Numerical Modelling of Sintering of Alumina

- Pore shrinkage and Grain growth

Bo Fan
Aug 26th, 2013

Overview

- Introduction
- Background Knowledge
- Models & Examples
  - Particle – Number Continuity Equation
  - Isolated Pore Shrinkage Model
  - Isolated Grain Growth Model
  - Combination of Pore Shrinkage Model and Grain Growth Model
- Conclusions and Future Work

Introduction

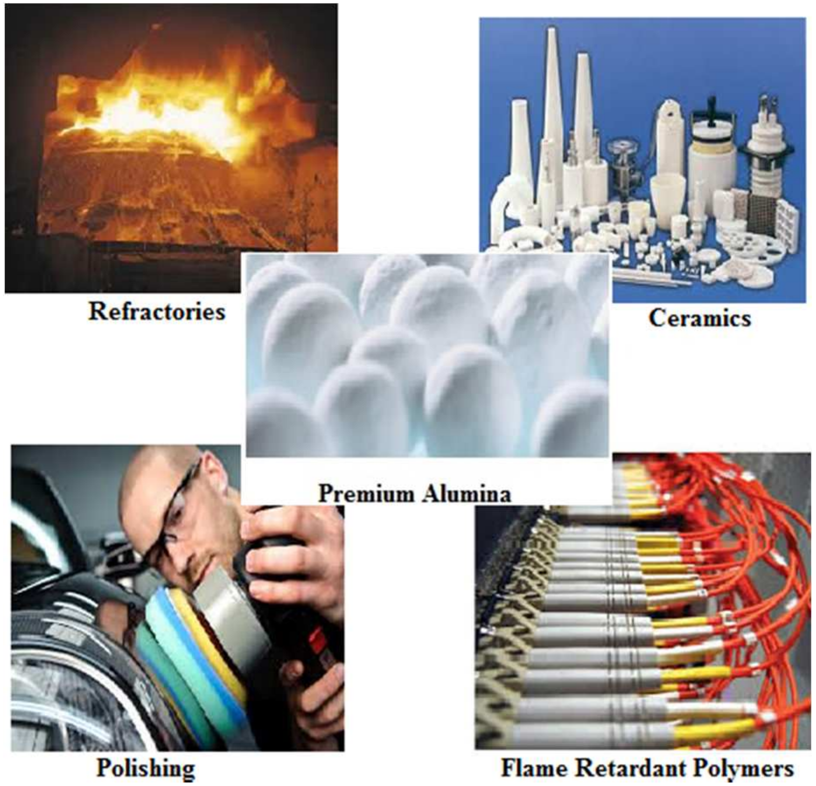
- Almatis and this project
  - Why do we do this project?
  - What do we have?
  - What do we want from this project?
  - What did we do?

Introduction

- Almatis and this project

As a leading producer of premium alumina in the market, Almatis is pursuing higher quality products so as to support and enhance the customers' business.

Sintering, which is a key process during the production of premium alumina, plays an important role on the quality of the final products.



Introduction

What do we want?

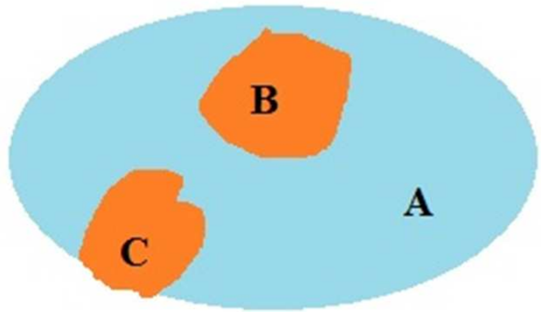
What's relative density? Why?

- Simulation of relative density
- Prediction using pre-defined temperature cycle

Background Knowledge

- Sintering Process of Alumina

Porosity



$$True\ Porosity = \frac{Total\ Pore\ Volume\ (B + C)}{Total\ Volume\ (A + B + C)}$$

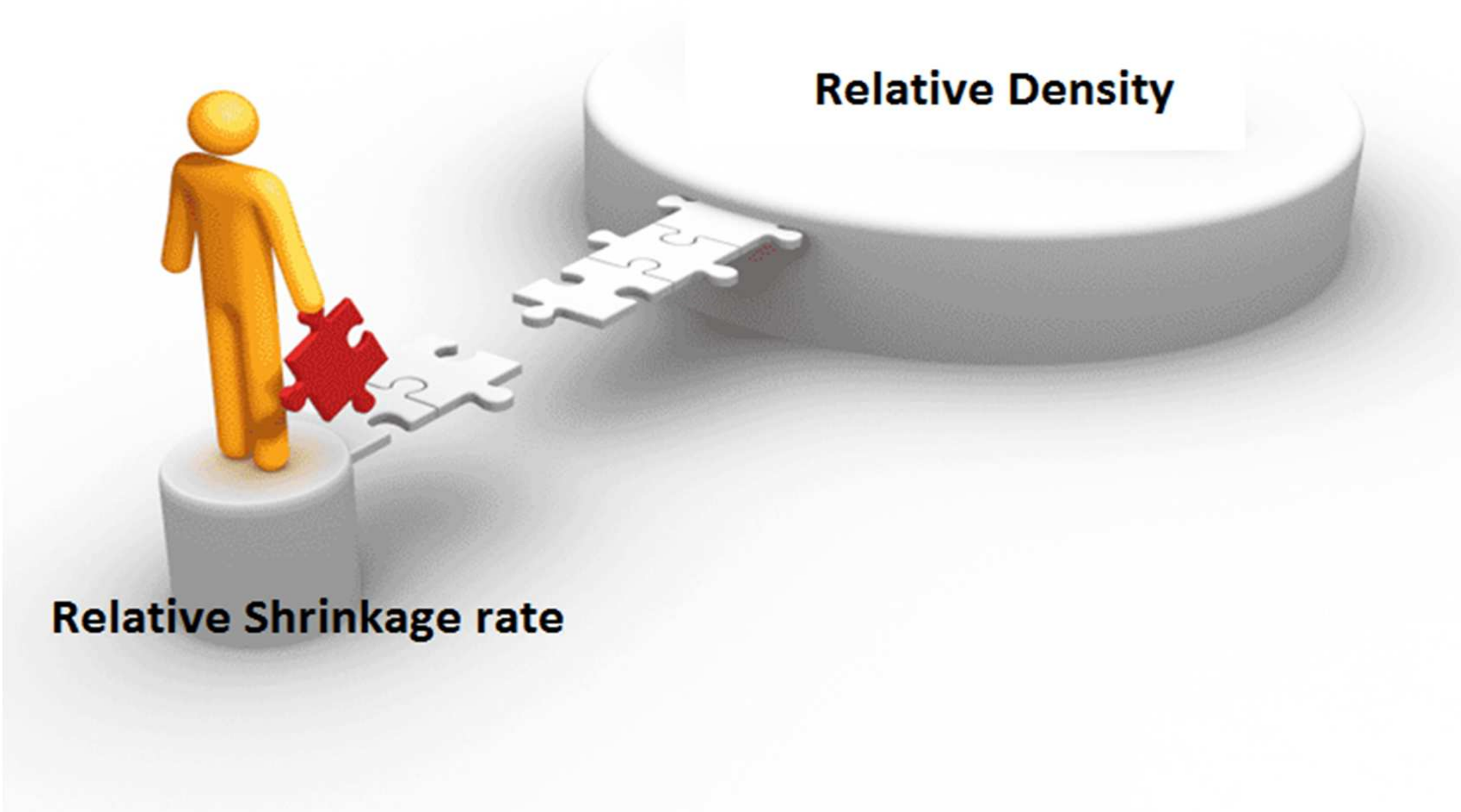
Relative Density (also called bulk specific gravity, i.e. BSG)

$$Relative\ Density = \frac{Bulk\ density}{True\ density} = \frac{\frac{mass}{total\ volume}}{\frac{mass}{solid\ volume}}$$

$$= \frac{solid\ volume\ (A)}{total\ volume\ (A + B + C)} = 1 - True\ Porosity$$

We'd like to use relative density in our project.

Introduction



Introduction

What kind of data do we have?

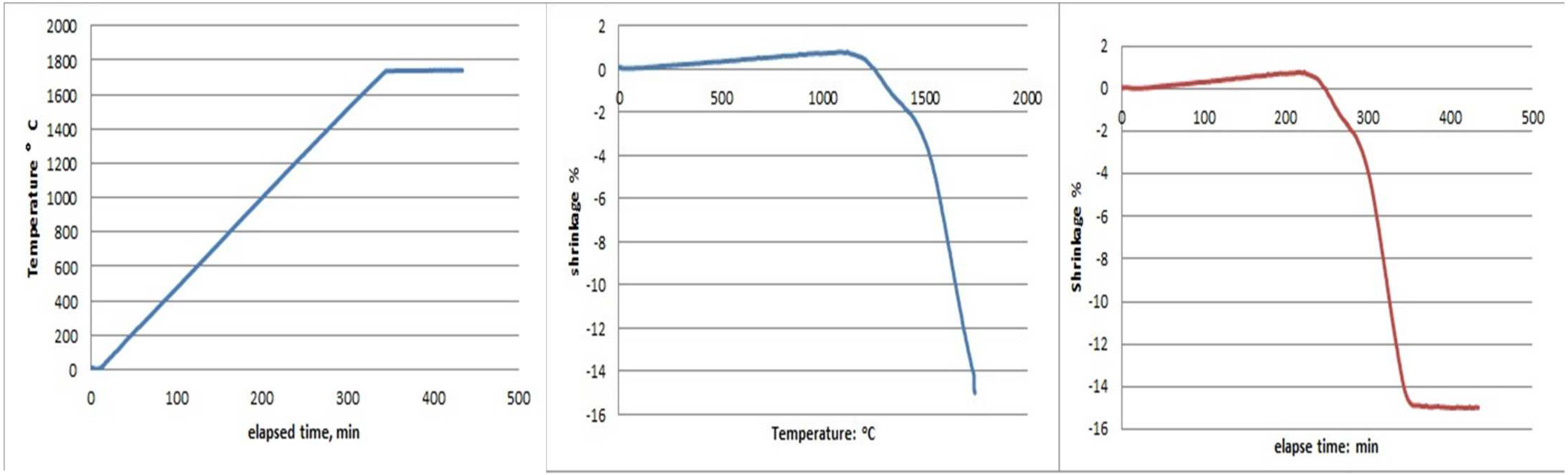
- Dilatometer test result (Dilatometer test is used to measure sintering kinetics)

What kind of data?

Introduction

- Result of Dilatometer Test

Temperature cycle and relative shrinkage rate (i.e. the volume change of the sample $\epsilon = \frac{\Delta V}{V_0}$)



Introduction

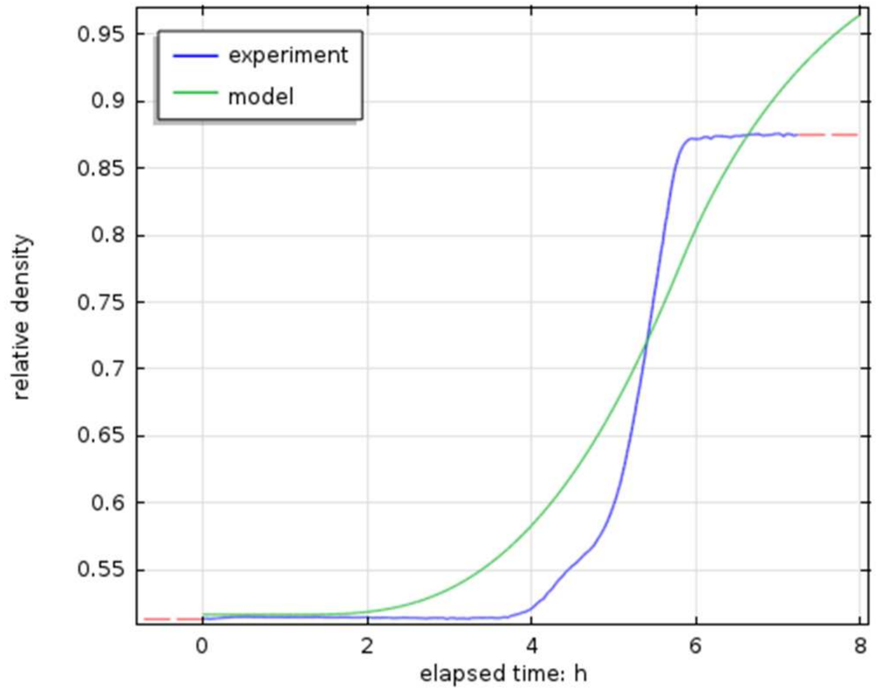
What did we do?

