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MECHANISMS AND MODELING OF CEMENT HYDRATION *Time and Temperature Effects*

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Cement Hydration involves Nucleation and Growth

- Hancock and Sharp proposed analysis methodology for comparing the kinetics of isothermal solid-state reactions based on the classical equation for analysis of nucleation and growth processes.

- Reaction mechanisms obtained by linearizing the general Avrami model:

  Fraction reacted $Q/Q_{max} = [\ 1 - \exp(-\ k\ t^m\ )\ ]$

  Model linearization for quantifying k & m:

  $Y = \ln[-\ln(1 - Q/Q_{max})] = \ln(k) + m \ln(t)$

  The characteristic ranges of m are a measure of

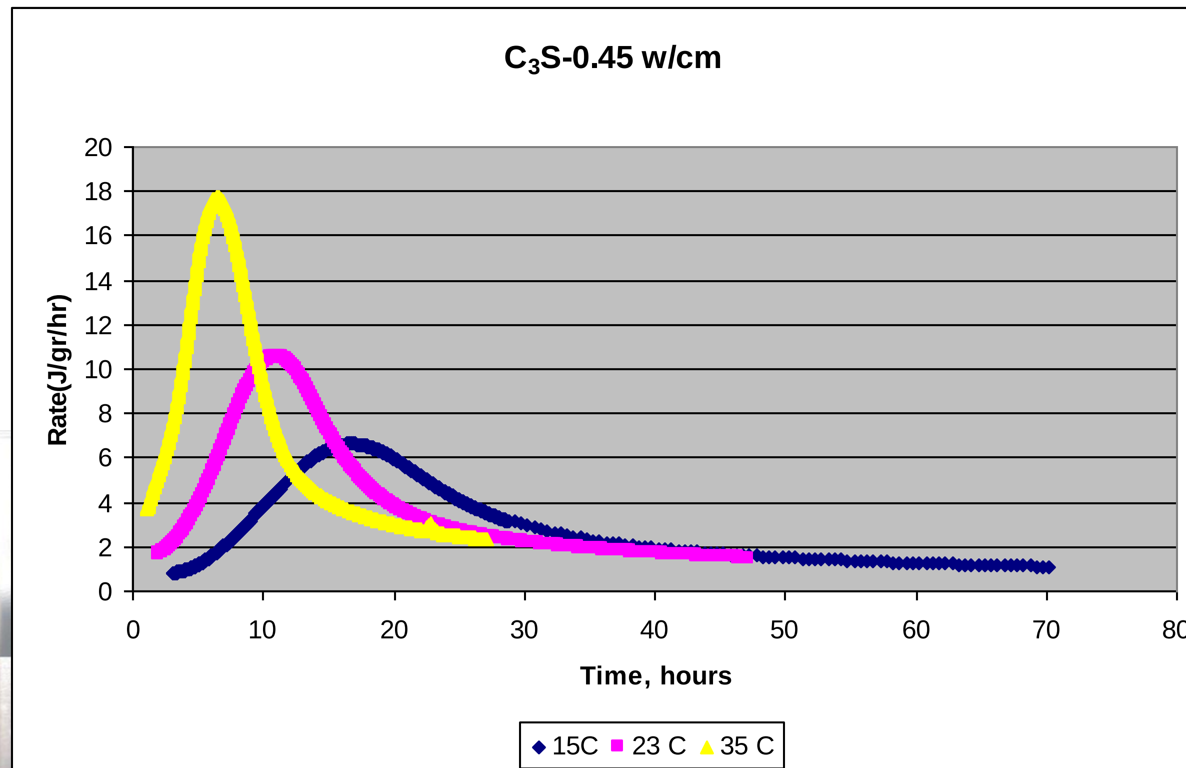
  - $m \sim 0.5$ Diffusion controlled process
  - $m \sim 1$ Phase boundary controlled process
  - $m \sim 2\text{-}3$ Chemical controlled process

J.D. Hancock and J.H. Sharp, "Method of Comparing Solid State Kinetic Data and its Application to the Decomposition of Kaolinite, Brucite, and BaCO3", Journal of American Ceramic Society, Vol. 55, No. 2, p74, 1972.

