# Dehydroxylation kinetics of kaolinite and montmorillonite examined using isoconversional methods

Oluwadamilare Charles Adesina<sup>1</sup>, Sayee Srikarah Volaity<sup>1</sup>, Bryan K. Aylas-Paredes<sup>2</sup>, Chengqing Qi<sup>3</sup>, Aditya Kumar<sup>2</sup>, Narayanan Neithalath<sup>\*1</sup>

<sup>1</sup> School of Sustainable Engineering and the Built Environment, Arizona State University, Tempe, AZ \* <u>Narayanan.Neithalath@asu.edu</u>

<sup>2</sup> Department of Materials Science and Engineering, Missouri University of Science and Technology, Rolla, MO

<sup>3</sup> Ash Grove Cement Company, Overland Park, Kansas

Presenter: Avinaya Tripathi





## **This Presentation...**

- Discusses the kinetics of the dehydroxylation of kaolinite and montmorillonite investigated under nonisothermal conditions.
- Presents a framework for accurately estimating kinetic parameters and conversion-time  $(\alpha t)$  relationships using isoconversional methods.
- Explains the experimental validation of the estimated kinetic triplets used to predict isothermal calcination conditions.
- Highlights the relevance of the framework in generating novel SCMs from conventional and nonconventional clay sources, including various potentially reactive aluminosilicate wastes that require thermal activation through optimized and energy-efficient calcination schemas.





## **Background: Cement**

- Concrete most widely used construction material; second only to water in terms of global usage.
- Production of Portland cement key concrete component; accounts for ~8% of anthropogenic CO<sub>2</sub> emissions, 7% of global energy use and 4% of global warming.
- Emission, energy and decarbonization strategies reducing clinker content using SCMs is a promising and widely adopted lever, among others.
- Clays from geologically abundant and cost-effective sources offer sustainable alternatives; also help offset the scarcity of industrial by-products like fly ash and slags used as SCMs.





**Arizona State** 

**University** 



## Clay minerals and their activation

- Clays contains minerals like kaolinite, montmorillonite, illite etc.
- Clay minerals fundamental crystal structure contains stacking layers of tetrahedral (T) and octahedral
   (O) sheets.
- Kaolinite and montmorillonite notable for their pozzolanic properties when activated.
  - Kaolinite 1:1 ratio of T- and O- sheets; adjacent layers are joined together by hydrogen bonds; kaolin clay from US Silica
  - Montmorillonite 2:1 clay mineral from the smectite group; isomorphous substitution within the O-sheet; presence of
    interlayer exchangeable cations such as Ca<sup>2+</sup>, Na<sup>+</sup> or K<sup>+</sup>; interlayer cations facilitate water adsorption; Sodium (Na)
    montmorillonite bentonite from American Colloid Company



## Clay minerals and their activation

- Both clay minerals contain OH groups chemically bonded in their lattices that must be removed to cause structural disorder and exposure of reactive sites.
- Dehydroxylation (thermal treatment) is the process of OH group removal to activate them as viable SCMs
- Many studies on clay calcination implement conditions involving longer durations at high temperatures than necessary.
- Over-calcination, due to exceedingly high temperatures or prolonged durations, not only cause energy wastage but also diminishes reactivity due to possible recrystallization of the clay structure.
- Dehydroxylation kinetics can be assessed from temperature programs revealing thermal behavior e.g.,
   Thermogravimetric analysis (TGA), heat flow experiments like DSC, DTA, etc.



zona State

## Kinetic modeling: Isoconversional method

- Reaction-model fitting methods capable of fitting hypothetical reaction models in the general rate equation; however, yields uncertain and sometimes uninterpretable kinetic results.
- Isoconversional (reaction model-free) kinetic analysis solely temperature/time-dependent analysis of the general rate equation; assumption of reaction model not required; can determine the kinetic triplets that quantitatively characterizes a reaction.
- Kinetic triplets Activation energy (E), reaction model ( $f(\alpha)$ ), and pre-exponential factor (A)

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha)h(P) \qquad \beta \frac{\mathrm{d}\alpha}{\mathrm{d}T} = A\exp\left(\frac{-E}{RT}\right)f(\alpha) \qquad g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T \exp\left(\frac{-E}{RT}\right)\mathrm{d}T$$



Arizona State

## Kinetic modeling: Determination of $E_{\alpha}$

- Rigid integral isoconversional methods incorporate approximations of the kinetic temperature integral;
   examples are Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS) and Starink methods.
- Flexible integral isoconversional methods:
  - Vyazovkin incremental method no approximations; based on numerical integration of the temperature integral over small time or temperature increment;  $E_{\alpha}$  is obtained by minimizing the objective function  $\varphi(E_{\alpha})$ .