- Transfer the result of Dilatometer test to desification curve (relative density v.s. temperture)
- Build a model for calculating relativety density
- Model validation and calibration
- Prediction with exsiting model
- Additional models used to better understand the sintering process

Introduction

- Simulation Result

Main Result: comparison of experiment data and model result:



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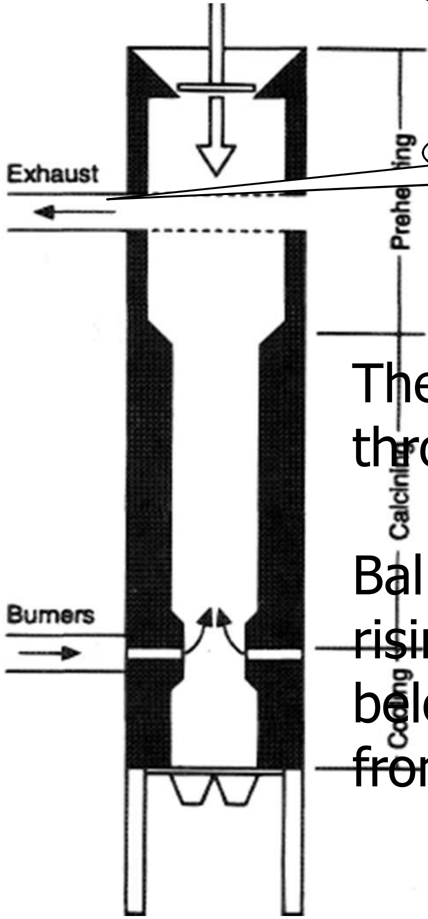
Background Knowledge

- What’s happened in the real industry field?
- What’s sintering?
- Sintering and microstructure

Background Knowledge



ring (converter)

green balls enter

The balls move slowly downwards through the vertical shaft kiln.

Balls above are preheated by rising hot exhaust gases and balls below are cooled by incoming air from the bottom.

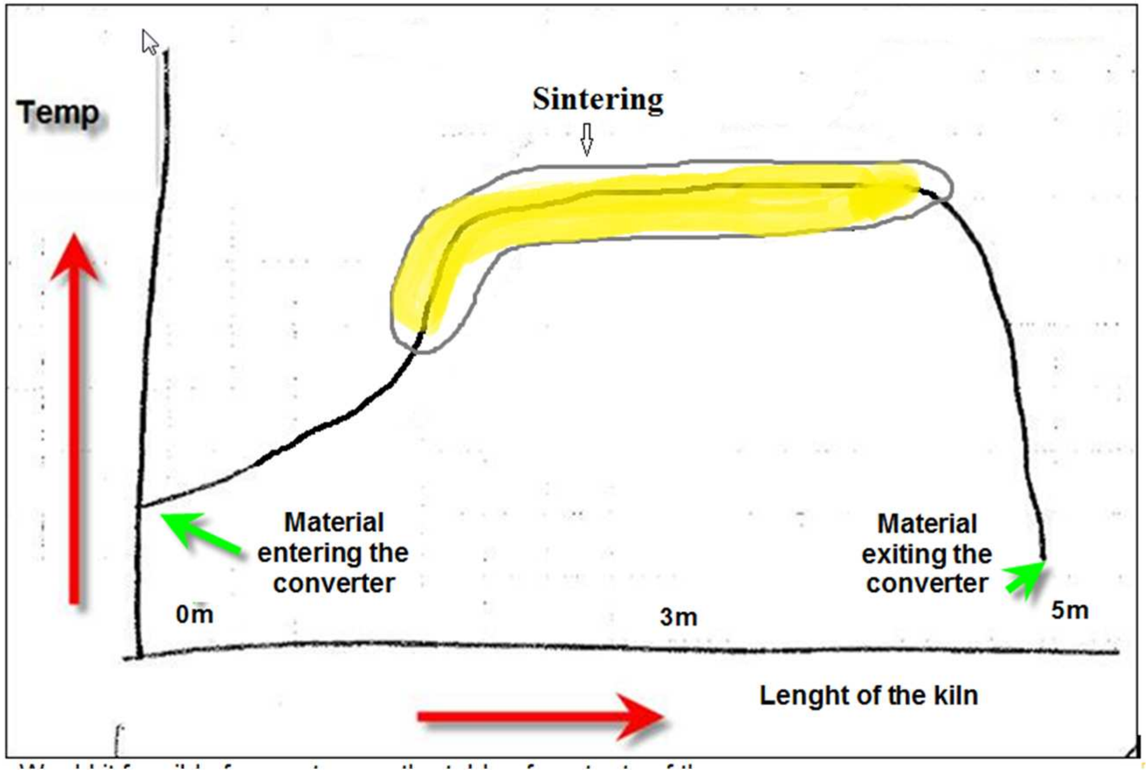
sintered converter discharge (CD) balls

Background Knowledge

- Temperature in the converter

The sintering temperature of high purity alumina is generally above 1600 ^{o}C, and blow the melting point of α-alumina 2050 ^{o}C.

In different cases, the sintering temperatures are different.



Temperature in the shaft kiln

Background Knowledge

- Definition of sintering

Definition of Sintering: "When thermal energy is applied to a powder compact, the compact is densified and the average grain size increases. The basic phenomena occurring during this process, called sintering, are densification and grain growth." - Suk-Joong L.Kang (2005)

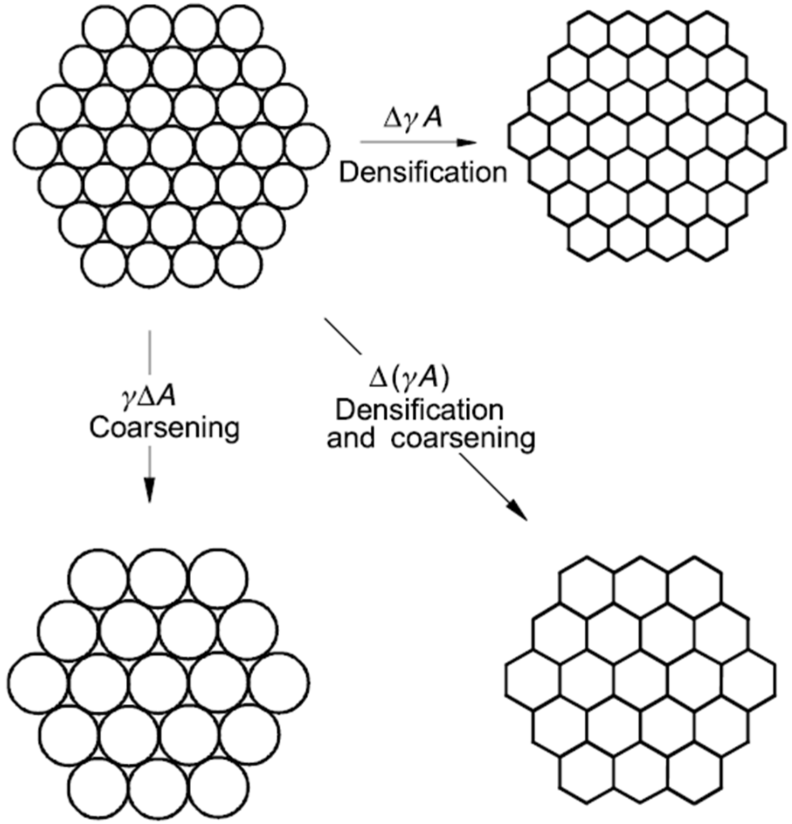
Background Knowledge

– Two basic microstructure phenomena of sintering

For densification: the solid-gas interfaces (surfaces) is replaced by grain boundaries.

For grain growth: the ratio of the interfacial area per volume of the grains are reduced.

Optimization of alumina sintering is to achieve zero porosity (fully dense compact) with minimum possible grain growth.



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Model & Examples

- Particle Number Continuity Equation
- Isolated Pore Shrinkage Model
  - Introduction of the model
  - Validation
  - Looking for proper parameters
  - Sensitive Analysis
- Isolated Grain Growth Model
- Combination of Pore Shrinkage Model and Grain Growth Model

Model - Particle-Number Continuity Equation

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial r}(v_r n) = 0$$

The basic idea behind this equation is conservation of particle number.

- Assumptions behind this equation
  - The sample is spacially homogenous and sintering is a convectionless batch process.
  - Sintering is coalescence free.
  - The velocity is only determined by radius r.

- In our project, we use this equation for the pore shrinkage ($n = n_p$) as well as grain growth process ($n = n_g$) .

Model & Examples

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Model - Isolated Pore Shrinkage

$$\frac{\partial n_p(r_p,t)}{\partial t} + \frac{\partial}{\partial r_p}(v_{r_p} n_p(r_p,t)) = 0$$

- n_p - the number density function of pores. $n_p(r_p,t)dr_p$ is the number of pores whose radius is between r_p and $r_p + dr_p$. (unit of n_p: $\mu m^{-3} \mu m^{-1}$).
- r_p - pore size (unit: μm).
- t – time
- $v_{r_p} = -\frac{k_p}{r_p^m}$ is the rate of pore shrinkage.
- m - is a floating model parameters influenced by the material transport mechanism (unit: 1) .

Model - Isolated Pore Shrinkage

$$\frac{\partial n_p(r_p,t)}{\partial t} + \frac{\partial}{\partial r_p}(v_{r_p} n_p(r_p,t)) = 0$$

- k_p (unit: $\mu m^{(m+1)}/h$) is a rate constant decided by Arrhenius equation.

$$k_p = k_{p0} e^{-\frac{Q_p}{RT}}$$

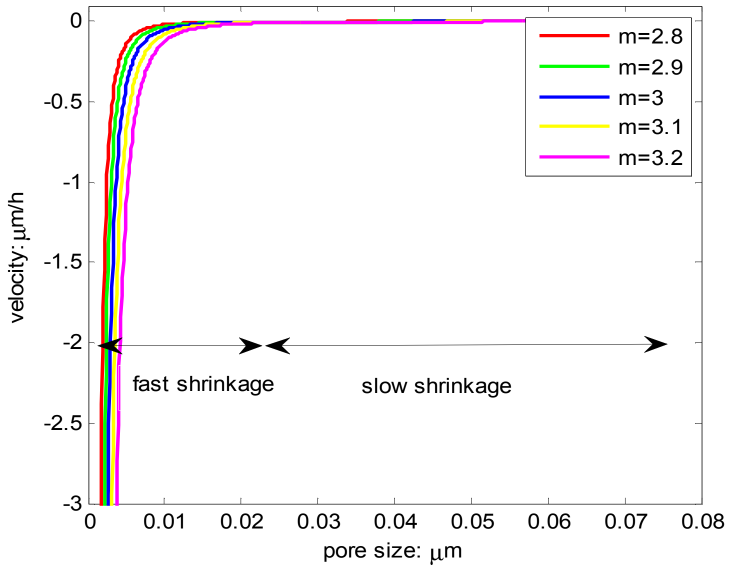
- Where
  - R - the gas constant (unit: $J \cdot K^{-1} mol^{-1}$)
  - T - the absolute temperature (unit: K)
  - Q_p - the activation energy for densification result (unit: J)
  - k_{p0} - pre-exponential factor (unit: depends on the order of reaction and is same as k_p) .

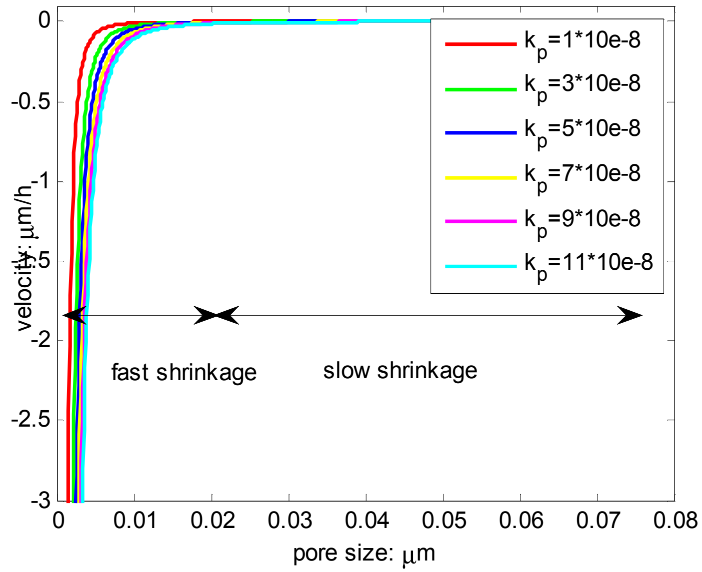
Model - Isolated Pore Shrinkage

$$\frac{\partial n_p(r_p,t)}{\partial t} + \frac{\partial}{\partial r_p}(v_{r_p} n_p(r_p,t)) = 0$$

- $v_{r_p} = -\frac{k_p}{r_p^m}$ is the rate of pore shrinkage.