Heat of Hydration as a measure of reactivity

Paste samples ~10g

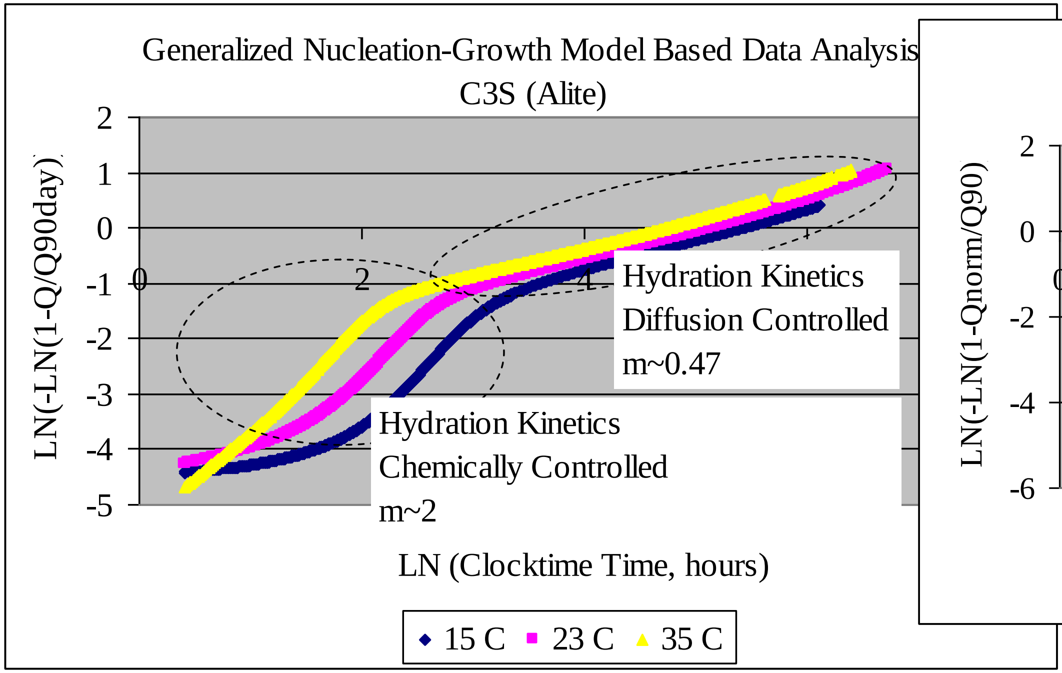
Isothermal calorimetry

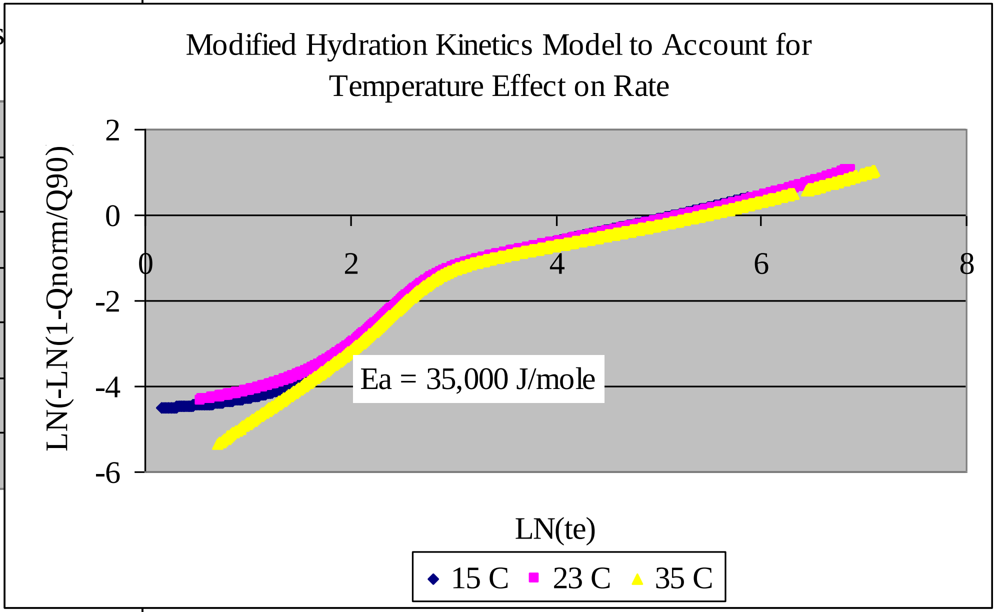


Exponent m in the Avrami Equation & Temp Normalization through Equivalent time, te.

$$Q/Qmax = [\ 1 - \exp(-\ k\ te^{\ m}\ )\ ]$$

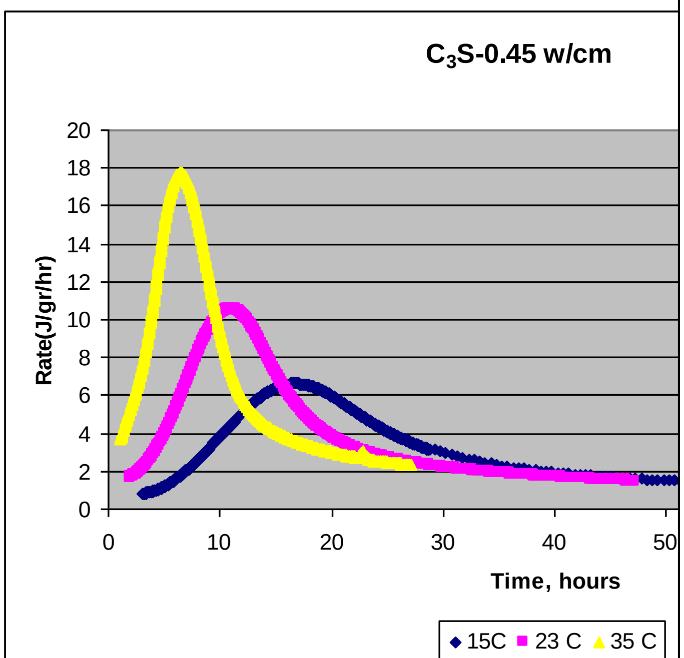
$$Y = \ln[-\ln(1 - Q/Qmax)] = \ln(k) + m\ \ln(te)$$

