ECerS XII

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Evolution of heat capacity of clay-based materials after a thermal treatment : influence of dehydroxylation

S. Ben Lakhal, G.L. Lecomte, H. Lemercier*, B. Naït-Ali, D.S. Smith

Heterogenous Materials Research Group (Limoges)/*TERREAL

Outline

Figures and Facts

Heavy clay production

- Turnover in France for 2009: 888 M€
- 149 factories and 5600 employees
- Key sector of european ceramics

Challenges

- Clay products: manufacturing is energy consuming
- Mastering energy consumption is now vital
- Raw Materials + firing techniques + bio-energy sources

Figures and Facts

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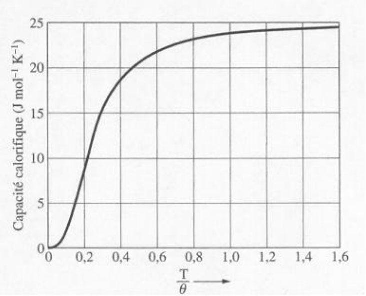
Key Parameter: Heat capacity

Definition

- Heat capacity: Amount of heat required to change a substance's temperature by 1K
- In solids : $C = \left(\frac{dU}{dT}\right)_V \approx Cp$
- $E = \int mC_p(T)dT + \Delta H$

Debye's model

- Evolution of C with T for a crystalline solid: Debye's model
- Hypothesis:
  - Monatomic system
  - Cubic
  - $\omega = v_0 k$: same for longitudinal and transverse vibrations



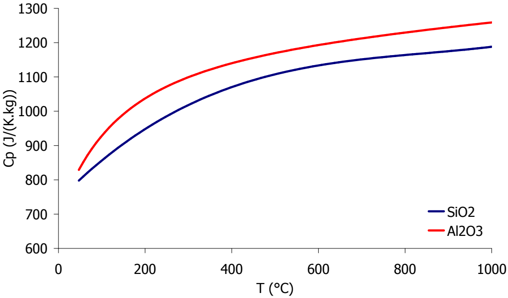
Evaluation of Cp for complex materials

Neumann-Kopp's Law, or rule of mixtures :

$$Cp(T) = \sum_{i=1}^{n} Cp_i(T).x_i$$

with x_i: Mass fraction

Dehydroxylated kaolinite: $Al_2O_3 + 2\,SiO_2$



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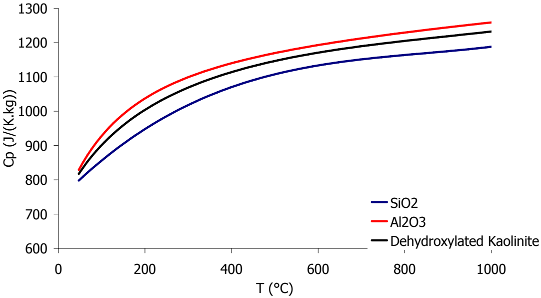

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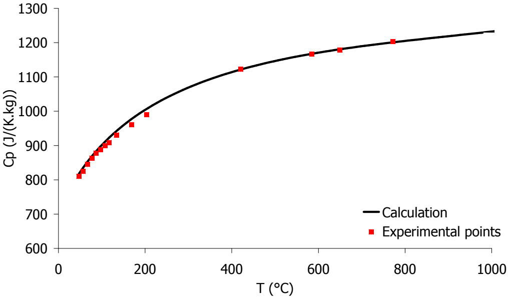
Validated for model kaolinite after dehydroxylation



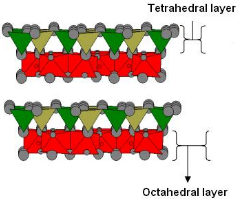
Materials

Model materials :

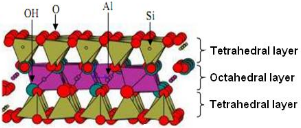
- Kaolin (1:1)
- Muscovite (2:1)
- Illite (2:1)
- Montmorillonite (2:1)

Industrial material:

Illite, kaolinite, quartz, feldspar,...



1:1 Phyllosilicate

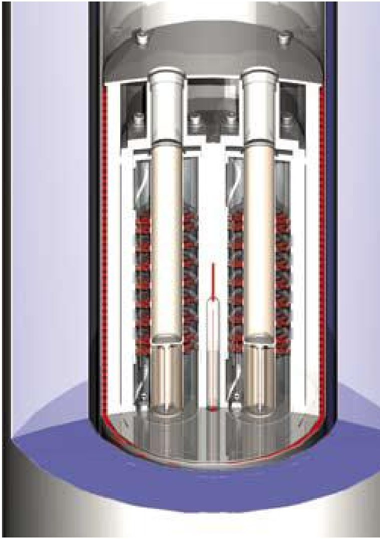


2:1 Phyllosilicate

Calorimetry measurement

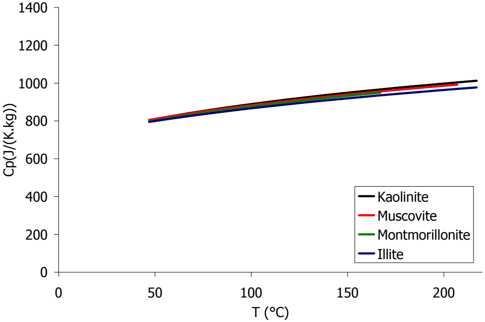
Measurement of heat flow between the sample and a reference material