The smaller the pore is, the faster it shrinks.
For the small pores, the larger m is, the faster the shrinkage rate is. And the larger k_p is, the faster the shrinkage rate is.





Model - Isolated Pore Shrinkage

$$\frac{\partial n_p(r_p,t)}{\partial t} + \frac{\partial}{\partial r_p}(v_{r_p} n_p(r_p,t)) = 0$$

At sintering time t, the cumulative pore size distribution is

$$F_v(r_p,t) = \frac{\int_{r_p}^{\infty} n_p(r'_p,t) r'^3_p dr'_p}{\int_0^{\infty} n_0(r_p) r_p^3 dr_p}$$

and the total pore volume (unit: 1) is

$$V_p(t) = C \int_0^{\infty} n_p(r_p,t) r_p^3 dr_p$$

where C is a dimensionless constant for given geometry.

Then the relative density can be calculated from the simulation result of this model

$$\rho_r(t) = \frac{1}{1 + \frac{V_p(t)}{V_p(0)}[\frac{1}{\rho_r(0)} - 1]}$$

$\rho_r(0)$ is the initial relative density.

Model - Isolated Pore Shrinkage

Validation of the Model:

- Analytical Solution

For initial pore size distribution $n_0(r_p)$, the analytical solution for the PDE is

$$n_p\left(r_p(t), t\right) = \frac{n_0([r_p^{m+1} + (m+1)\int_0^t k_p dt']^{1/(m+1)})}{(1 + (m+1){r_p}^{-(m+1)} \int_0^t k_p dt')^{m/(m+1)}}$$

- FDM Solution (forward Euler method)

Solving two ODEs $\longrightarrow$

$$\frac{dr_p}{dt} = -\frac{k_p}{r_p^m}$$

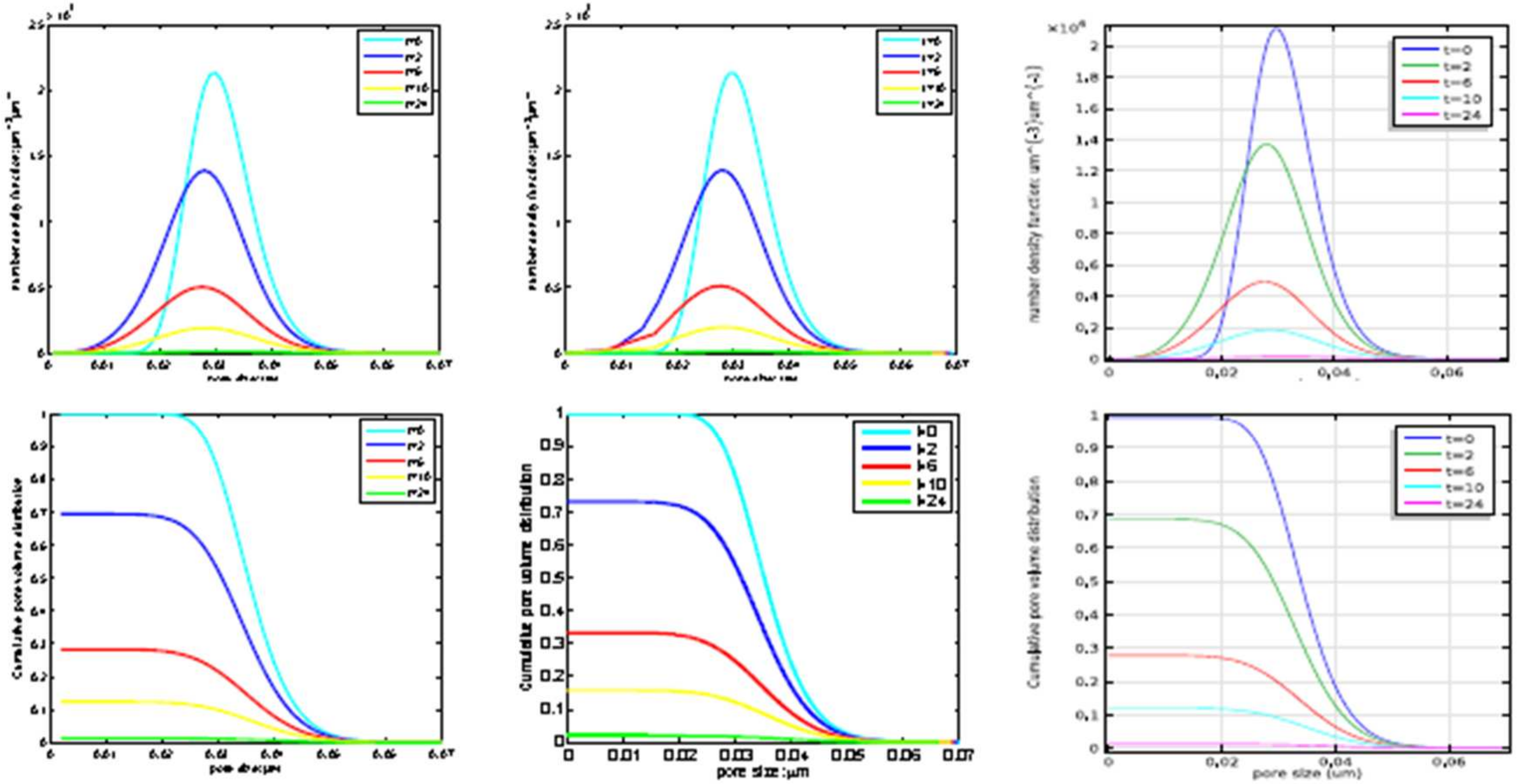
$$\frac{dn_p}{dt} = -n_p(r_p, t)\frac{k_p m}{r_p^{m+1}}$$

- FEM Solution (Streamline diffusion method)

Solving the PDE with COMSOL $\longrightarrow$ $\dfrac{\partial n_p(r_p,t)}{\partial t} + \dfrac{\partial}{\partial r_p}(v_{r_p} n_p(r_p,t)) = 0$

Model - Isolated Pore Shrinkage

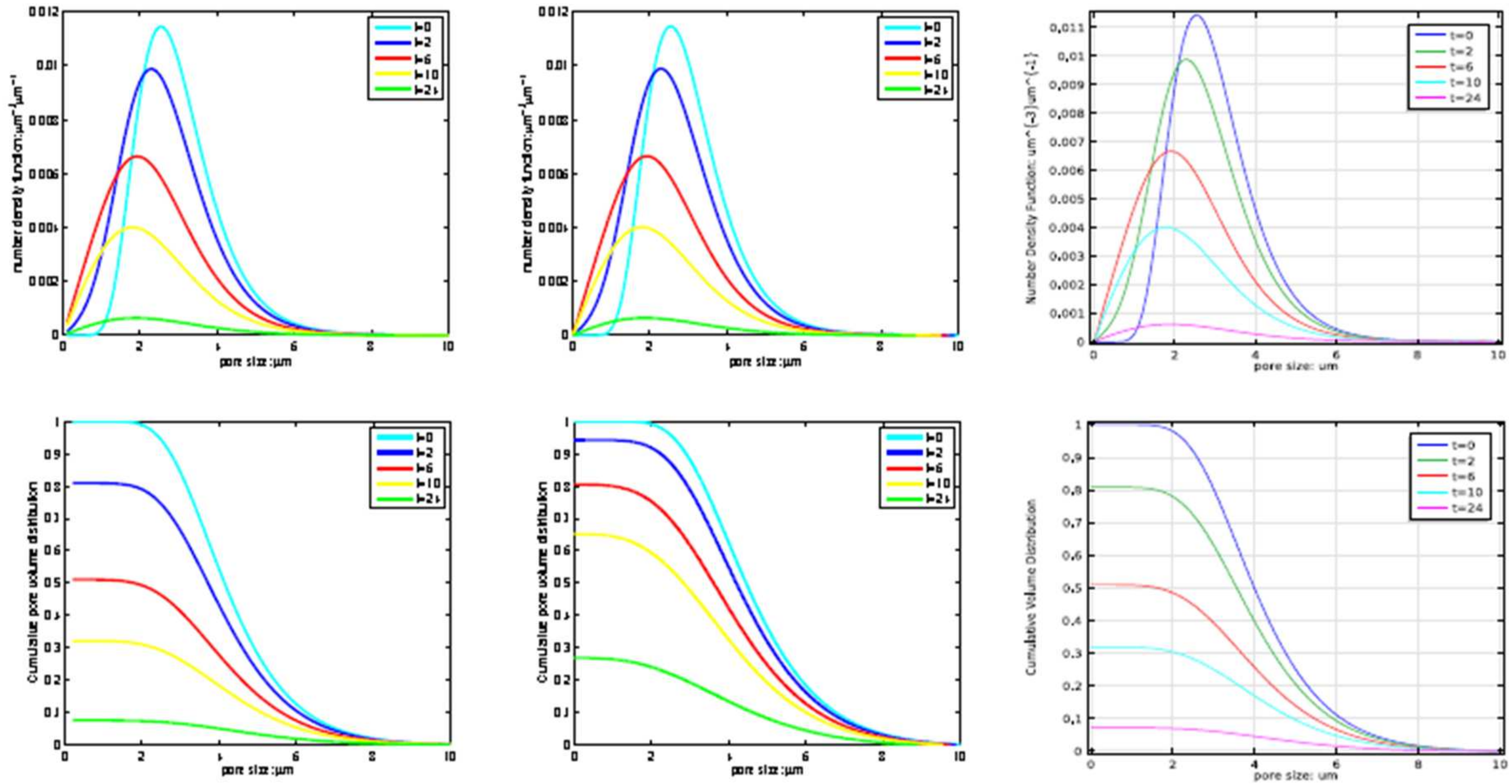
Validation of the Model – Example Alumina A16:



(a) analytical result (b) 2-ODE model (c) FEM result

Model - Isolated Pore Shrinkage

Validation of the Model – Example Zirconia SYP5.2:



Model - Isolated Pore Shrinkage

An example with data from literature:

Here we use

$$k_p(T) = \exp(k_{p0} - \frac{Q_p}{RT})$$

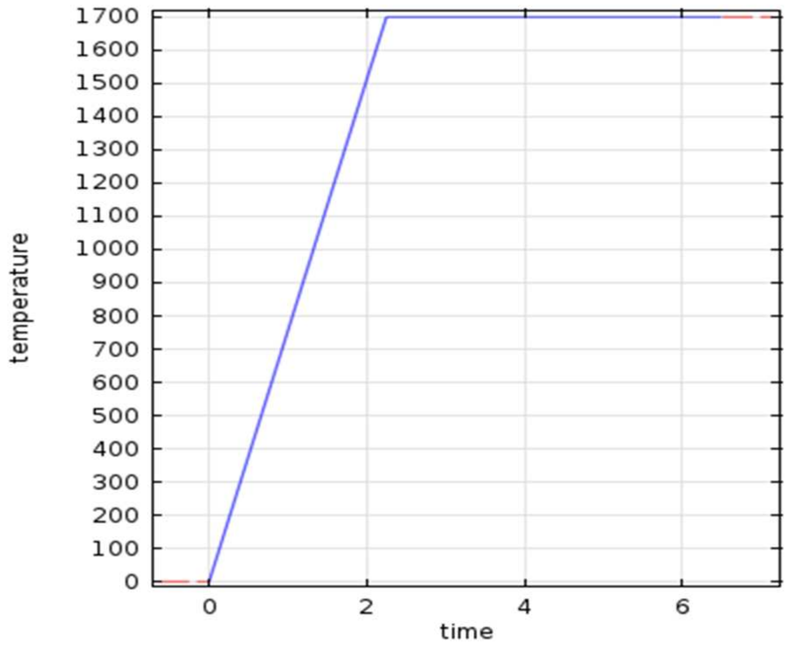
to generate parameter k_p

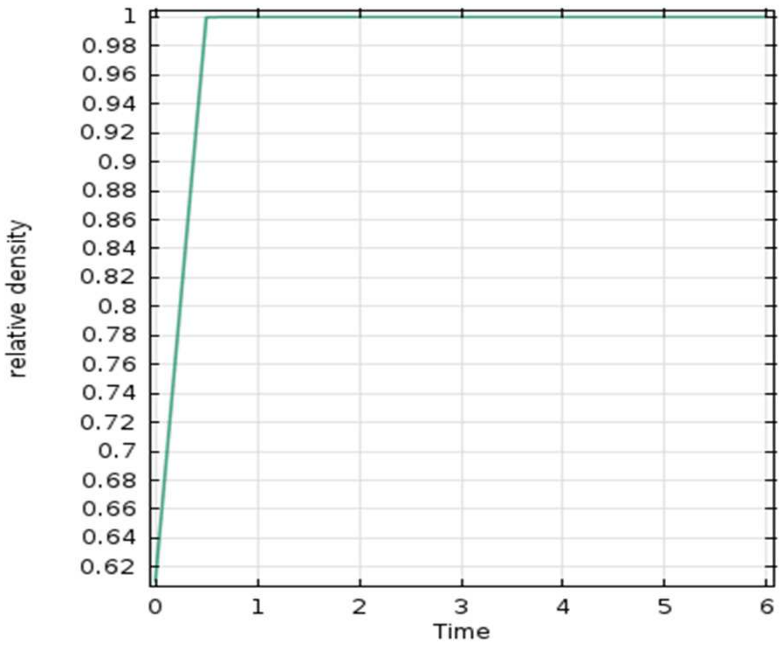
$$pore\ shrinkage\ parameters:$$

$$m = 4,\ k_{p0} = 12.2, Q_P = 131, \rho(0) = 0.61$$

Model - Isolated Pore Shrinkage

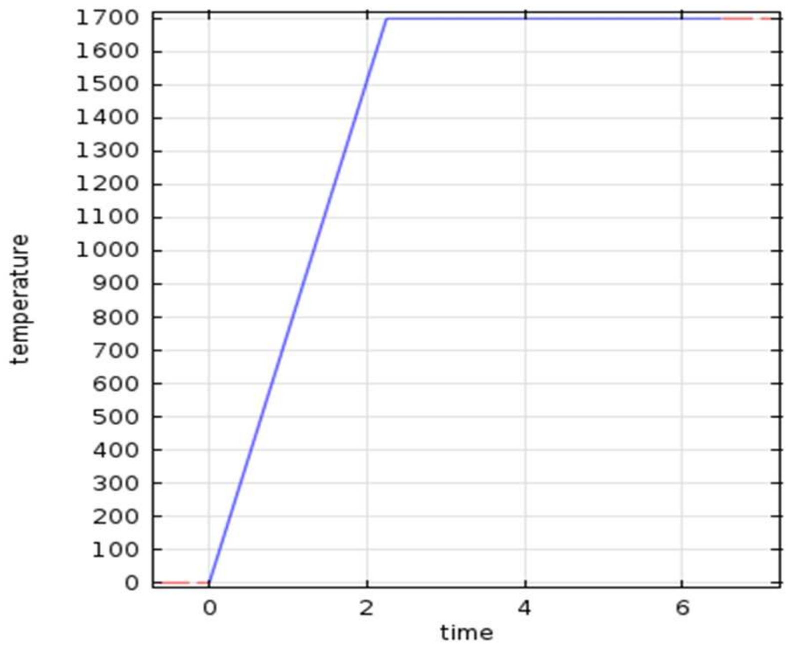
For initial pore size distribution: lognormal $r_m = 0.034, \sigma = 1.2$

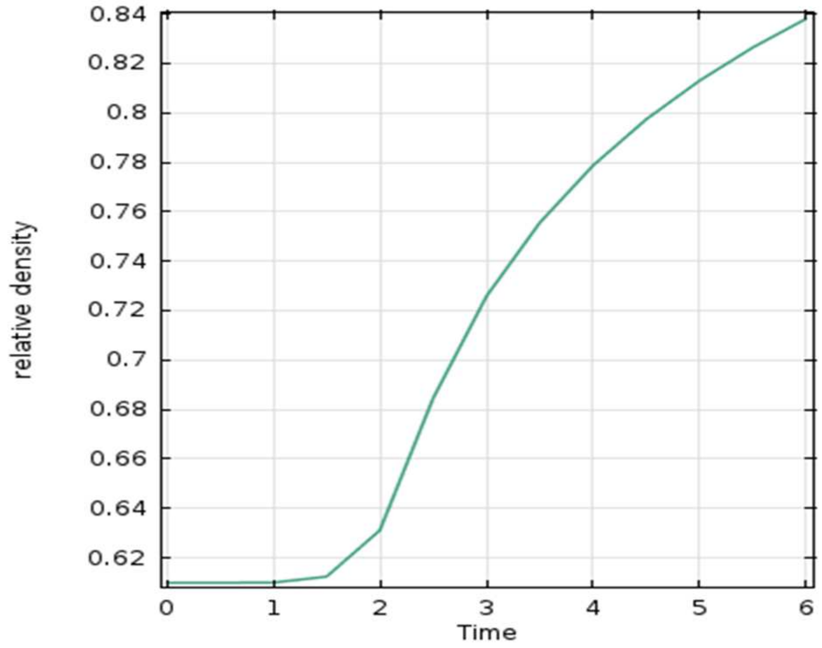




Model - Isolated Pore Shrinkage

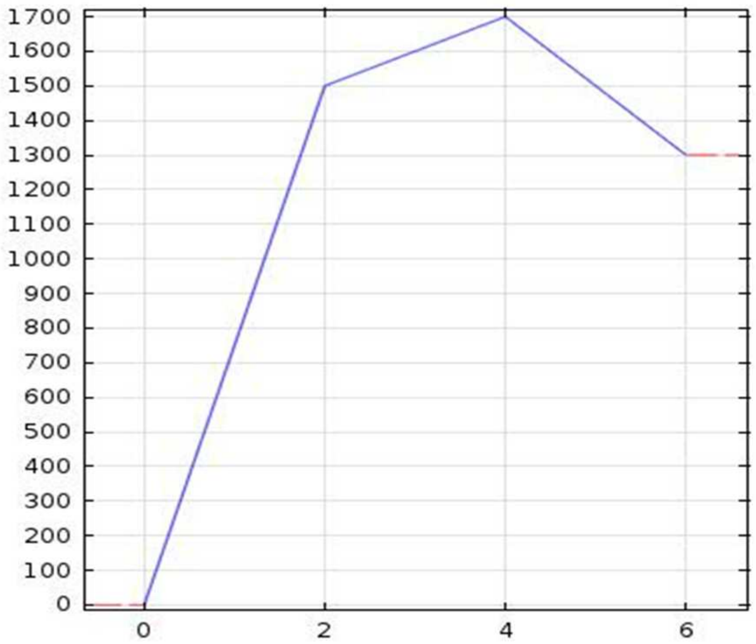
For initial pore size distribution: lognormal $r_m = 4, \sigma = 1.4$





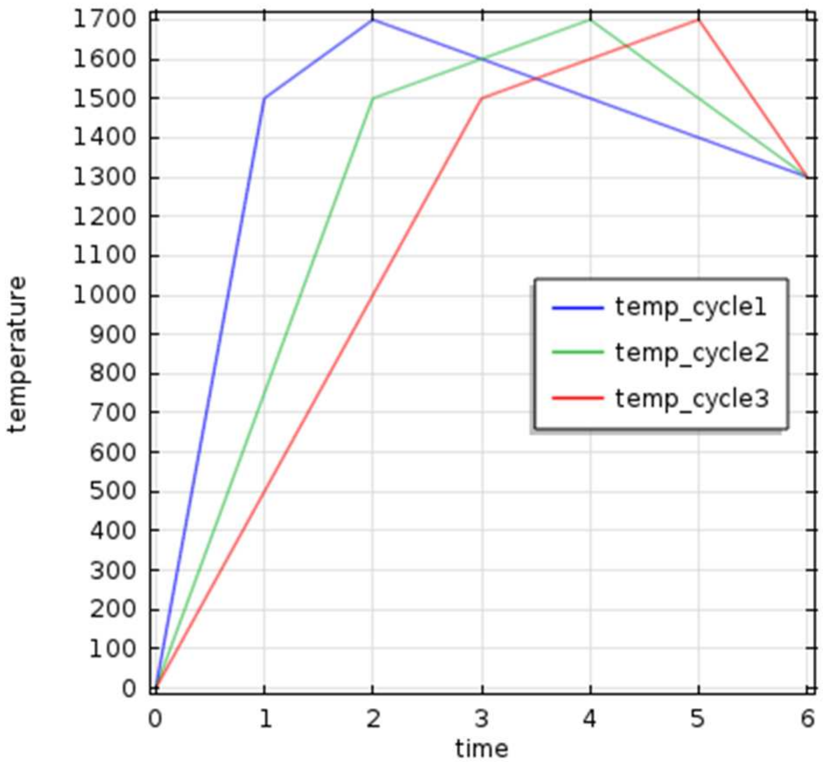
Model - Isolated Pore Shrinkage

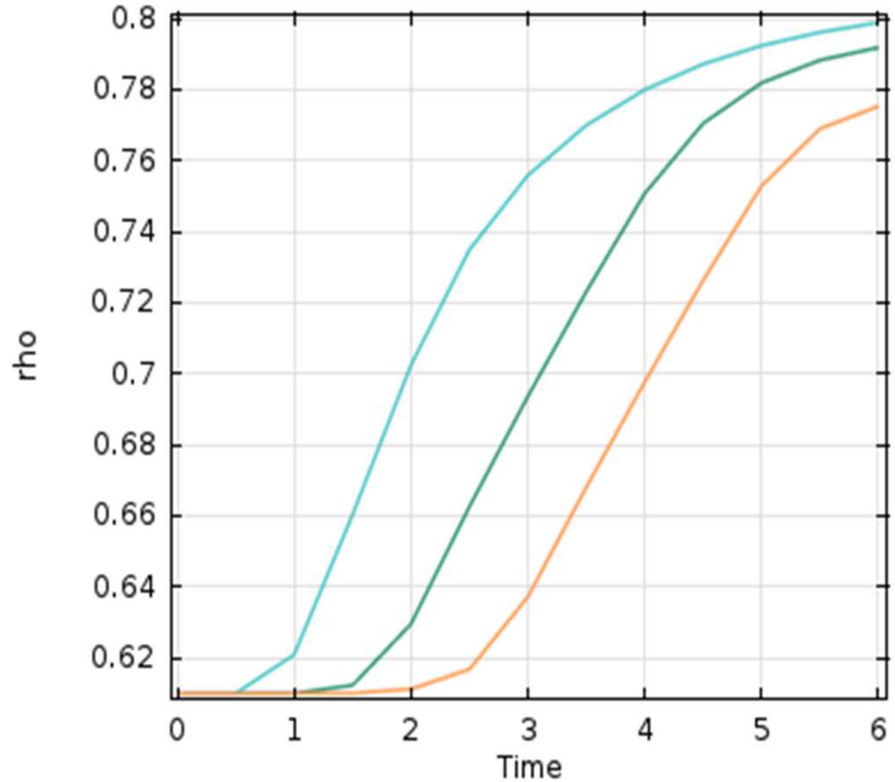
Parameters same as that in last slide.
Consider the temperature in the shaft kiln (increase in the preheating zone, then decrease in the cooling zone)



Model - Isolated Pore Shrinkage

For initial pore size distribution: lognormal $r_m = 4, \sigma = 1.4$





Model - Isolated Pore Shrinkage

Looking for proper parameters for our own case:

- Initial pore size distribution – from literature (log-normal distribution) and image analysis

$$n_0(r) = \frac{1}{r^4\sqrt{2\pi}\ln\sigma} e^{-\frac{1}{2}\left(\frac{\ln r - \ln r_m}{\ln\sigma}\right)^2}$$

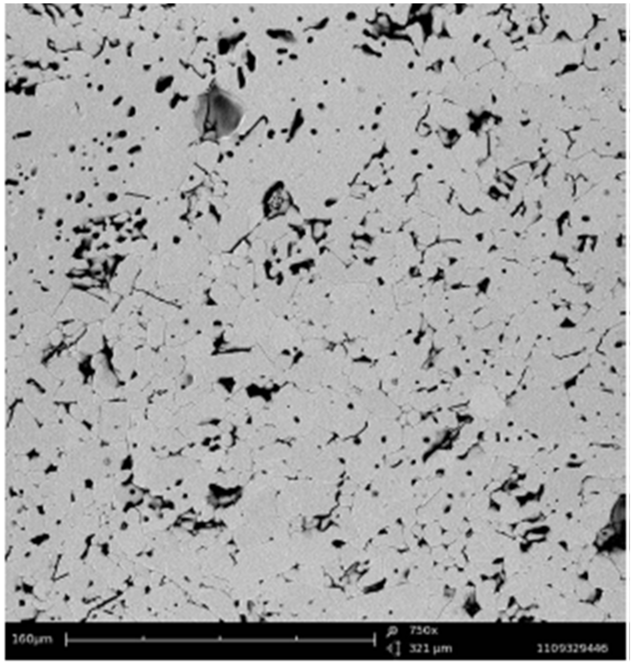
  r_m ($3.747\mu m$) and σ (5.925) are got from image analysis