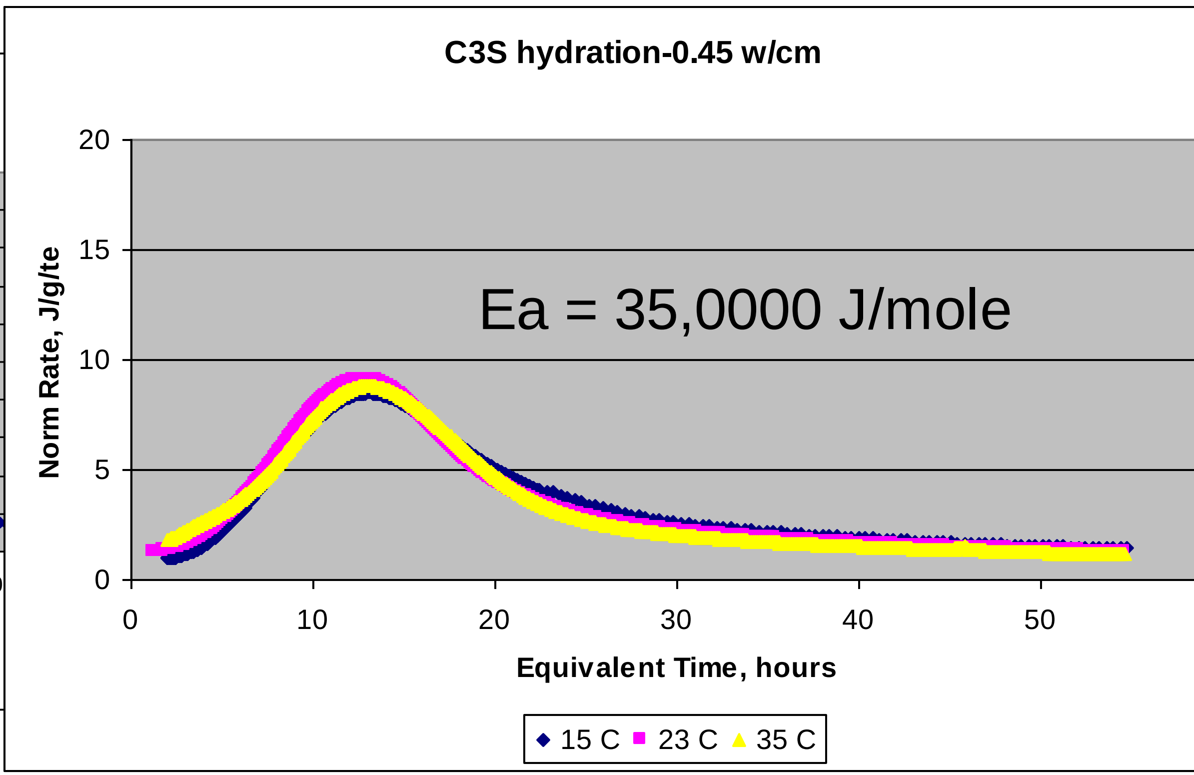




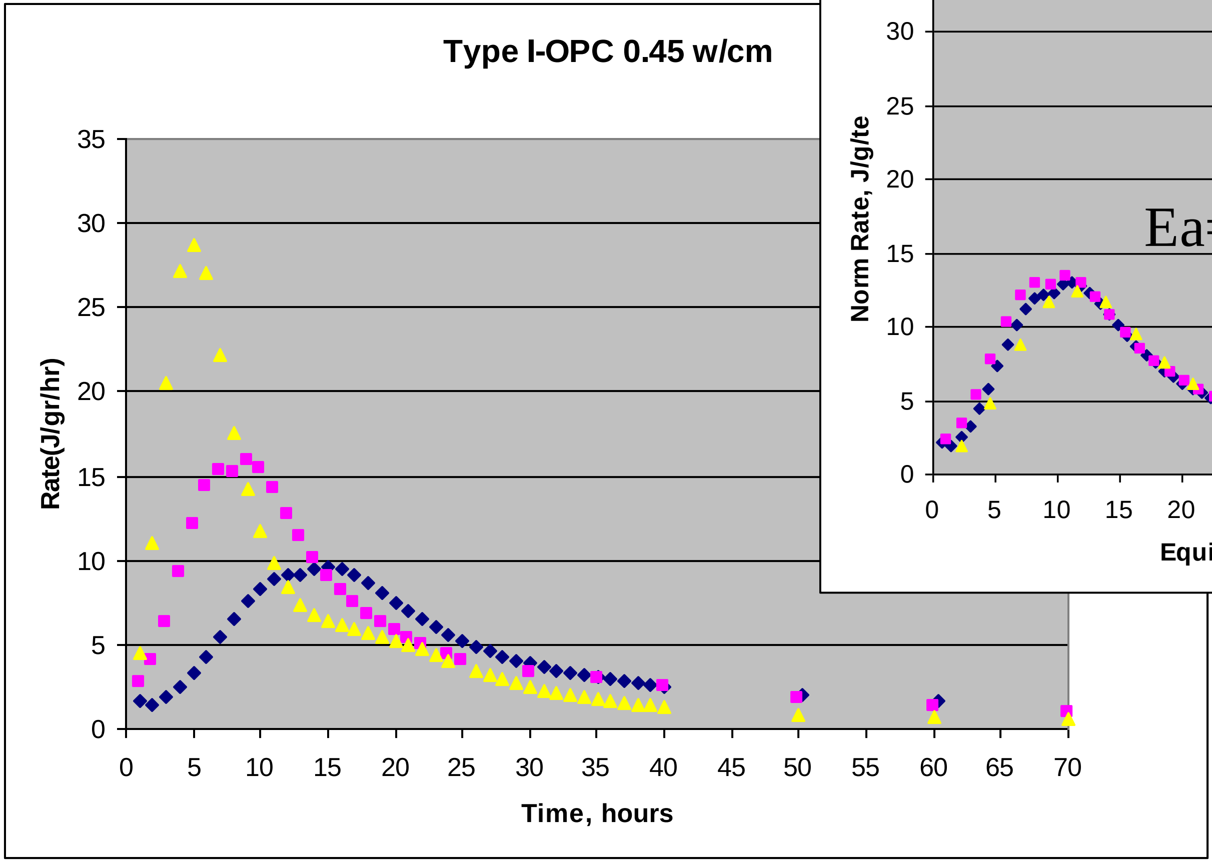
Normalizing for Temperature Effect-Arrhenius-Based Function

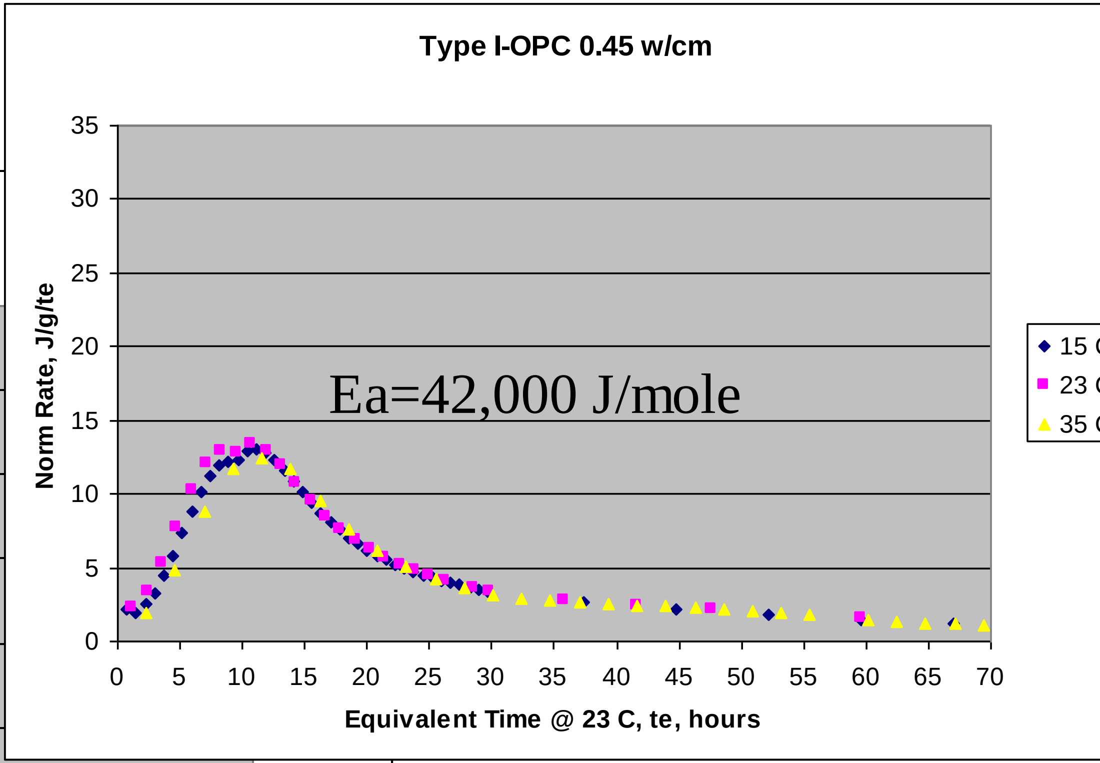
- Relative Rate = EXP (-Ea/R*[(1/Tref(^{0}K)-1/Tref (^{0}K)+T (^{0}C))]
- Isothermal Condition: Equivalent Time @ 20 ^{0}C, te, (hours) = Rel. Rate * t (@ temp of Interest))



