}}) + \frac{D_{OH_{O}}^{\ast}}{D_{v_{O}}^{\ast}} y_{OH_{O}}] (1 - \frac{X_{\text{II}}}{X_{\mu} - X_{I}})^{m}
\]

Effect of steam fraction and temperature on the proton defects

proton defects diffuse faster than oxygen vacancies. increasing steam fraction, proton defect increases, whereas oxygen vacancies decreases.

further increasing steam has no big effect, because the amount of H\(_2\)O molecule dissociation is limited by the density of oxygen vacancies.

\[2[v_{O}^{\ast\ast}] + [OH_{O}^{\ast}] = [A]\]
increasing temperature, proton defect decreases, whereas the oxygen vacancy diffusion coefficient and oxygen vacancy fraction increased. Consequently, the weak steam-induced enhancement effect on carbonation ensued.
Rate Equation Method

Effect of steam fraction on CaO conversion in the fast reaction stage in TGA with 15 vol% CO$_2$.

Two stages: fast and slower stages

The developed model can reasonably predict CaO conversion in the kinetically controlled stage, diffusion-limited regime, and transition without/with steam.
Validation: indirect sulphation & catalytic NH\textsubscript{3} oxidation


The enhancement of steam on the sulphation behavior can also be explained and predicted with the developed methods.

Steam fraction increases, OH\textsuperscript{•} increases, while V\textsubscript{O}\textsuperscript{**} decreases. The fraction of NH\textsubscript{3} oxidation decreases while the fraction of NH3 for NO reduction increases, therefore, NO decreases with steam increasing.

\[ \text{NH}_3 + 1.25\text{O}_2 \overset{\text{V}^{**}}{\rightarrow} \text{NO} + 1.5\text{H}_2\text{O} \]

\[ \text{NH}_3 + \text{OH}^* \rightarrow \text{NH}_2 + \text{H}_2\text{O} \]

\[ \text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O} \]
Conclusions

- OH⁻ formation caused by the dissociation of H₂O molecules may explain enhanced carbonation.
- The relationship of oxygen vacancies with OH⁻ was established and integrated into a new carbonation model.
- This new model included a simplified rate equation model to describe product island formation and a multi-ion diffusion model to describes product layer diffusion.
- Carbonation and sorption-enhanced water gas shift reactions in a fluidized bed reactor were conducted to validate the formation of OH⁻.
- The new developed models were validated by experimental data.
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