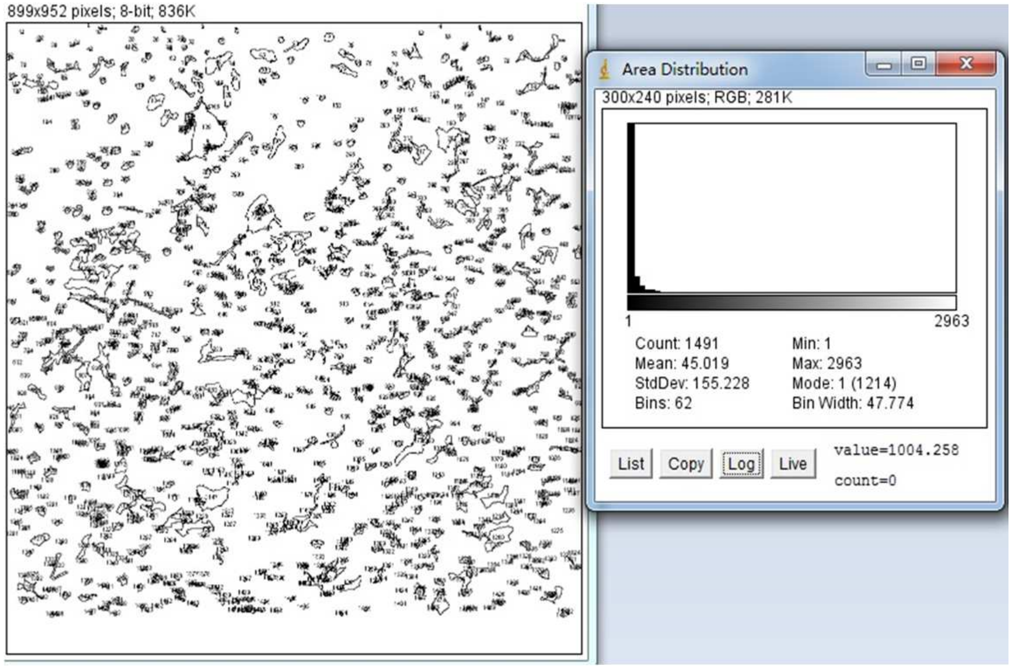
- Initial relative density – from literature or measurements 0.515
- Rate constant k_p - decided by Arrhenius equation
  - activation energy Q_p
  - pre-exponential factor k_{p0} - from trial and error
- Model parameter m - from trial and error

Model - Isolated Pore Shrinkage

$$\frac{\partial n_p(r_p,t)}{\partial t} + \frac{\partial}{\partial r_p}\left(v_{r_p} n_p(r_p,t)\right) = 0$$

- Initial pore size distribution $n_0(r_p)$



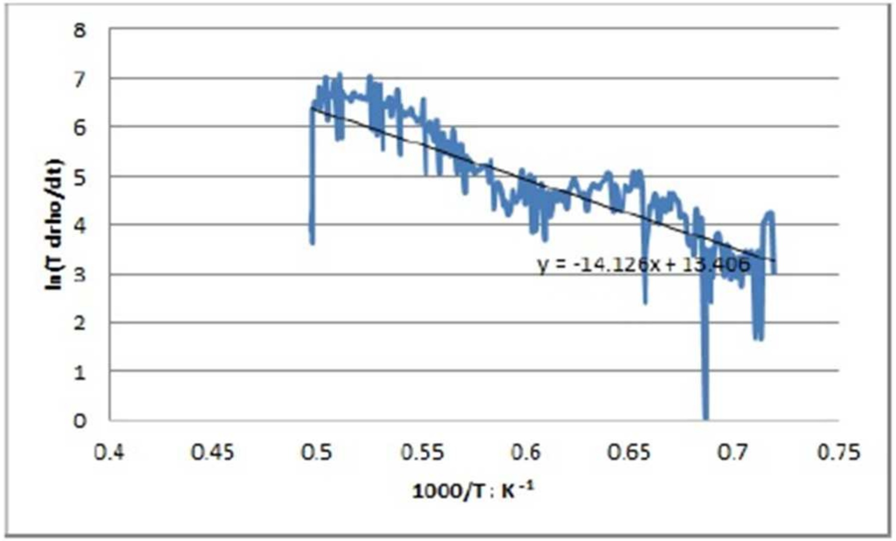


Model - Isolated Pore Shrinkage

Looking for proper parameters for our own case – Calculating activation energy Q_p

$$\ln(TT'\frac{d\rho}{dT}) = -\frac{Q_p}{RT} + \ln(f(\rho)) + k_{p0}$$

A plot of $\ln(TT'\frac{d\rho}{dT})$ v.s. $\frac{1}{T}$ would give the value of Q_p.



The slope is $-\frac{Q_p}{R}$, its value is -14.12,

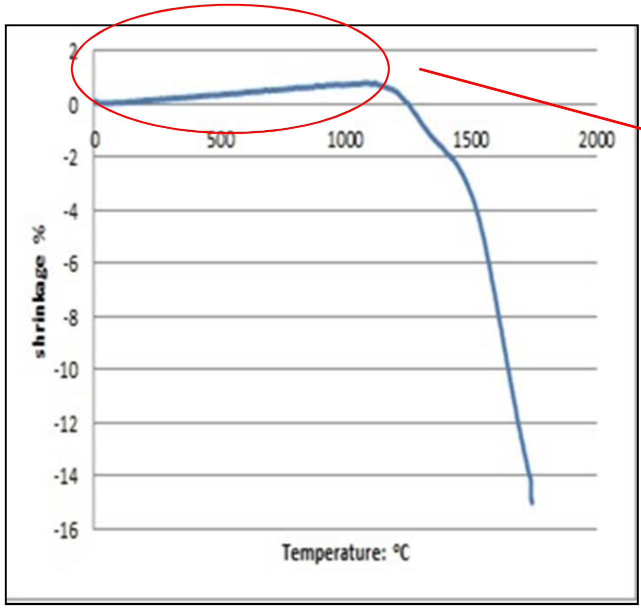
R is 8.314 $J \cdot K^{-1}mol^{-1}$

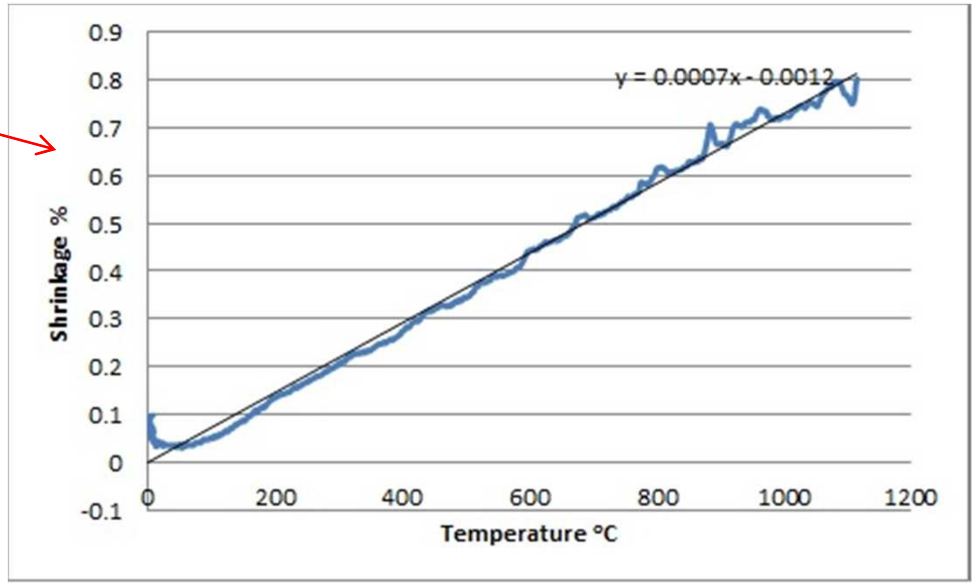
Q_p = 14.12∗8.314=117.39 kJ/mol.

Model - Isolated Pore Shrinkage

Looking for proper parameters for our own case – k_{p0} and m

Thermal expansion coefficient $\alpha = \frac{\Delta V}{V_0 \Delta T}$

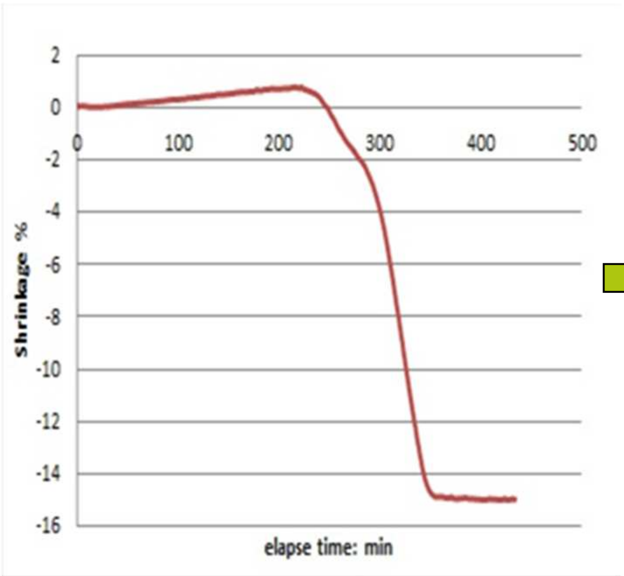


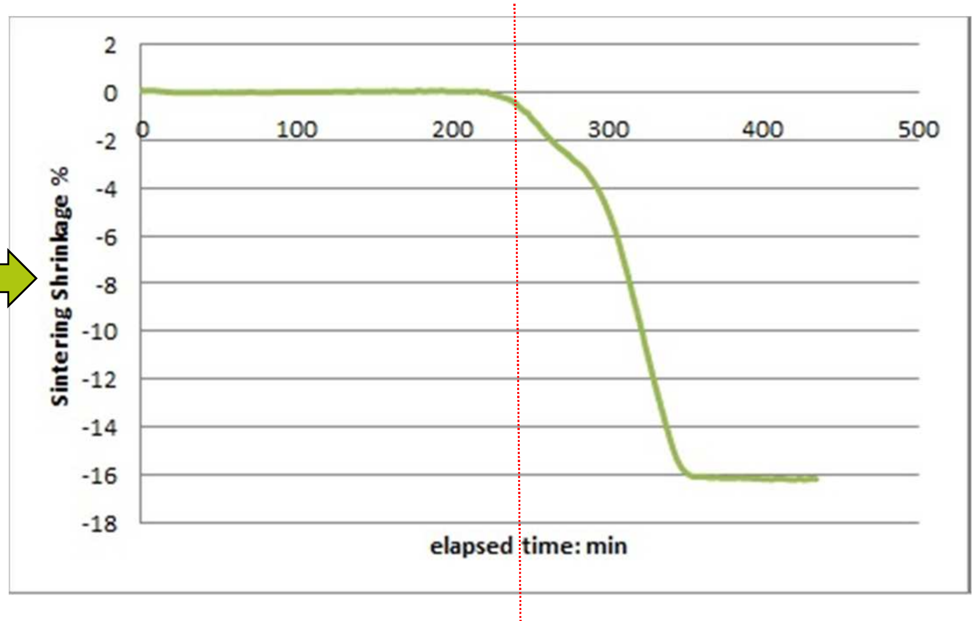


Model - Isolated Pore Shrinkage

Looking for proper parameters for our own case – k_{p0} and m

Sintering shrinkage $\epsilon_{tech} = \varepsilon - \alpha * 100 * (T - T_{room})$