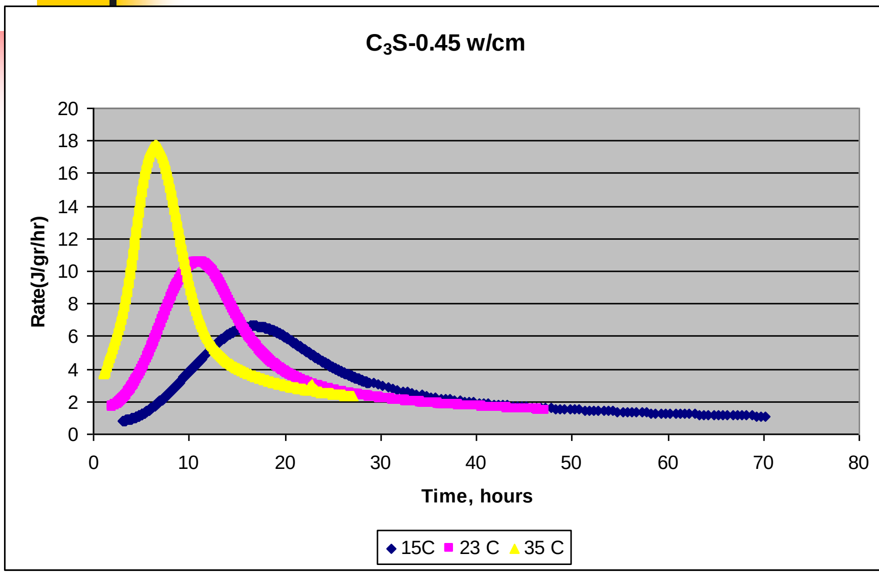


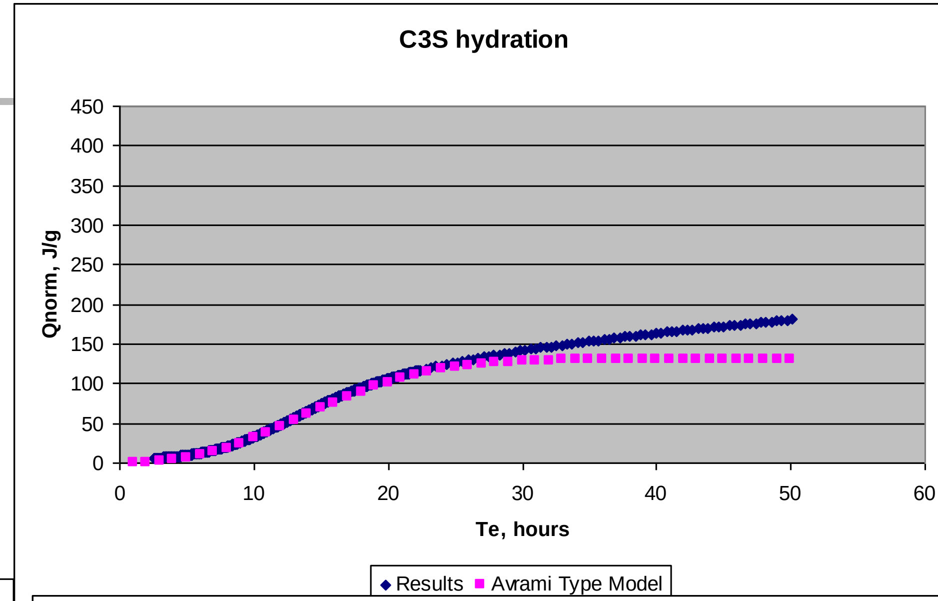
Type I Portland Cement-0.45 w/cm ratio paste

