

S[☀]CRATCES

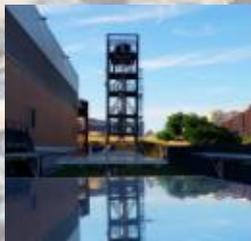
Use of steam during calcination in the CaL-CSP process: Kinetics and cyclability

Juan Arcenegui-Troya



CSIC

CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS



S[☀]CRATCES WEBINAR 10 June 2021

SOLAR CALCIUM-LOOPING INTEGRATION FOR THERMO-CHEMICAL ENERGY STORAGE



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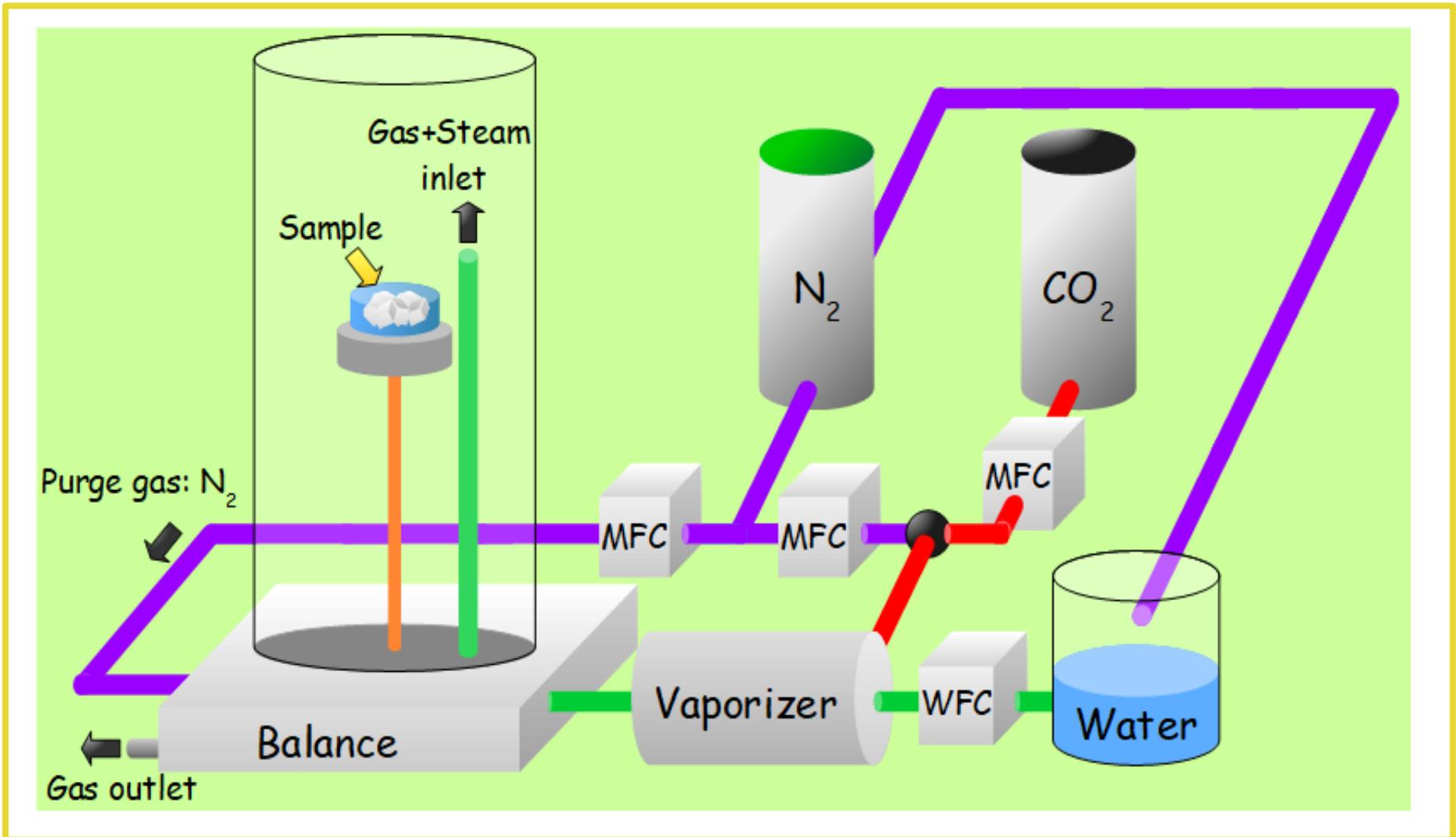