$$\varphi(E_{\alpha}) = \sum_{i=1}^{n} \sum_{j\neq 1}^{n} \frac{J[E_{\alpha}, T_{i}(t_{\alpha})]}{J[E_{\alpha}, T_{j}(t_{\alpha})]}$$
$$J[E_{\alpha}, T_{i}(t_{\alpha})] = \int_{t_{\alpha} - \Delta \alpha}^{t_{\alpha}} \exp\left(\frac{-E_{\alpha}}{RT(t)}\right) dt$$

- Differential isoconversional method
  - The Friedman method based on straightforward rearrangement and logarithmic transformation of the general kinetic rate equation.  $E_{\alpha}$  is determined from the slope of the linear plot. ln  $A_{\alpha}$  is obtained from the y-intercept

$$\ln\left[\beta_{i}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\alpha,i}\right] = \ln[A_{\alpha}f(\alpha)] - \frac{E_{\alpha}}{RT_{\alpha,i}}$$

Arizona State



## Kinetic modeling: Determination of $f(\alpha)$

- The master plot method involves comparing experimental plots informed by the kinetic parameters of the process with reference theoretical curves representing different possible reaction mechanisms; the best match is then selected by graphical or regression analysis; functions are normalized at reference conversion point  $\alpha = 0.5$
- Differential master plot approach,  $y(\alpha)$  based entirely on the differential form of the general kinetic equation

$$\frac{y(\alpha)}{y(0.5)} = \frac{f(\alpha)}{f(0.5)} \qquad \qquad \frac{y(\alpha)}{y(0.5)} = \frac{\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha}}{\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{0.5}} \cdot \exp\left[\frac{E_{\mathrm{a}}}{R}\left(\frac{1}{T_{\alpha}} - \frac{1}{T_{0.5}}\right)\right]$$

• Combined differential and integral master plot approach,  $Z(\alpha)$  – based on the combination of the differential and integral forms of the general kinetic equation; simplifying the resulting expression predominantly reflects only the experimental data ( $d\alpha/dt$  and T).

$$\frac{Z(\alpha)}{Z(0.5)} = \frac{f(\alpha)g(\alpha)}{f(0.5)g(0.5)}$$

 $\frac{Z(\alpha)}{Z(0.5)} = \frac{\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha}}{\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{0.5}} \cdot \frac{T_{\alpha}^{2}}{T_{0.5}^{2}}$   $\mathbf{Arizona State}_{\mathbf{University}} \qquad \mathbf{CONCRETE}_{\mathbf{CONVENTION}}$ 

# Kinetic modeling: Determination of $f(\alpha)$

#### • Theoretical curves representing different possible reaction mechanisms



Reaction mechanism	Code	$f(\alpha)$	$g(\alpha)$	$- Z(\alpha) = f(\alpha)g(\alpha)$
Reaction order				=
First order	F1	$1 - \alpha$	$-ln(1-\alpha)$	Z(0.5) = f(0.5)a(0.5)
Second order	F2	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$	$Z(0.5) = \int (0.5)g(0.5)$
Third order	F3	$(1 - \alpha)^3$	$\frac{1}{2}[(1-\alpha)^{-2}-1]$	2 + D2
$n^{th}$ order	Fn	$(1-\alpha)^n$	$\frac{1}{n-1}[(1-\alpha)^{1-n}-1]$	- — D3, R3 — D4 —
Geometrical contraction				$1.6 - F_{1, A(n)}$
2D (contracting cylinder)	R2	$2(1-\alpha)^{\frac{1}{2}}$	$1-(1-\alpha)^{\frac{1}{2}}$	$\hat{\boldsymbol{\nabla}}$ $\begin{bmatrix} -F_2 \\ -F_3 \\ -F_3 \end{bmatrix}$
3D (contracting sphere)	R3	$3(1-\alpha)^{\frac{2}{3}}$	$1-(1-\alpha)^{\frac{1}{3}}$	$\tilde{N}_{1.2}$
Random nucleation and growth	of nuclei		ize	
	A2	$2(1-\alpha)[-ln(1-\alpha)]^{\frac{1}{2}}$	$\left[-ln(1-\alpha)\right]^{\frac{1}{2}}$	те 0.8-
Johnson-Mehl-Avrami equations	A3	$3(1-\alpha)[-ln(1-\alpha)]^{\frac{2}{3}}$	$\left[-ln(1-\alpha)\right]^{\frac{1}{3}}$	ōz .
	A4	$4(1-\alpha)[-ln(1-\alpha)]^{\frac{3}{4}}$	$\left[-ln(1-\alpha)\right]^{\frac{1}{4}}$	0.4-
Diffusion				
2D (Valensi equation)	D2	$[-ln(1-\alpha)]^{-1}$	$\alpha + (1-\alpha)ln(1-\alpha)$	
3D (Jander equation)	D3	$\frac{3}{2}(1-\alpha)^{\frac{2}{3}}\left[1-(1-\alpha)^{\frac{1}{3}}\right]^{-1}$	$\left[1-(1-\alpha)^{\frac{1}{3}}\right]^2$	0 0.2 0.4 0.6 0.8 1 Degree of conversion, α
3D (Ginstling–Brounshtein equation)	D4	$\frac{3}{2} \left[ (1-\alpha)^{\frac{-1}{3}} - 1 \right]^{-1}$	$1-\frac{2\alpha}{3}-(1-\alpha)^{\frac{2}{3}}$	