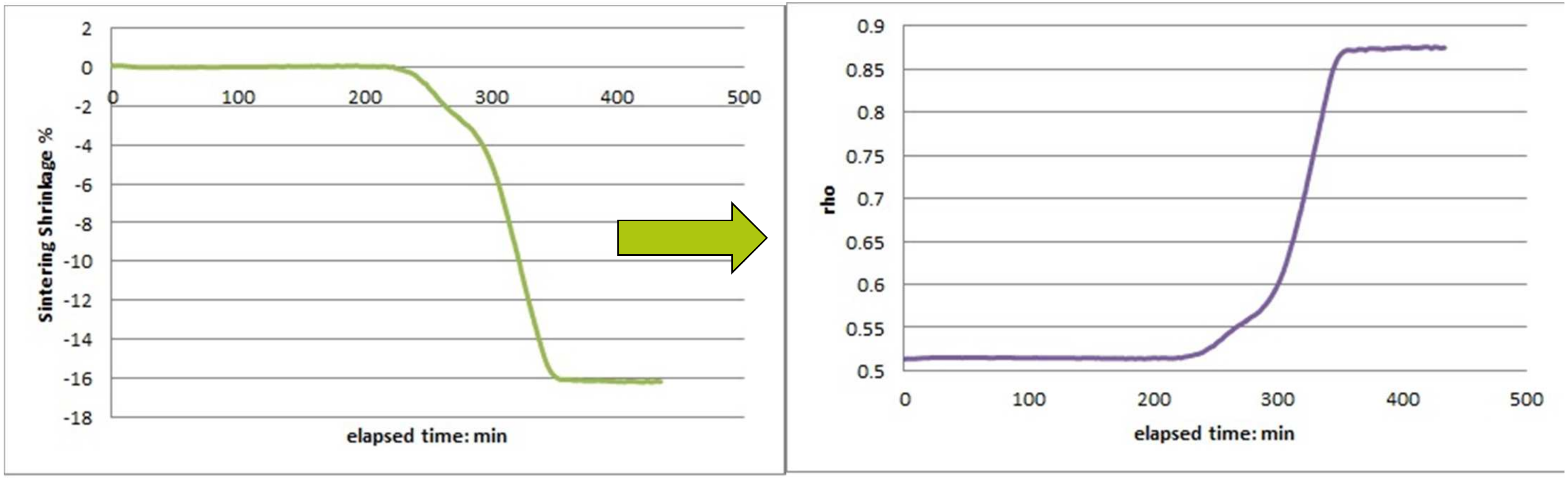


around 1200℃

Model - Isolated Pore Shrinkage

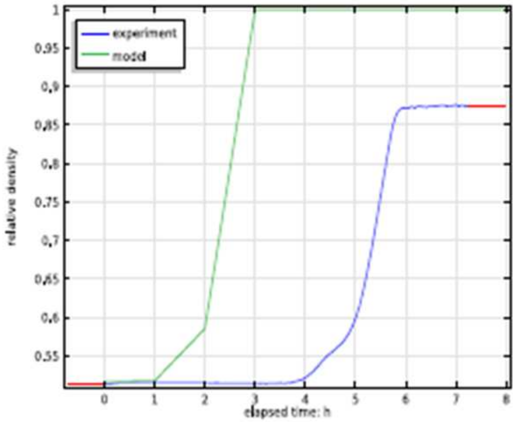
Looking for proper parameters for our own case – k_{p0} and m

Sintering densification curve $\rho = \rho_{gd} \frac{100^3}{(100+\varepsilon_{tech})^3}$

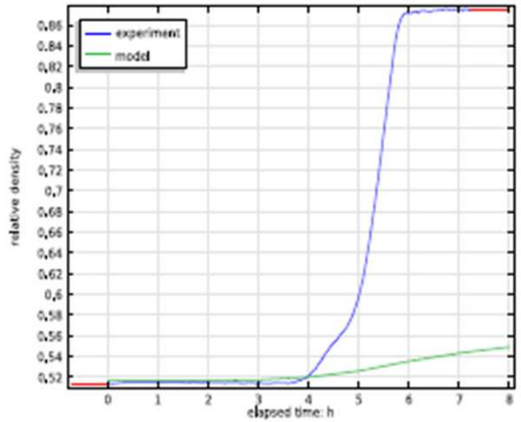


Model - Isolated Pore Shrinkage

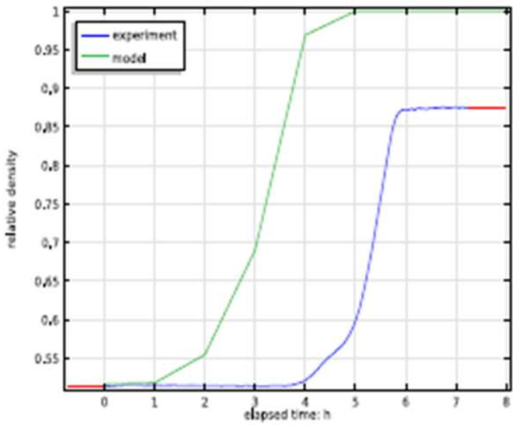
Looking for proper parameters for our own case – k_{p0} and m



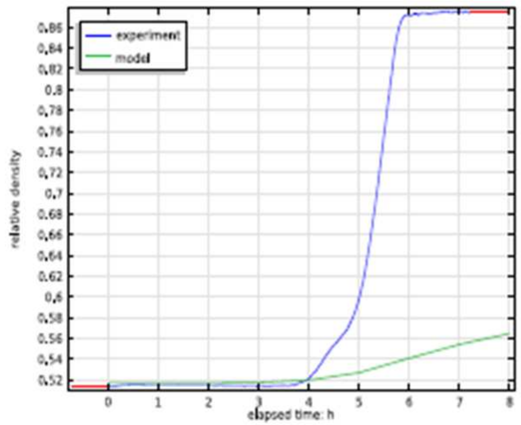
(a) m=3, $k_{p0} = 4$



(b) m=3, $k_{p0} = 4.5 * 10^{-6}$



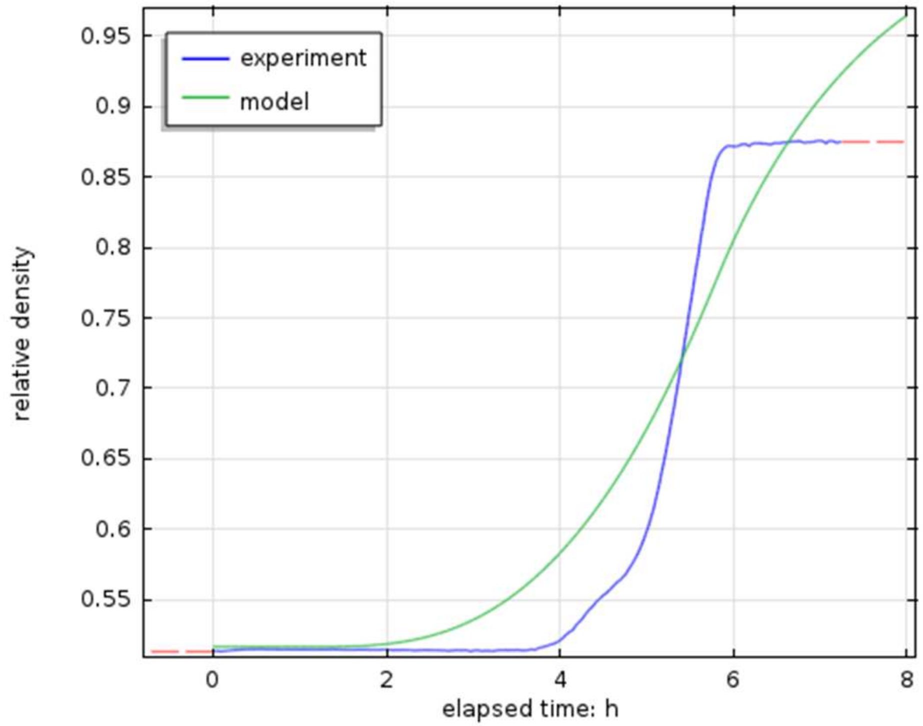
(c) m=5, $k_{p0} = 4.5 * 10^{-4}$



(d) m=2, $k_{p0} = 4.5 * 10^{-4}$

Model - Isolated Pore Shrinkage

Looking for proper parameters for our own case – k_{p0} and m



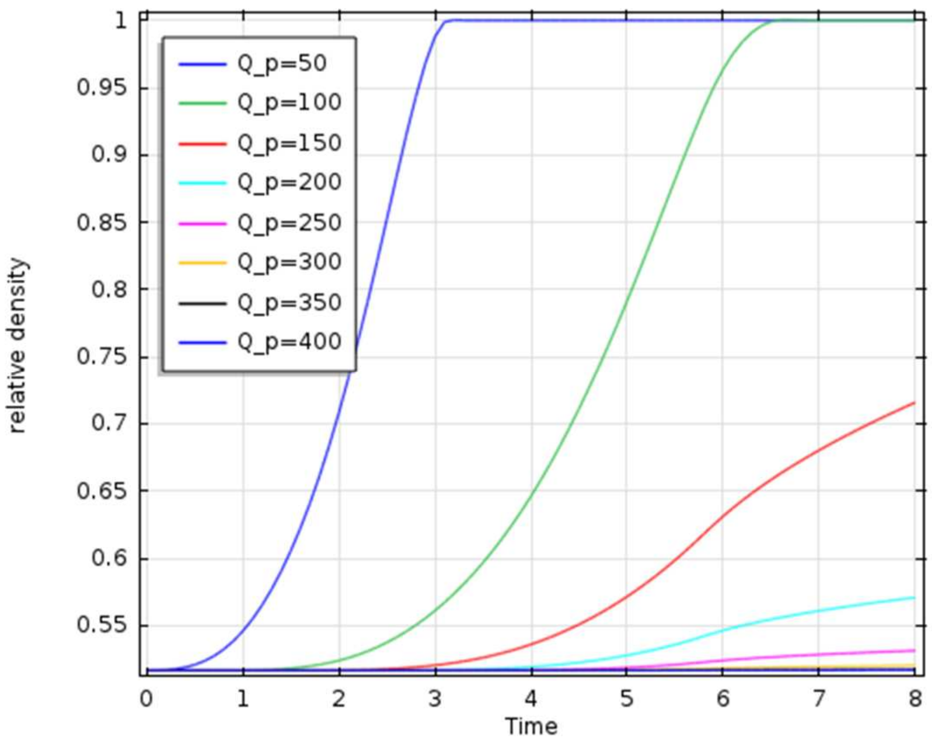
$$k_{p0} = 3.5 * 10^{-4}, \mathrm{m} = 3.4,\ Q_p = 117.39$$

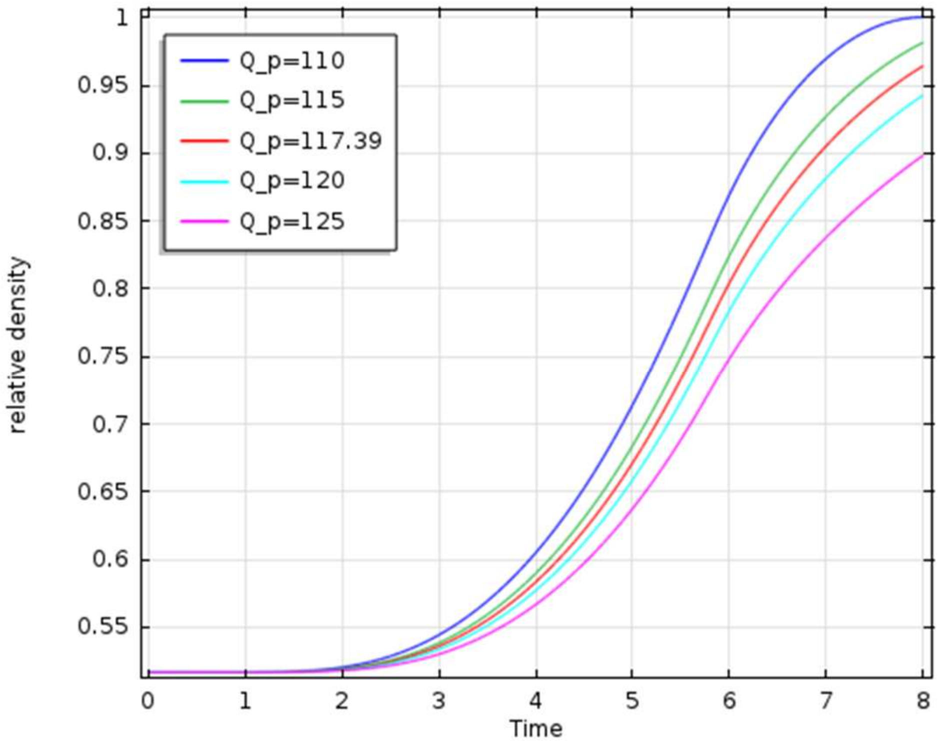
$$\rho(0) = 0.515, r_m = 3.747, \text{ and } \sigma = 5.925.$$