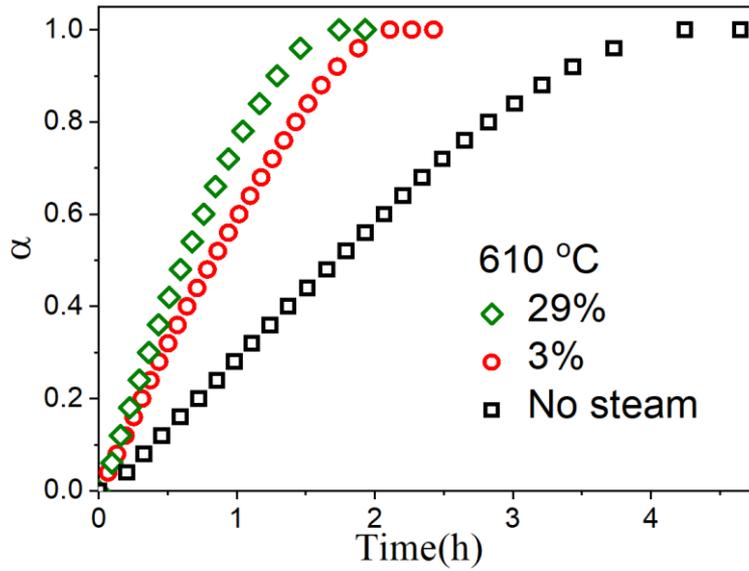
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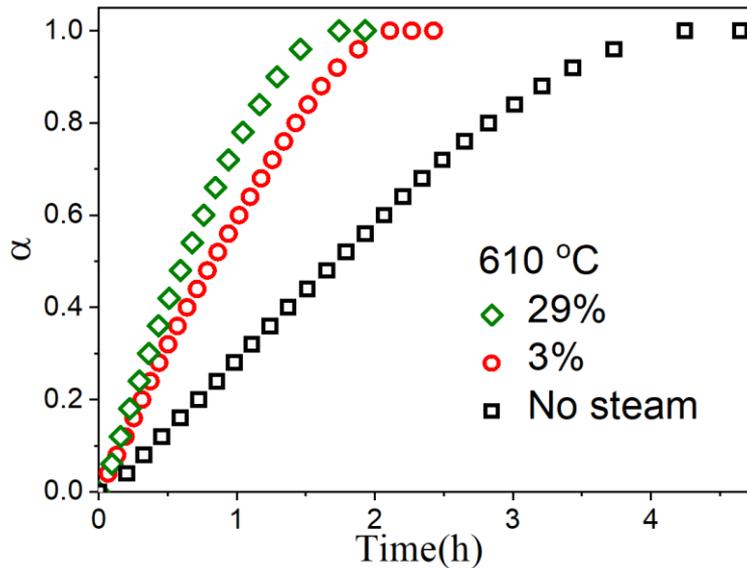
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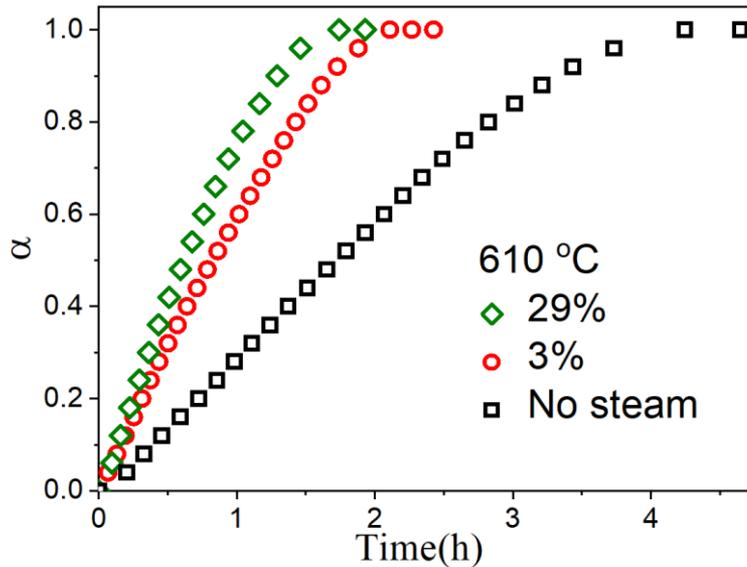
Non-parametric kinetic method