**Arizona State** 

University

(aci)<sub>CO</sub>

CONVENT

## Kinetic modeling: Determination of A

The pre-exponential factor A – obtained from the second derivative of the general rate equation after determining other components of the kinetic triplets; determined for each temperature program employed; there are other applicable methods to determine A

$$A_{i} = \frac{-\beta_{i}E_{a}}{RT_{m}^{2}f'(\alpha_{m})}\exp\left(\frac{E_{a}}{RT_{m}}\right)$$



Universitv

## Kinetic modeling: Estimation of conversion time

Time predictions for calcination – The estimated kinetic triplets can be subsequently implemented to predict duration,  $t_{\alpha}$ , required to reach a given conversion,  $\alpha$  in an isothermal temperature program at a fixed temperature

$$t_{\alpha} = \frac{g(\alpha)}{A} \exp\left(\frac{E_{a}}{RT_{0}}\right)$$



### **Kinetic framework**

 $\alpha, \frac{\mathrm{d}\alpha}{\mathrm{d}t}, T, t, \beta$  $\varphi(E_{\alpha}) = \sum_{i=1}^{n} \sum_{j\neq 1}^{n} \frac{J[E_{\alpha}, T_i(t_{\alpha})]}{J[E_{\alpha}, T_j(t_{\alpha})]}$  $\ln\left[\beta_i\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\alpha,i}\right]$  $= \ln[A_{\alpha}f(\alpha)] - \frac{E_{\alpha}}{RT_{\alpha,i}}$  $J[E_{\alpha}, T_{i}(t_{\alpha})] = \int_{t_{\alpha-\Delta\alpha}}^{t_{\alpha}} \exp\left(\frac{-E_{\alpha}}{RT(t)}\right) dt$  $f = \frac{f(\alpha)}{f(0.5)} = \frac{\left(\frac{d\alpha}{dt}\right)_{\alpha}}{\left(\frac{d\alpha}{dt}\right)_{0.5}} \cdot \exp\left[\frac{E_a}{R}\left(\frac{1}{T_{\alpha}} - \frac{1}{T_{0.5}}\right)\right]$  $\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha}$  $=\frac{f(\alpha)g(\alpha)}{f(0.5)g(0.5)}=$  $\cdot \frac{T_\alpha^2}{T_{0.5}^2}$  $\frac{Z(\alpha)}{Z(0.5)} =$  $\frac{y(\alpha)}{y(0.5)}$  $\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)$  $A_{i} = \frac{-\beta_{i}E_{a}}{RT_{m}^{2}f'(\alpha_{m})}\exp\left(\frac{E_{a}}{RT_{m}}\right)$  $t_{\alpha} = \frac{g(\alpha)}{A} \exp\left(\frac{E_{a}}{RT_{0}}\right)$ 



**Arizona State** 

University

## Kinetic data: Heating rate experiment

• Linear non-isothermal TGA experiments – revealing thermal decomposition of kaolinite and montmorillonite at different heating rates,  $\beta$ ; High purge gas flow rate to facilitate removal of water vapor

during dehydroxylation; experiments follows the guidelines of ICTAC.



University

# Kinetic analysis: E<sub>a</sub> from isoconversional methods

The Friedman method –  $E_{\alpha}$  is determined from the slope of

Vyazovkin incremental method –  $E_{\alpha}$  is obtained by

University

CONVEN

minimizing the objective function  $\varphi(E_{\alpha})$ .

the linear plot.



# Kaolinite: Reaction model and contextualization

- Dehydroxylation follows a reaction (n<sup>th</sup>) order mechanism.
   Regression analysis of Kinetic compensation effect (KCE) yielded the reaction order exponent, n as 2.3.
- From the crystal particle structure's perspective, the mechanism implies that reaction rate is proportional to the concentration of unreacted material, resembling a second order reaction.
- During dehydroxylation, OH units become mobile, displaced from their original position, react together forming water molecules which migrates out through the interlayer channels.
- The loss of OH groups induces structural distortion in the Osheets, changing the coordination of octahedral (Al) cation and transforming kaolinite to amorphous metakaolin.