Introduction

- Simulation Result

Sensitive analysis - Q_p

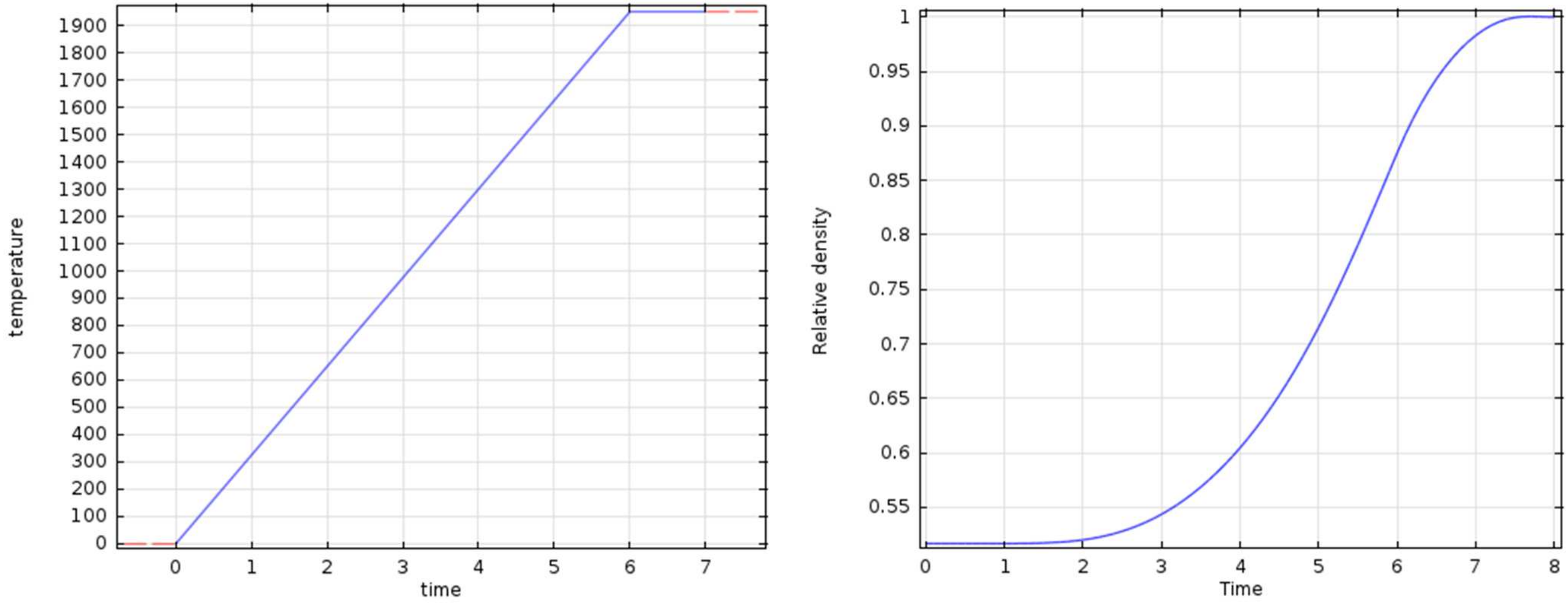




Model - Isolated Pore Shrinkage

– Prediction for different temperature cycle

Example: change the temperature cycle and use our model to try to predict other situations



Model & Examples

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- Combination of Pore Shrinkage Model and Grain Growth Model

Model – Isolated Grain Growth

$$\frac{\partial n_g(r_g,t)}{\partial t} + \frac{\partial}{\partial r_g}(v_{r_g} n_p(r_g,t)) = 0$$

- n_g - the number density function of grain size. (unit: $\mu m^{-3} \mu m^{-1}$)
- r_g - radius of grain. (unit:μm)
- Similar to pore size distribution, the initial grain size distribution $n_0(r_g)$ needs to be defined in the beginning. This can be also got from literature study and image analysis

Model – Isolated Grain Growth

$$\frac{\partial n_g(r_g,t)}{\partial t} + \frac{\partial}{\partial r_g}(v_{r_g} n_p(r_g,t)) = 0$$

- $v_{r_g} = \frac{dr_g}{dt} = \frac{k_g}{r_g^n}(\frac{1}{r_c} - \frac{1}{r_g})$, is the rate of grain growth.
  - k_g - temperature constant (unit: $\mu m^{n+2}/h$)

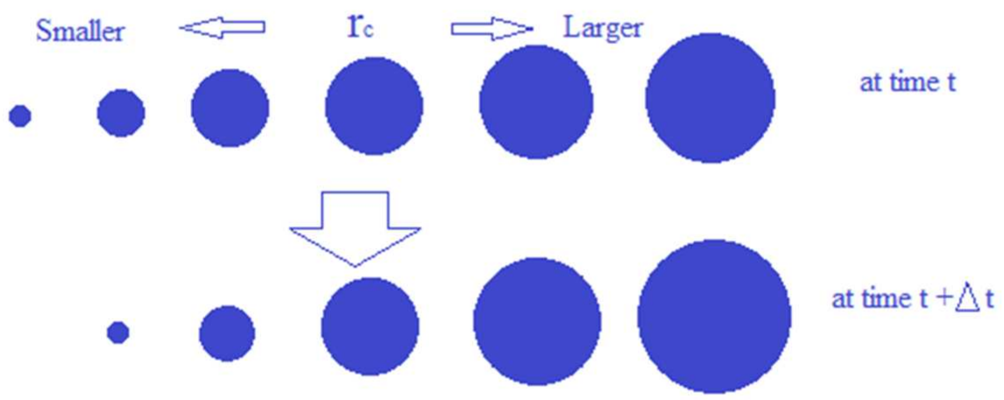
    Can be got from Arrhenius equation $k_g = k_{g0} e^{-\frac{Q_g}{RT}}$
  - n – model parameter which depends on transport mechanisms. (unit: 1)

Calculation of Q_g, k_{g0}, and n are similar to calculation of k_{p0}, Q_p and m in the pore shrinkage model and are going to be discussed in the future study.

Model – Isolated Grain Growth

$$\frac{\partial n_g(r_g,t)}{\partial t} + \frac{\partial}{\partial r_g}(v_{r_g} n_p(r_g,t)) = 0$$

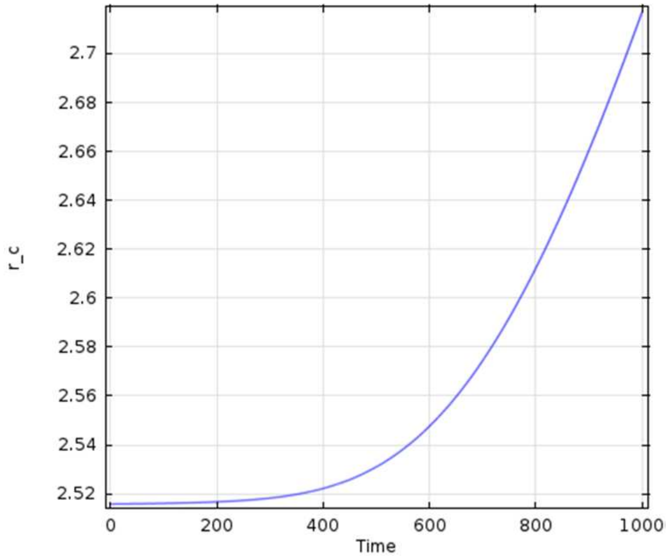
- $v_{r_g} = \frac{dr_g}{dt} = \frac{k_g}{r_g^n}(\frac{1}{r_c} - \frac{1}{r_g})$, is the rate of grain growth.
  - r_c - instantaneous critical radius. Grain in this radius size neither shrinks nor grows at any instant of time. (unit: μm)



Model – Isolated Grain Growth

$$\frac{\partial n_g(r_g,t)}{\partial t} + \frac{\partial}{\partial r_g}(v_{r_g} n_p(r_g,t)) = 0$$

- $v_{r_g} = \frac{dr_g}{dt} = \frac{k_g}{r_g^n}(\frac{1}{r_c} - \frac{1}{r_g})$, is the rate of grain growth.
  - r_c - instantaneous critical radius. Grain in this radius size neither shrinks nor grows at any instant of time. (unit: μm)

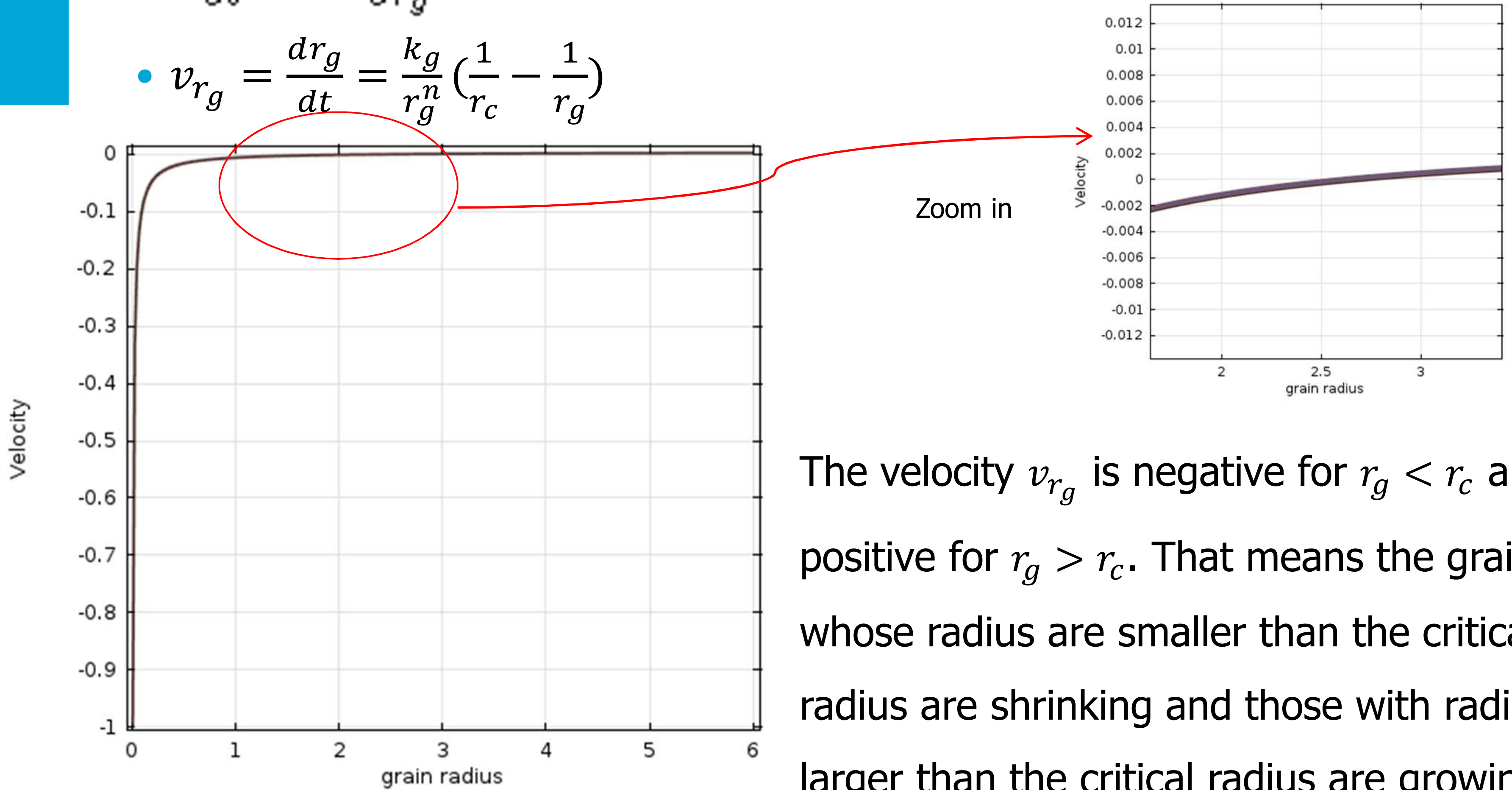


The critical radius r_c is a function of time t.

Model – Isolated Grain Growth

$$\frac{\partial n_g(r_g,t)}{\partial t} + \frac{\partial}{\partial r_g}\left(v_{r_g} n_p(r_g,t)\right) = 0$$

- $v_{r_g} = \frac{dr_g}{dt} = \frac{k_g}{r_g^n}\left(\frac{1}{r_c} - \frac{1}{r_g}\right)$



The velocity v_{r_g} is negative for $r_g < r_c$ and positive for $r_g > r_c$. That means the grains whose radius are smaller than the critical radius are shrinking and those with radius larger than the critical radius are growing.