J. Sempere, R. Nomen, R. Serra, J. Soravilla. *The NPK method an innovative approach for kinetic analysis of data from thermal analysis and calorimetry. Thermochim. Acta. 2002. 388: 407-414.*

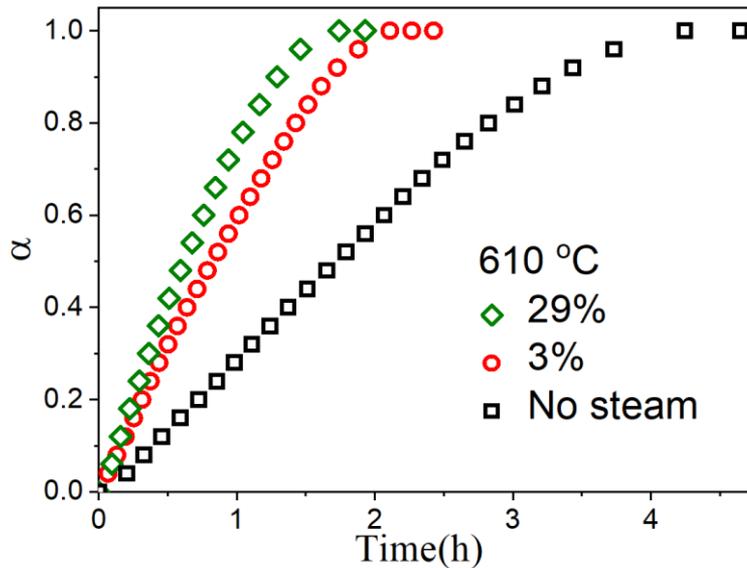
Non-parametric kinetic method

For isothermal conditions: $t = g(\alpha) \cdot (k(T))^{-1}$



Non-parametric kinetic method

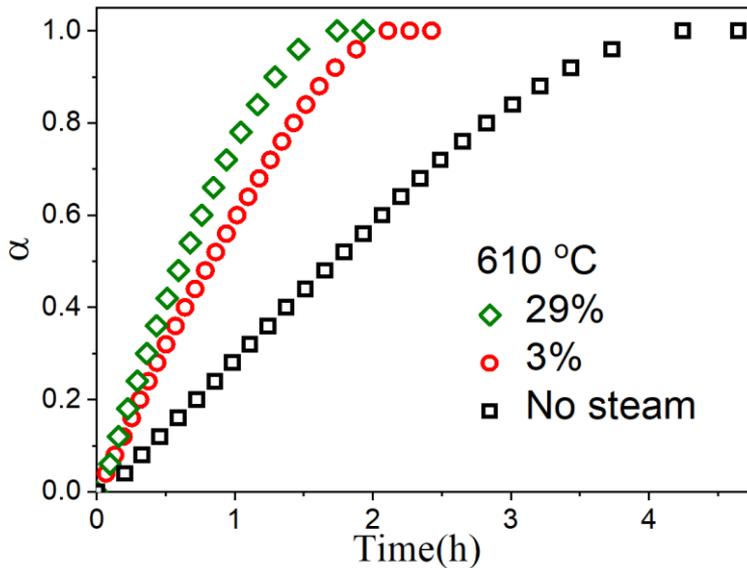
For isothermal conditions: $t = g(\alpha) \cdot (k(T))^{-1}$