- Acquisition between 40 and 220 °C
- Heating rate: 0.2°C/min
- Mass of sample ≈ 3 g



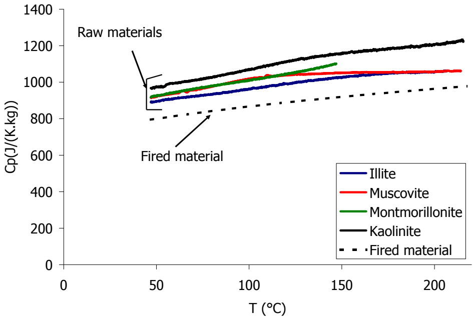
Fired Materials

- Evolution is comparable
- Influence of mineralogy is negligible



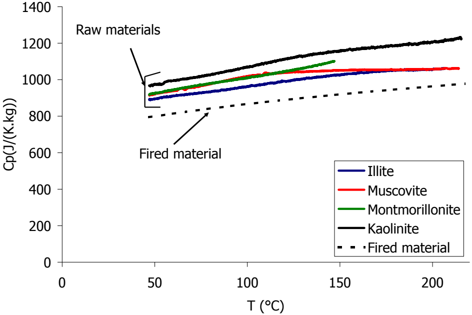
Raw materials

- Substantial difference with fired materials
- Different evolution depending on the material
- OH-groups content



Raw materials

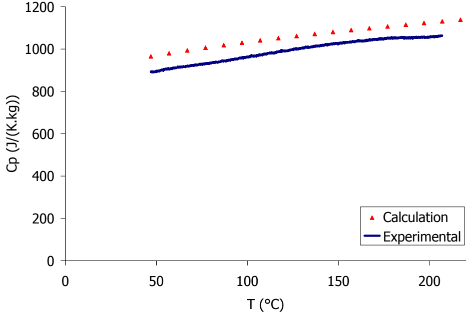
Mineral	Loss on ignition
Kaolinite	13.5 %
Muscovite	6 %
Montmorillonite	9.7 %
Illite	5 %



Extension of Rules of Mixtures to raw materials

Approach:

$$Cp_{raw} = (1 - \Delta m)Cp_{fired} + \Delta m Cp_{H_2O}$$
$$Cp_{H_2O} = 4186\ J.K^{-1}.kg^{-1}$$



Values of $Cp_{H_2O^*}$

$$Cp_{H_2O^*} = \frac{Cp_{raw} - (1 - \Delta m)Cp_{fired}}{\Delta m}$$

Values at 420K (147°C)

Mineral	Cp mineral$(J.K^{-1}.kg^{-1})$	$Cp_{H_2O^*}(J.K^{-1}.kg^{-1})$
Kaolinite	930	2625
Muscovite	937	3024
Montmorillonite	903	2950
Illite	916	2900

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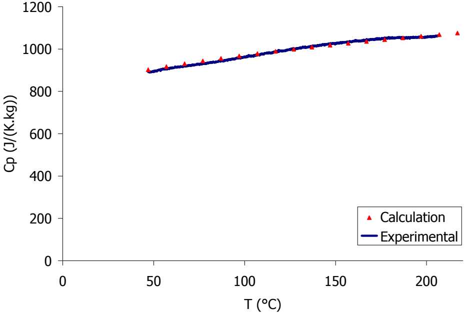
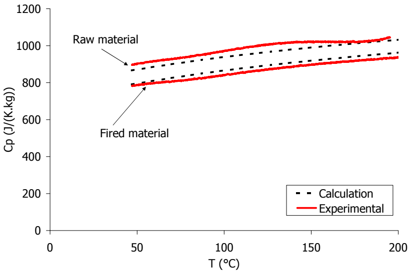


Application: Industrial material

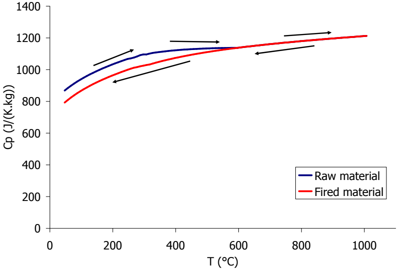
- Constant value Cp_{H_2O} : 2950 $J.K^{-1}.kg^{-1}$
- Weight Loss : 3.5%
- Close agreement with measurement: $<$ 2% after firing $<$ 4% before



Prediction of Cp variations with thermal treatment of green body

Hypothesis :

- Linear weight loss between 330 and 600°C
- Constant value of Cp_{H_2O}: 2950 $J.K^{-1}.kg^{-1}$



Conclusion

Achievements

- Good prediction of C_p for fired materials
- Influence of dehydroxylation
- New approach to estimate C_p for clay materials in general

Next Steps

- Variation of Cp_{H_2O} with T
- Influence of decarbonation

Thank you for your attention

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