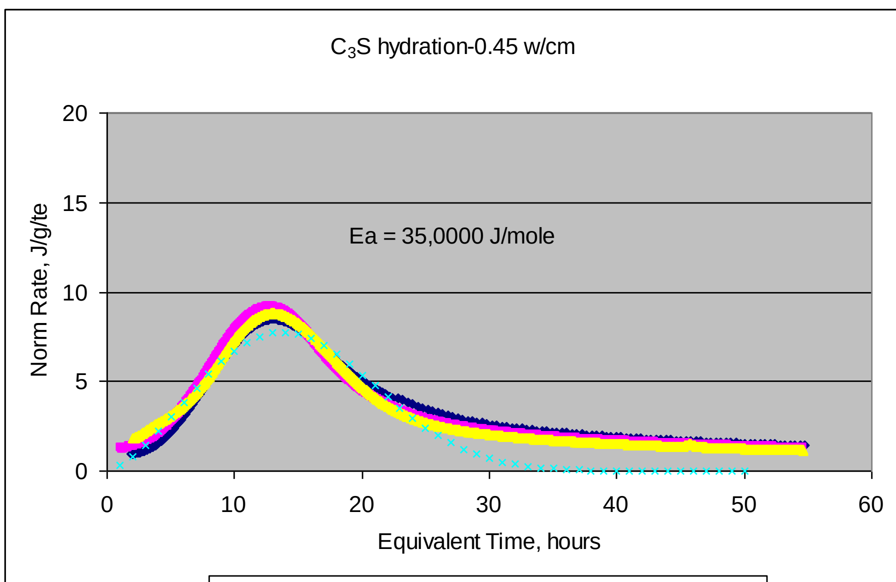


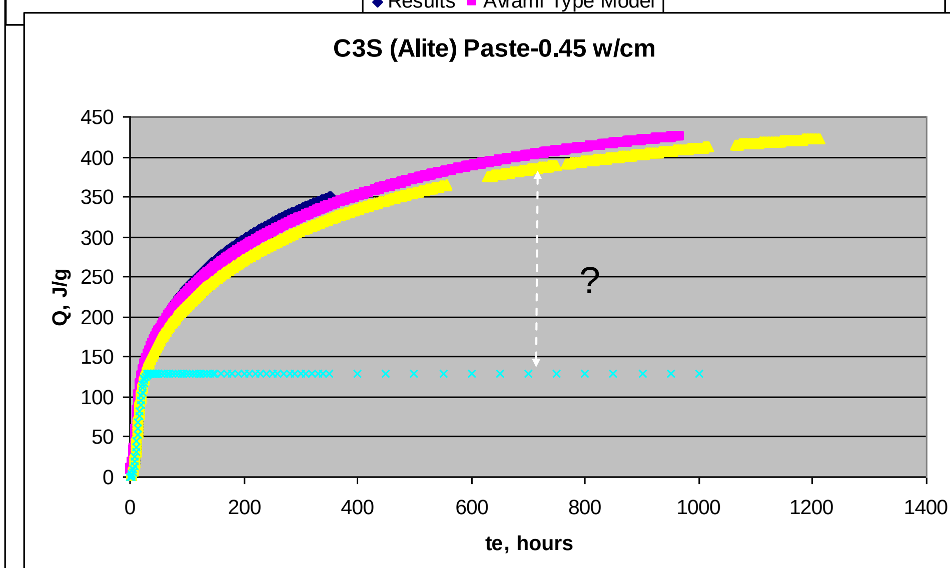


Mechanism-Based Hydration Kinetics Modeling

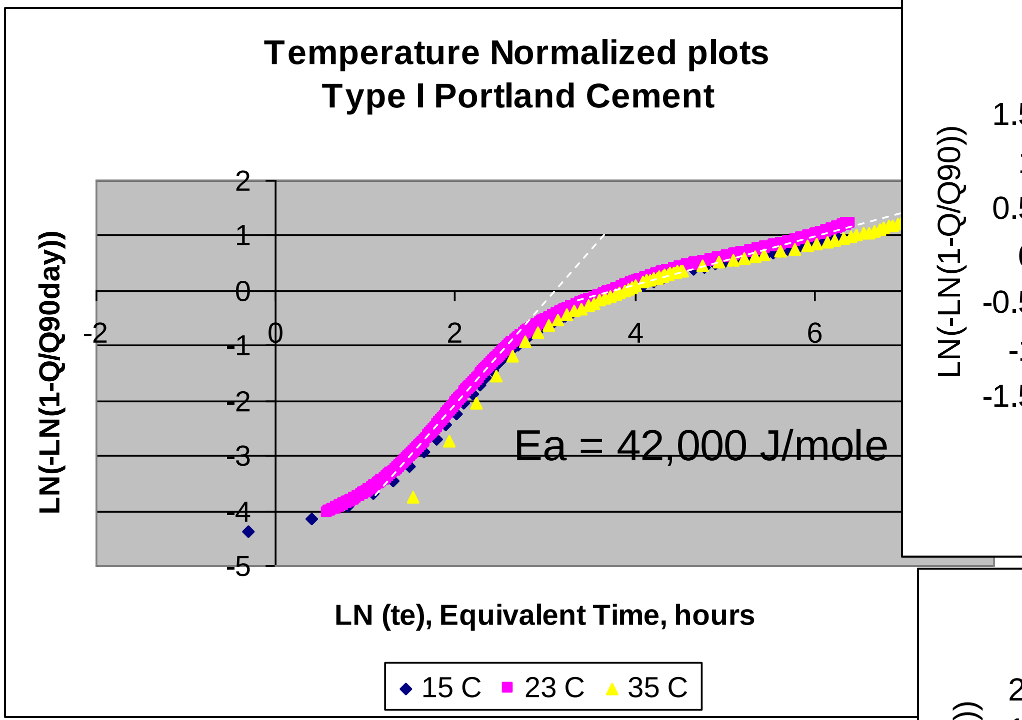


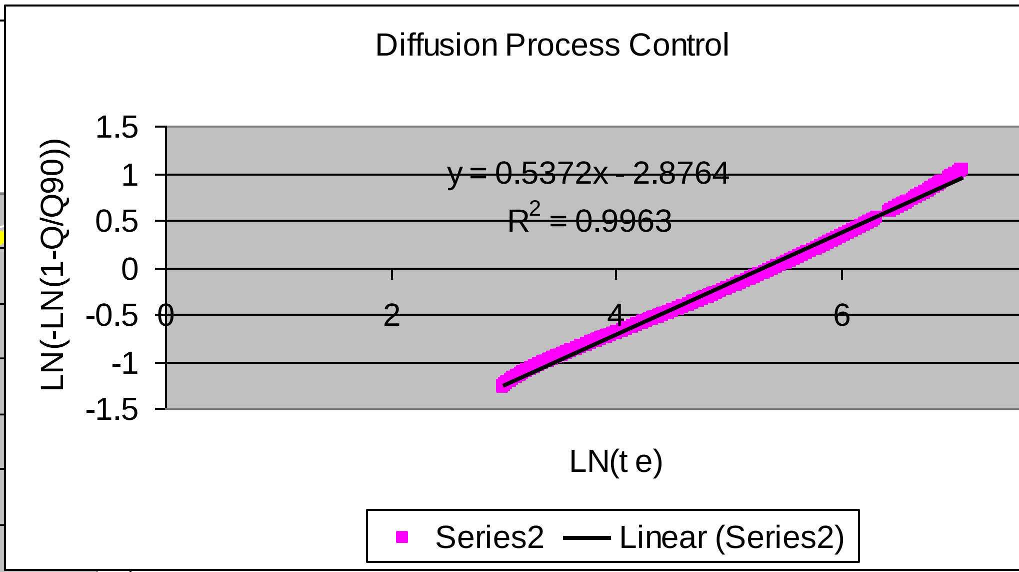


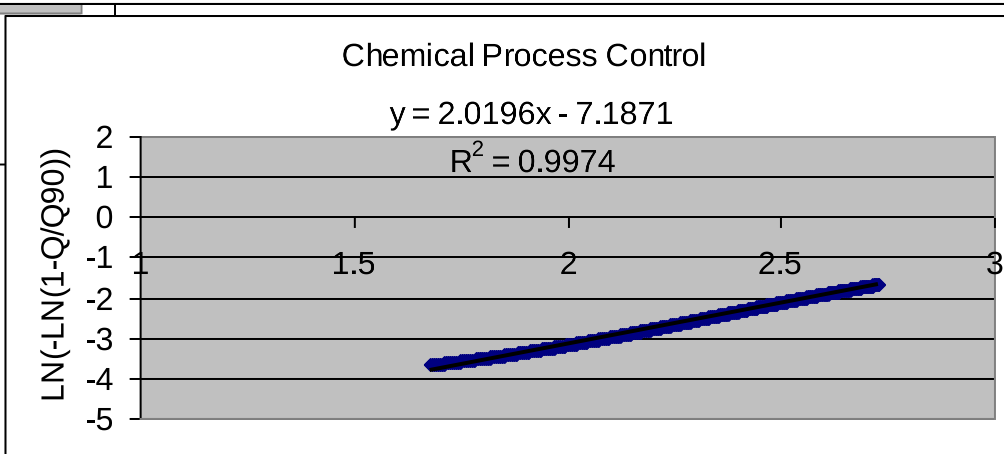




Nucleation & Growth – Temperature Normalization







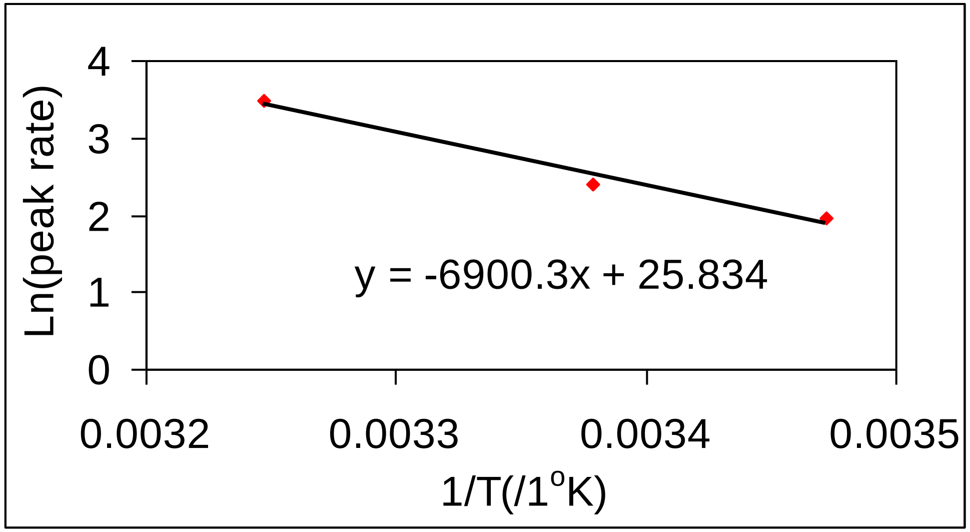
Modeling Hydration

$$\frac{dQ}{dt} = k(T)f(\hat{\alpha}) = k(T)f(\frac{Q}{Q_\infty})$$

Temperature effect

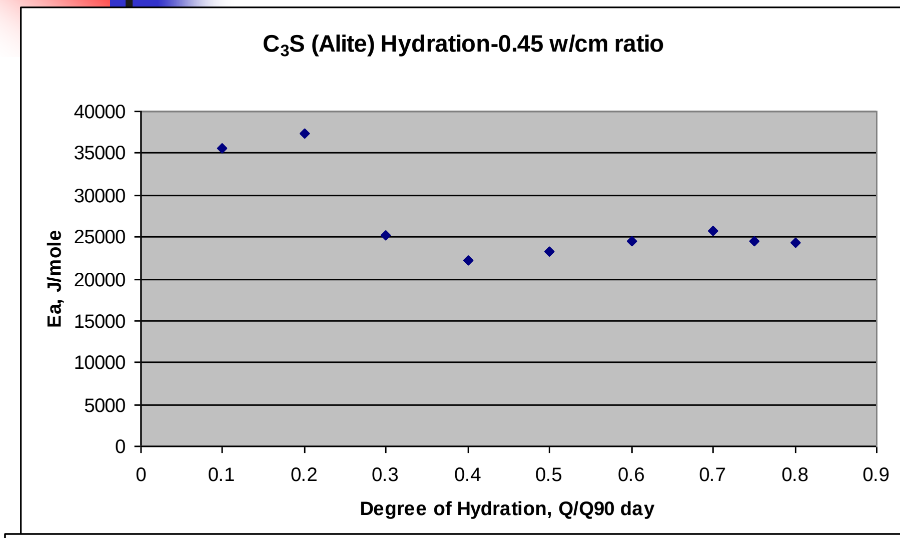
function of relative hydration (unique for a given system)