$$\begin{array}{ccc}
 T_1 & T_2 & T_3 \\
 \downarrow & \downarrow & \downarrow \\
 t = \begin{pmatrix} t_{11} & t_{12} & t_{13} \\ t_{21} & t_{22} & t_{23} \\ t_{31} & t_{32} & t_{33} \end{pmatrix} \begin{array}{l} \leftarrow \alpha_1 \\ \leftarrow \alpha_2 \\ \leftarrow \alpha_3 \end{array} & \rightarrow & t = u \cdot w \cdot v^T
 \end{array}$$

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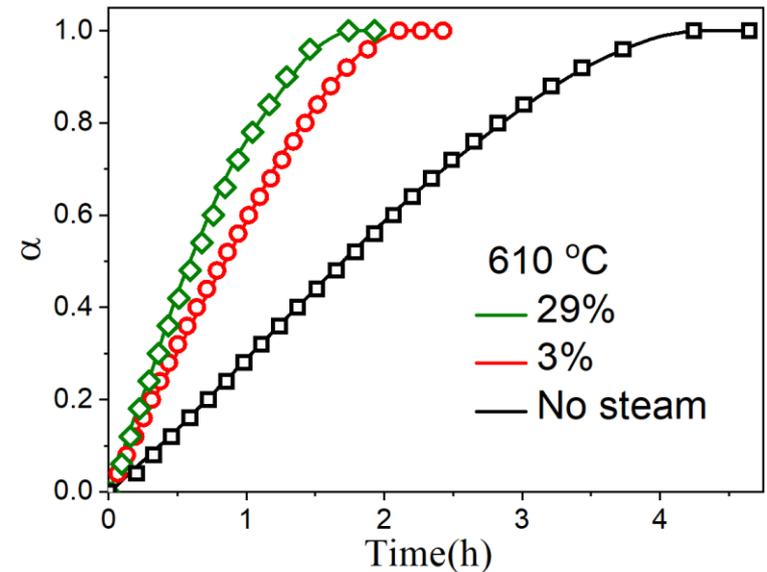
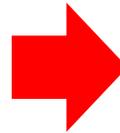
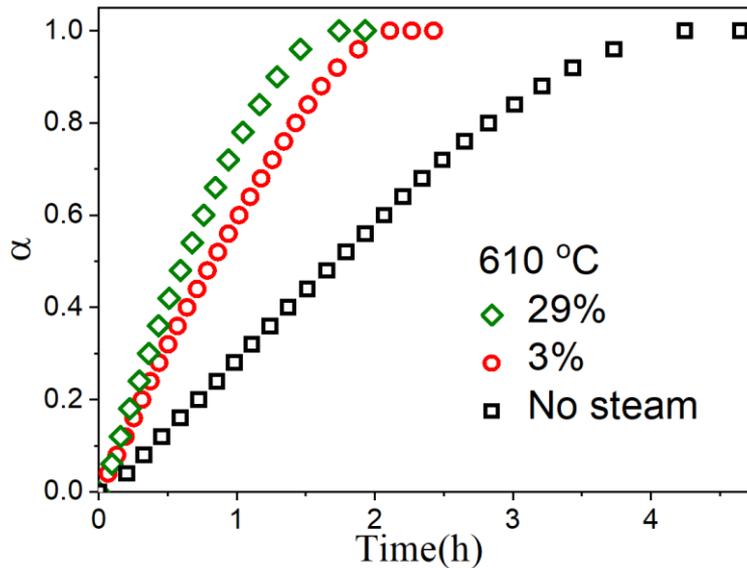
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 \end{array}$$