**Arizona State** 

Iniversitv



### Na-montmorillonite: Reaction model and contextualization

- Dehydroxylation is diffusion-controlled. Master plot model- fitting confirms the rate-controlling step as three-way transport model (D3).
- Mechanism is linked to removal of water molecules and its transport towards phase boundary of the spherical crystalline aggregate.
- The Na<sup>+</sup> interlayer cations influence diffusion rate of water molecules.
- Octahedral cations (Al) undergo changes in coordination with residual oxygen anions, resulting in a distorted, five-fold coordinated, trigonal bipyramidal structure.
- The layered structure is preserved during dehydroxylation; amorphization may occur subsequently.



### Kinetic analysis: Pre-exponential factor (ln A)

- Average  $E_a$  from Friedman and Vyazovkin methods are separately used to compute  $\ln A$ .
- Friedman and Vyazovkin methods yield identical ln A values.
- The pre-exponential factor is independent of heating rate.

Temperature programs, β (°C. min <sup>-1</sup> )	$\ln A (s^{-1})$						
	Kaolinite		Montmorillonite				
	Friedman	Advanced Vyazovkin	A Eriedman method	Advanced Vyazovkin			
	method	incremental method	i neuman methou	incremental method			
5	9.06	9.15	11.52	11.81			
10	9.08	9.17	11.46	11.74			
15	9.06	9.15	11.48	11.76			
20	9.08	9.16	11.51	11.79			
30	9.10	9.19	11.50	11.78			
Mean	9.08	9.16	11.50	11.78			



### **Kinetic predictions**

- Erroneous kinetic triplet estimations can lead to flawed predictions of heat treatment requirements with energy and economic implications.
- The isothermal prediction plots  $(\alpha t)$  are based on the clays' dehydroxylation ranges to optimize energy efficiency while avoiding over-calcination.
- Montmorillonite exhibits a rapid conversion to a peak value of 1.0, whereas kaolinite displays a more extended plateau near the maximum conversion.



### **Experimental verification: TGA**

- Bulk samples are calcined in a muffle furnace under the conditions based on kinetic predictions.
- The extent of dehydroxylation (conversion,  $\alpha$ ) of the calcined products was determined via mass loss (under TGA) within the dehydroxylation temperature range; degree of dehydroxylation  $\geq$  90%.
- The experimentally measured degrees of dehydroxylation were close to the target conversion values.
- Decomposition of impurities and temperature gradients in muffle furnace resulting in less-than-ideal heat transfer and consequently lower calcination efficiencies accounts for the residual mass loss during TGA validation.



### **Experimental verification: XRD**

- Bulk samples are calcined in a muffle furnace under the conditions based on kinetic predictions.
- The mineralogical and qualitative amorphous characterization of the calcined products was evaluated by via XRD; XRD results corroborate the TGA experimental verifications
- Kaolinite XRD patterns reveal absence of peaks of the clay mineral but show broad amorphous hump between 14° and 35°
   2θ; peaks of accompanied impurities persist; the amorphous hump signifies enhanced reactivity.
- Montmorillonite's layered structure is preserved in calcined sample, albeit show slight reductions or rounding off at higher calcination temperatures.



### **Evaluation of reactivity**

- Hydration kinetics, coupled with thermodynamic calculations using enthalpy of reaction of the samples with Ca(OH)<sub>2</sub> was studied through micro-calorimetry to accurately determine reactivity over 7 days
- Both raw clay minerals exhibit low reactivity (<6%); raw montmorillonite was more reactive.
- The calcination protocol improved the reactivity of kaolinite samples to a similar degree of ~50% due to structural disorder and increased number of Al<sup>V</sup> coordination sites.
- Calcined montmorillonite exhibiting lower reactivity (<25%) retains its structural order after calcination; Amorphization induced at extended calcination accounts for the different extent of reactivity.



### **Summary and conclusion**

• Phase transformation of potentially reactive virgin materials through sound fundamental methodology and framework

enables identification of energy-efficient activation pathways for novel SCM synthesis.



### Summary and conclusion

- Friedman differential and Vyazovkin incremental isoconversional methods were employed to accurately quantify kaolinite and montmorillonite dehydroxylation reaction yielding identical activation energy and pre-exponential factor for the respective clay mineral. Reaction models were identified using master plot approach based on isoconversional principle.
- The kinetic triplets representing the clay mineral dehydroxylation yielded reliable predictions across suitable temperature ranges for energy-efficient calcination to produce reactive and viable SCMs.
- TGA and XRD experiments confirmed complete or near complete dehydroxylation verifying the kinetic predictions.
- Reactivity of the synthesized SCM was a function of clay mineral structural disorder and the amorphousness induced during dehydroxylation.
- While the derived kinetic parameters and deductions are specific to the examined samples, they offer valuable insights that build on fundamental knowledge which can inform studies on related clay minerals.



Arizona State

University