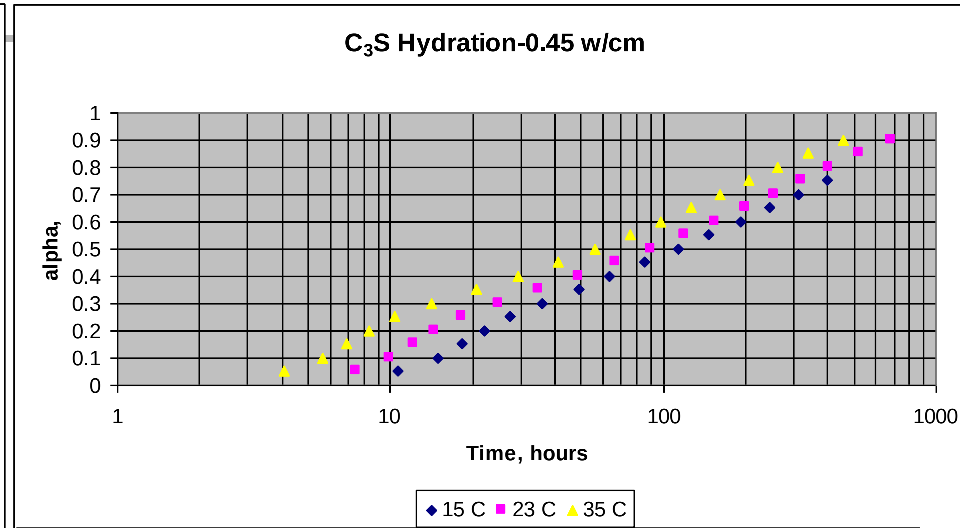
$$k(T) = A\exp[-(\frac{E_a}{RT})]$$

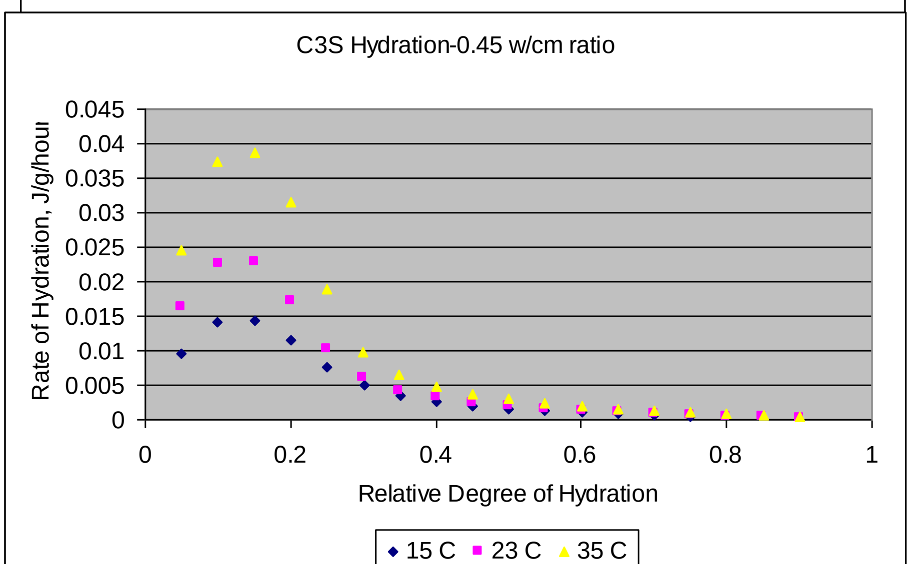


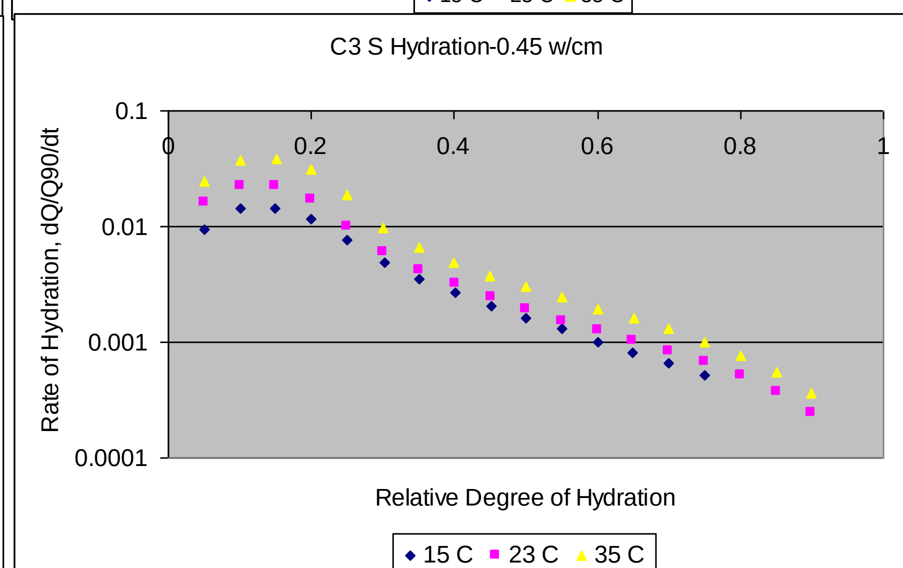
$$\hat{\alpha} = \frac{Q}{Q_\infty}$$

Hydration is affected by temperature at later stages although at a decreasing effect on total rate