$$u(i, 1) \propto g(\alpha_i) \quad \text{with } i = 1:3$$

$$v(j, 1) \propto (k(T_j))^{-1} \quad \text{with } j = 1:3$$

Non-parametric kinetic method

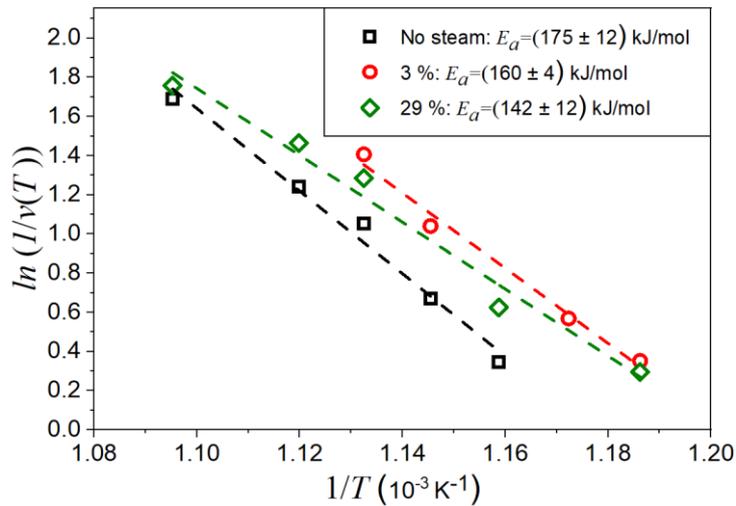
$$t_{ij} = u(i, 1) \cdot w(1, 1) \cdot v(j, 1)$$



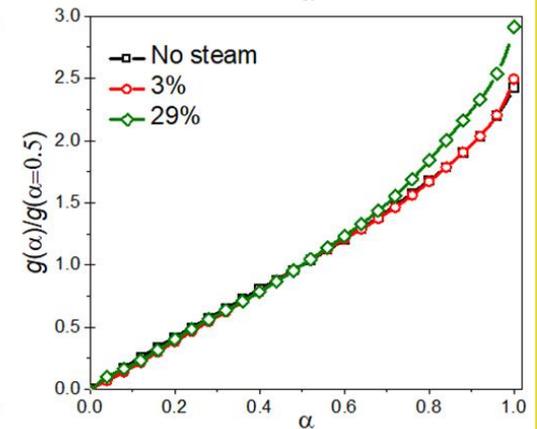
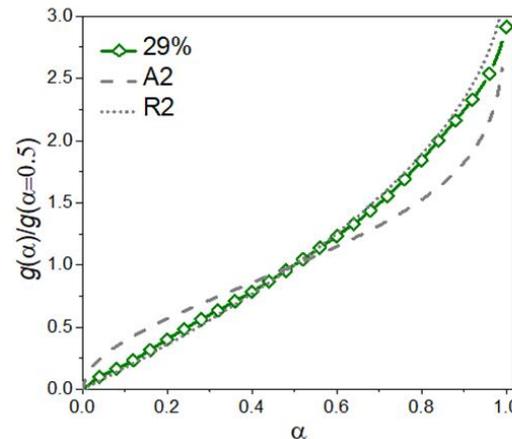
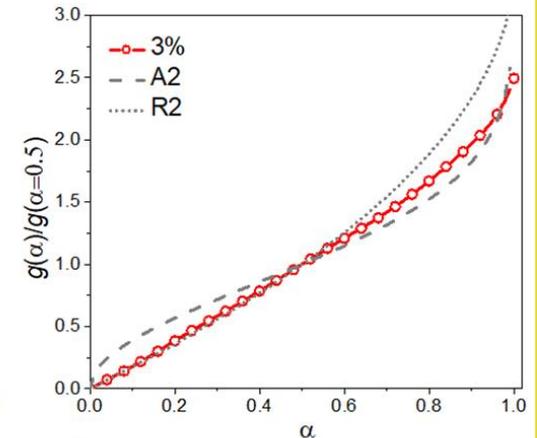
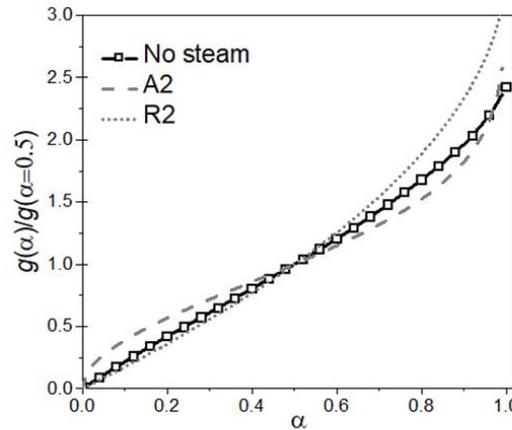
Non-parametric kinetic method

$$k(T) = A \cdot e^{-E_a/RT}$$

$$v(j, 1) \propto (k(T_j))^{-1}$$



$$u(i, 1) \propto g(\alpha_i)$$



Non-parametric kinetic method

Kinetic parameters		
Partial pressure of steam	E_a (kJ·mol ⁻¹)	A^* (s ⁻¹)
No steam	175 ± 12	(3.4 ± 0.1) · 10 ⁶
3 %	160 ± 4	(9.2 ± 0.2) · 10 ⁵
29 %	142 ± 12	(1.1 ± 0.4) · 10 ⁵

$$t = (1/A^*) \cdot (u(\alpha)/u(\alpha = 0.5)) \cdot e^{E_a/RT}$$

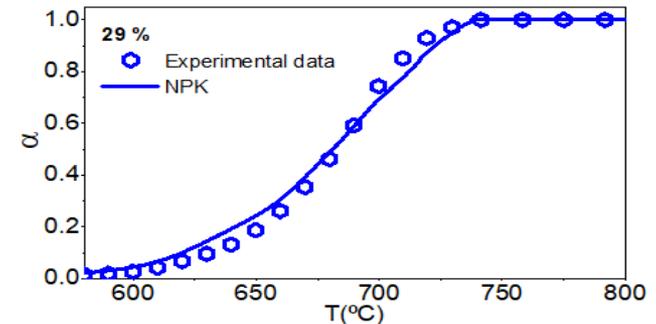
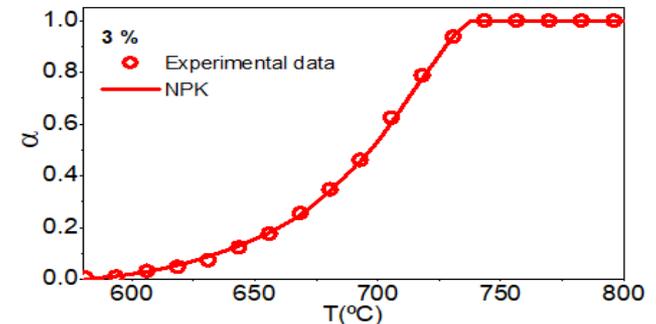
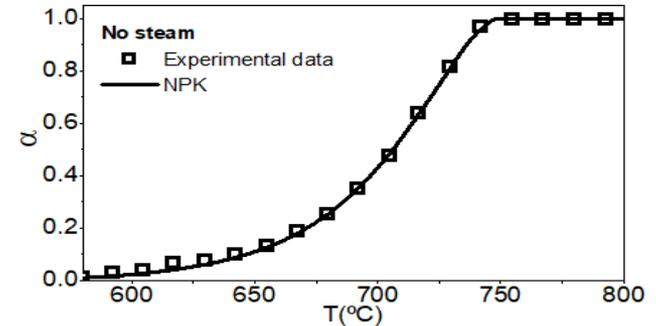
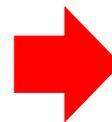
$$A^* = A/u(\alpha = 0.5)$$