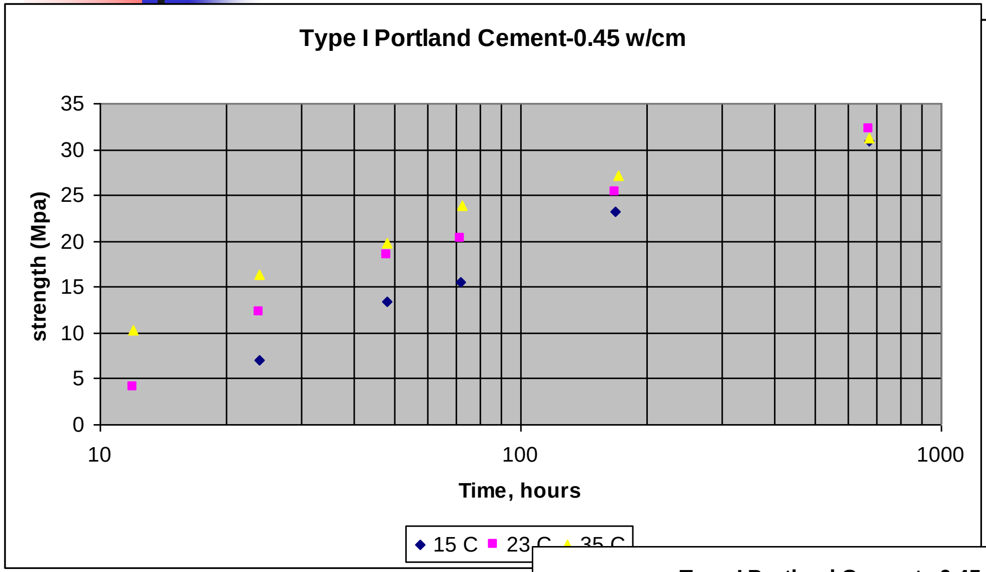


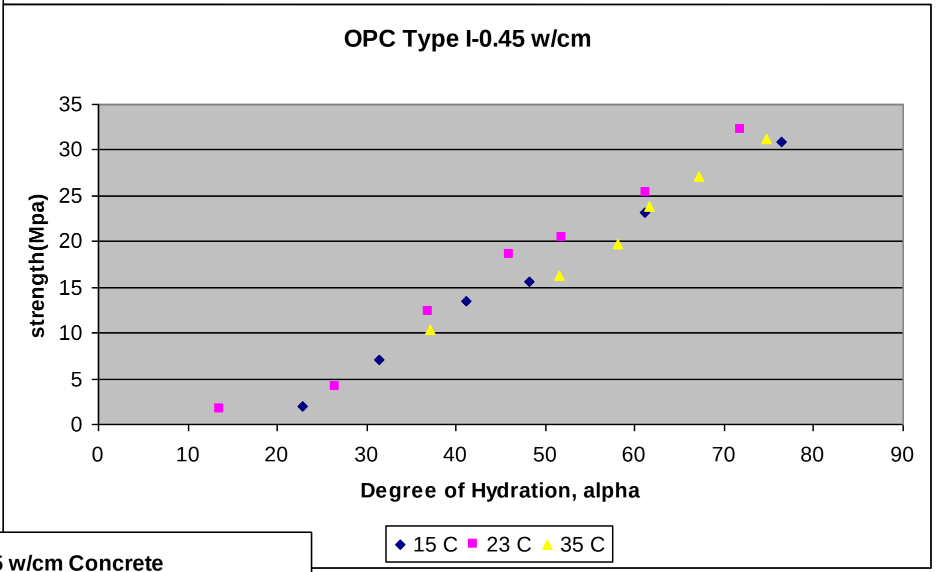


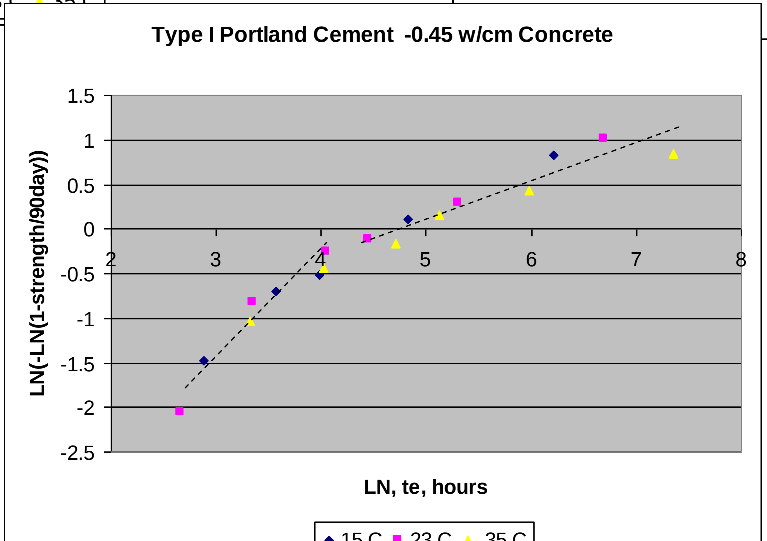




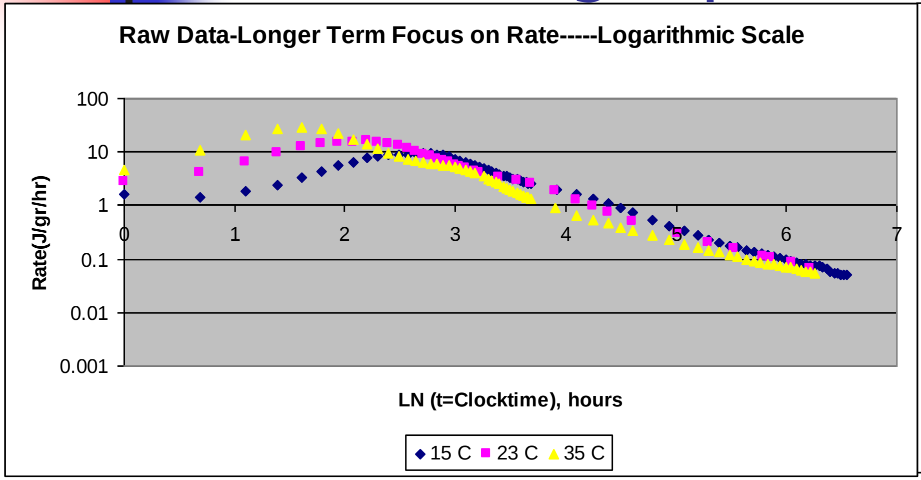
Two Different Stages from Concrete Strength Results