Non-parametric kinetic method

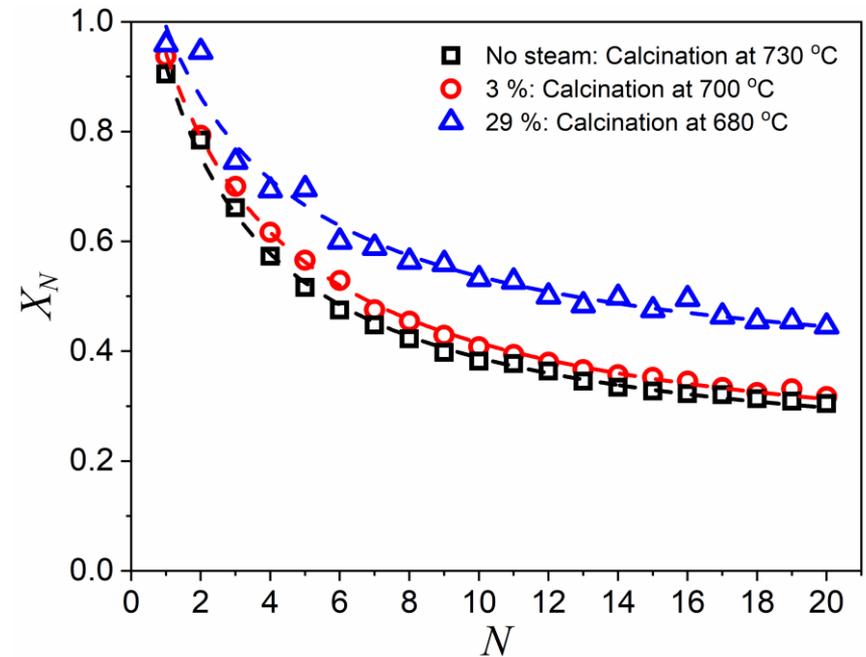
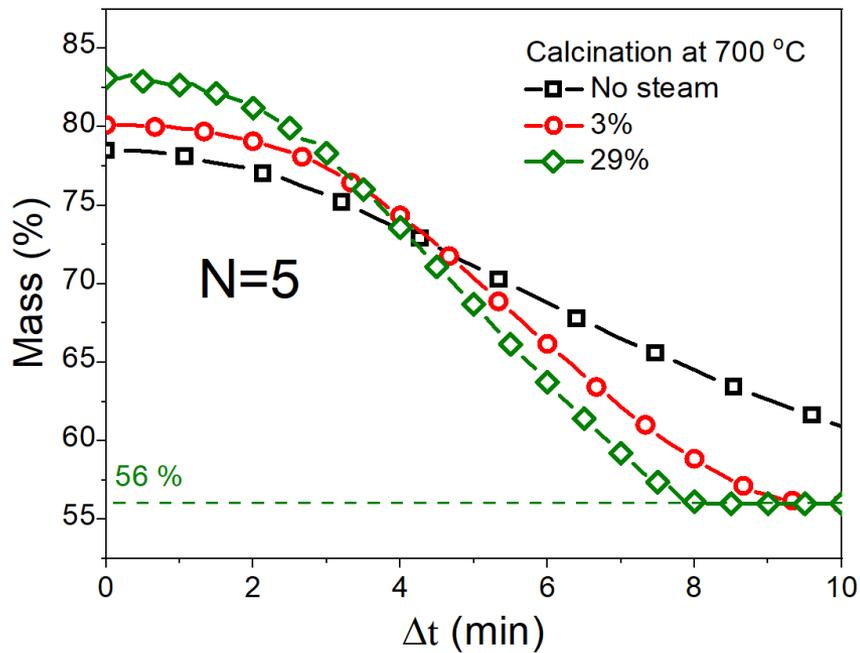
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29 %	142 ± 12	$(1.1 \pm 0.4) \cdot 10^5$

$$t = (1/A^*) \cdot (u(\alpha)/u(\alpha = 0.5)) \cdot e^{E_a/RT}$$

$$A^* = A/u(\alpha = 0.5)$$



Cyclability



Cyclability

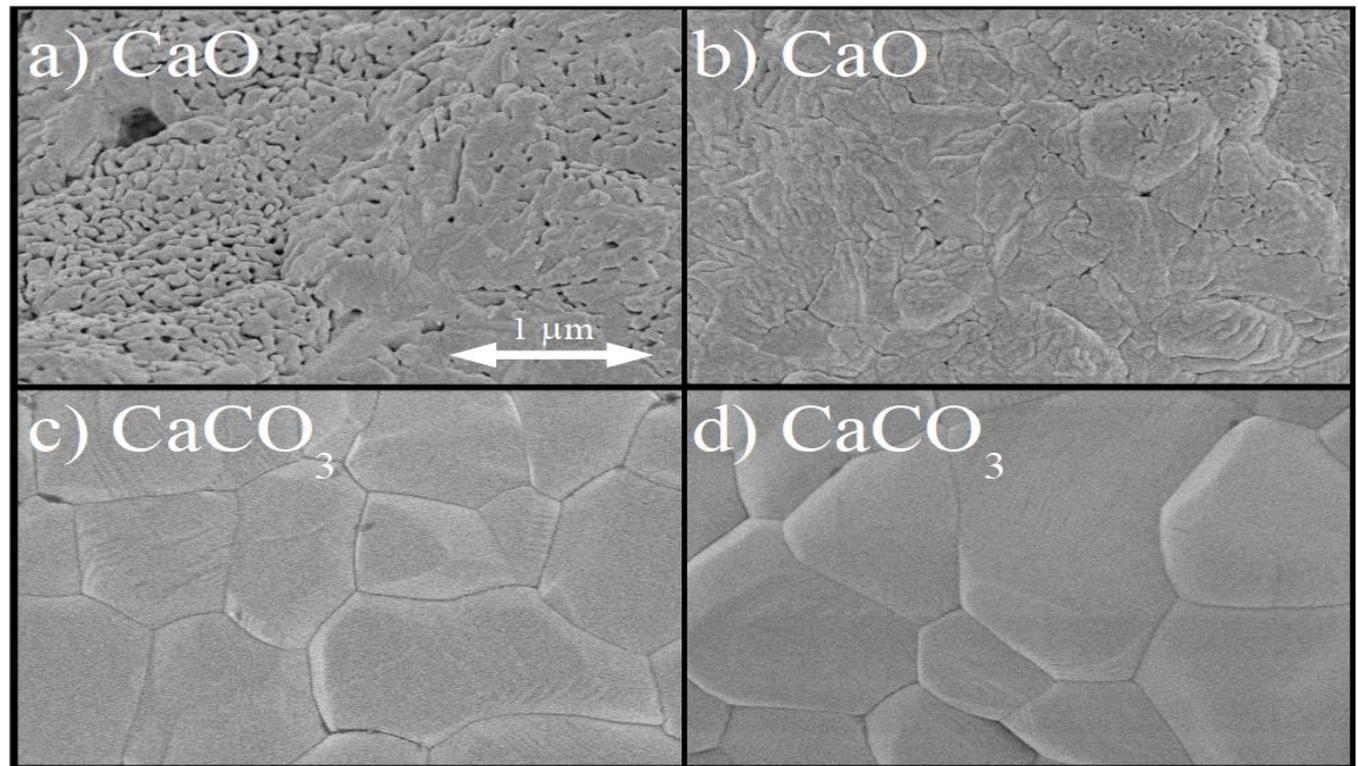
29 %

No steam

After 20
cycles:

$T_{\text{cal}} = 680 \text{ } ^\circ\text{C}$

$T_{\text{carb}} = 850 \text{ } ^\circ\text{C}$



Conclusions

- Steam addition decreases the apparent activation energy.
- The kinetic model is modified when a large amount of steam is employed.
- The temperature needed to attain full calcination can be decreased.
- Steam helps prevent the loss in reactivity and creates a more open structure resilient to pore plugging.

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Thanks for your attention



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