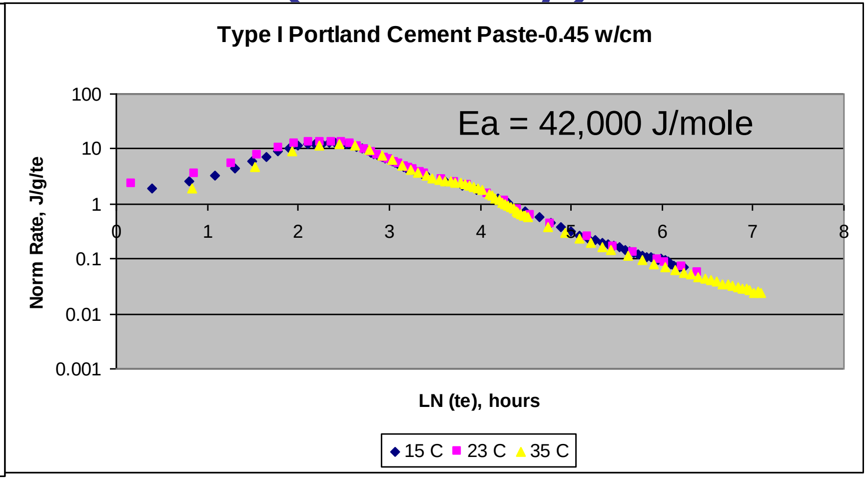


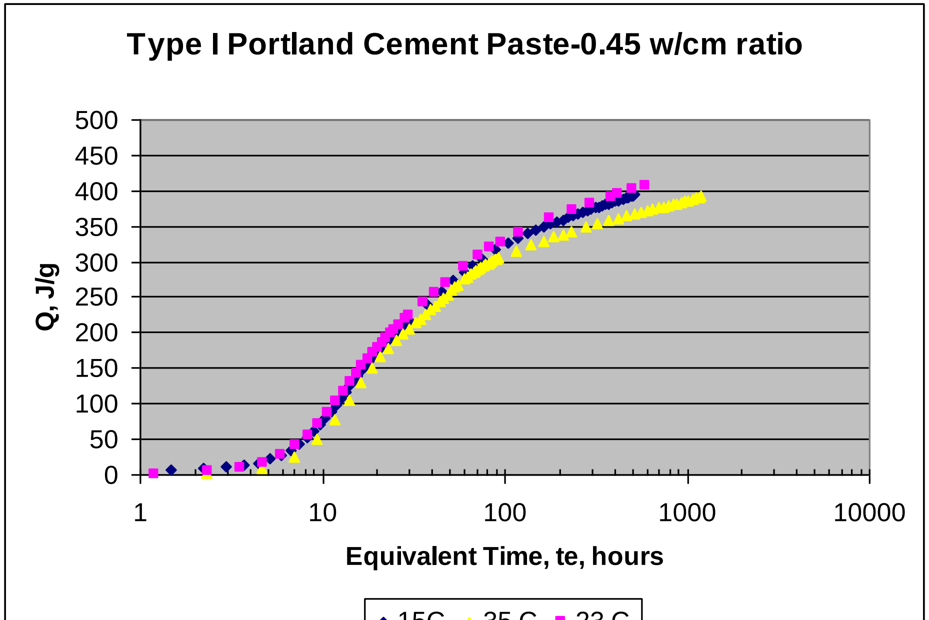




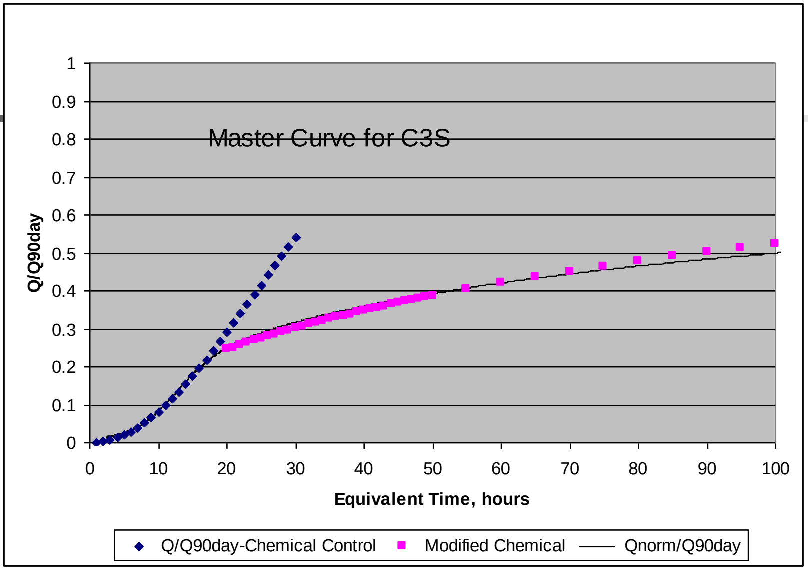
Normalize Hydration Curves for Temperature Effect using Equivalent Time (Maturity) Method

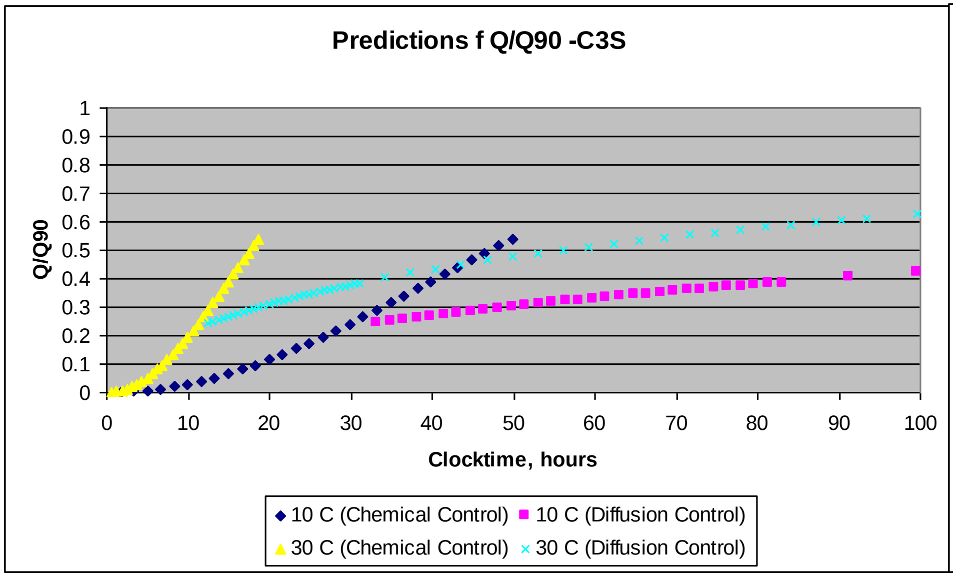


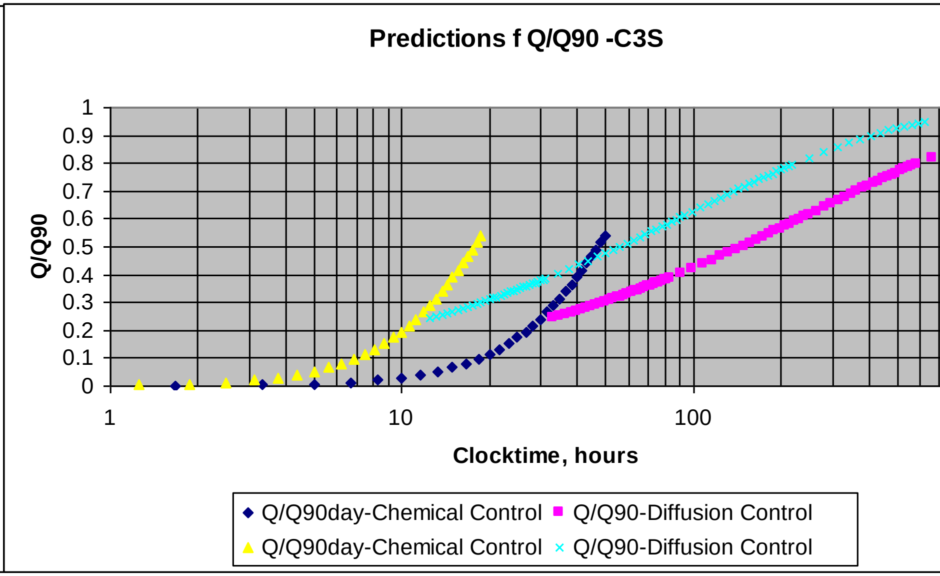




Mechanism-Based Modeling







Summary

- Two Distinct stages of hydration has been identified:
  - Initially rate is chemically Controlled
  - At later stages chemical control is gradually diminished due to diffusion process.

Thank You!