Model – Isolated Grain Growth

Model Validation:

- Analytical solution - It's hard to get because more complex velocity model ☹
- FDM solution with 2-ODEs – It's possible to transfer the PDE into two ODE equations.
- Asymptotic steady-state solution for some special cases (i.e. n=1)

$$n_g(u) = n_{g0}\frac{u^2}{(1.5-u)^{11/3}(3+u)^{7/3}}e^{\frac{-u}{1.5-u}} \qquad 0 \leq u < 1.5$$

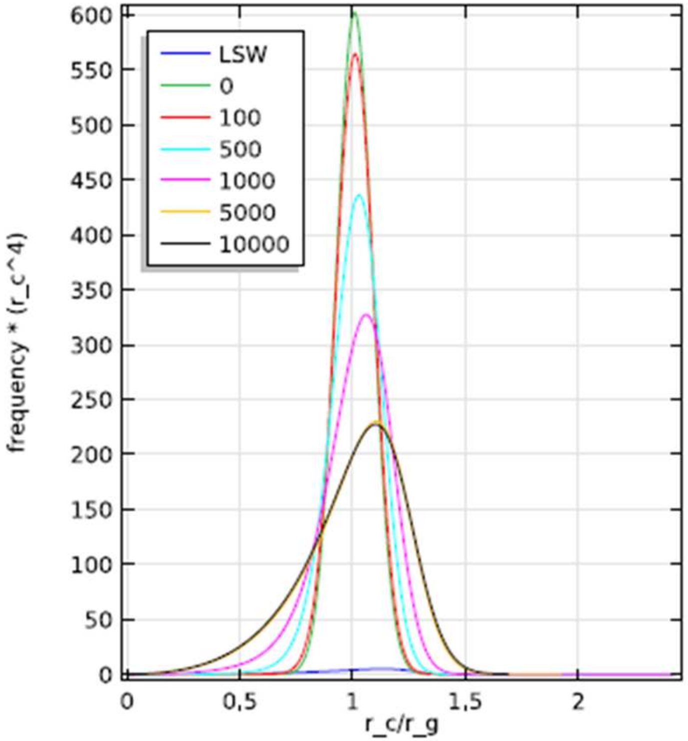
$$n_g(u) = 0 \qquad else$$

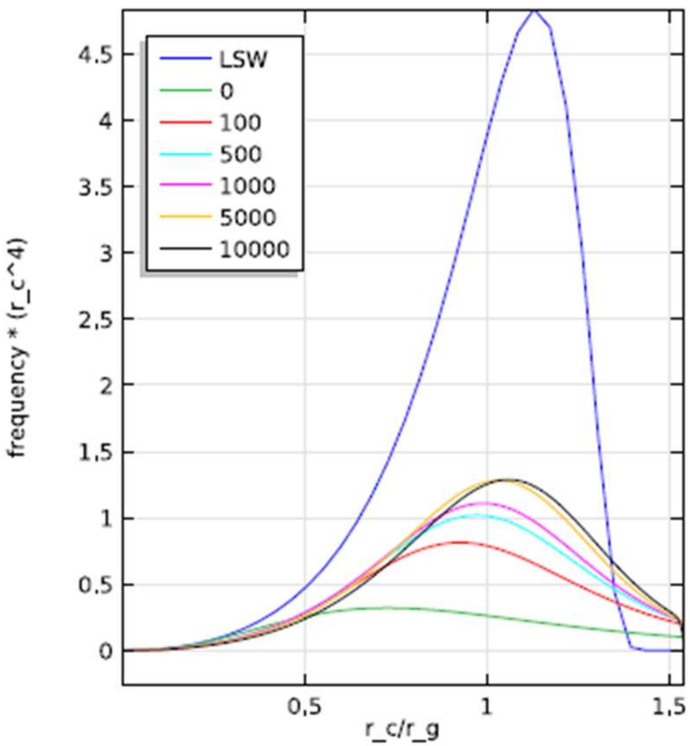
where n_{g0} is a normalizing constant and $u = \frac{r_g}{r_c}$, $n_g(u) = r_c^4 n_g(r_g)$. ☺

- FEM solution ☺

Model – Isolated Grain Growth

Model Validation (n=1):

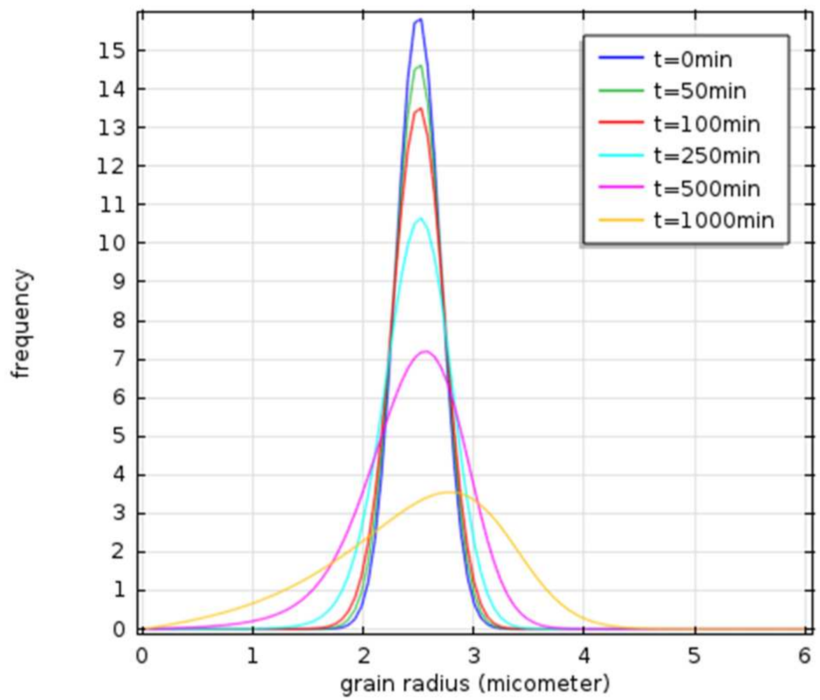


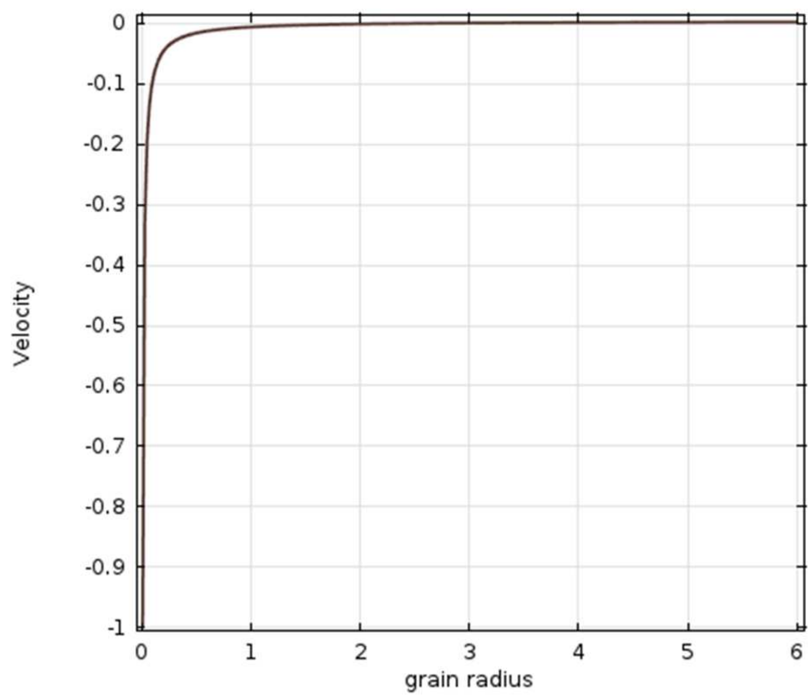


Model – Isolated Grain Growth

- Example: Initial grain size distribution: Gaussian distribution with mean 2.5 and standard deviation 0.2. Parameter values are $k_g = 0.01\mu m^2/min$, n=0.

As time going on, the average grain size is increasing, that is, grain growth.





Model & Examples

- Particle Number Continuity Equation
- Isolated Pore Shrinkage Model
    - Introduction of the model
    - Validation
    - Looking for proper parameters
    - Sensitive Analysis
- Isolated Grain Growth Model
- Combination of Pore Shrinkage Model and Grain Growth Model

Model – Combination of Two Models

- The coupling of pore shrinkage and grain growth is through the relative density $\rho(t)$:

Output variable from pore shrinkage model:
Number density function of pore size n_p

↓

Calculate total pore volume at sintering time t:
$$V(t) = C\int_0^\infty n_p(r_p,t)\,r_p^3\,dr_p$$

C is $\frac{4\pi}{3}$ in our case

↓

Calculate relative density by pore volume:
$$\rho(t) = \frac{1}{1+\frac{V(t)}{V(0)}\left(\frac{1}{\rho(0)}-1\right)}$$

B.S.G

↓

Grain growth model: use $\rho(t)$ as an input variable

$$v_{r_g} = \frac{k_g}{r_g^n\left(1-\rho(t)\right)^\alpha}\left(\frac{1}{r_c}-\frac{1}{r_g}\right)$$

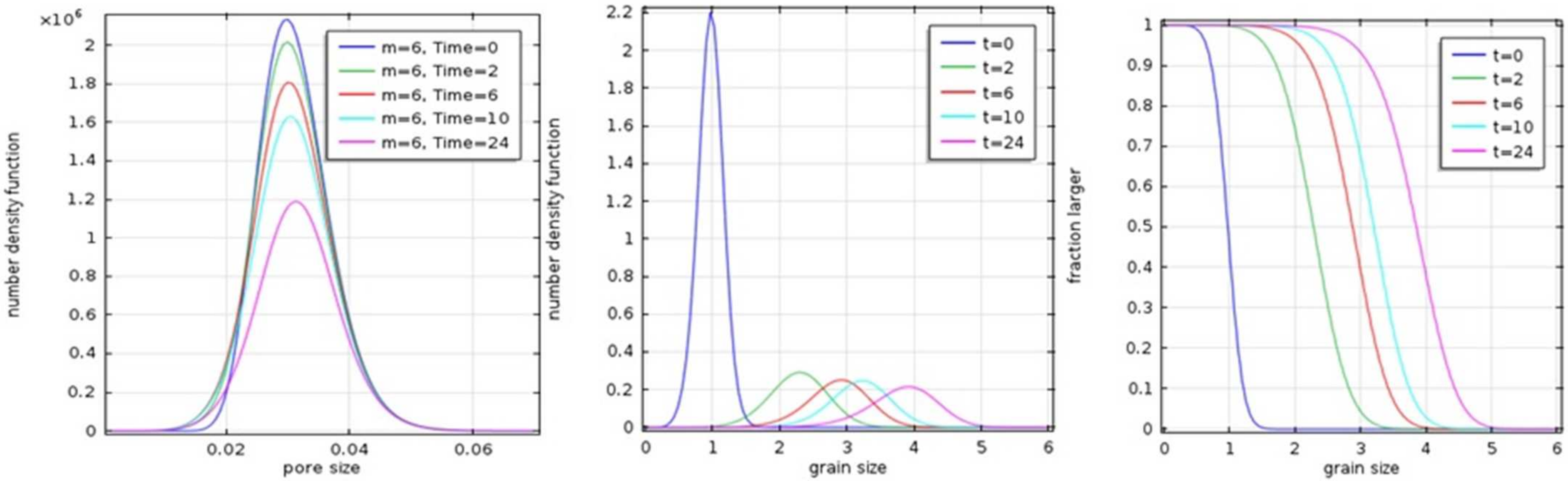
Model – Combination of Two Models

The initial distribution of pore size is log-normal with median size 0.034μm and geometric standard deviation 1.2.

$$m = 6,\ k_p = 1.00 * 10^{-13} \mu m^7/h,\ ,\ \rho(0) = 0.42$$

The initial distribution of grain size is log-normal with median size 0.98μm and geometric standard deviation 2.

$$n = 4,\ a = 1,\ k_g = 0.06\ \mu m^6/h.$$



Overview

- Introduction
- Background Knowledge
- Models & Examples
  - Particle – Number Continuity Equation
  - Isolated Pore Shrinkage Model
  - Isolated Grain Growth Model
  - Combination of Pore Shrinkage Model and Grain Growth Model
- Conclusions and Future Work

Conclusions and Future Work

For the pore shrinkage model

1. Many kinds of methods can be used to get the solution, so it's easy for us to use several methods to validate the model.

2. Easy to solve and time used to solve this problem can be almost ignored.

3. The result of this model can be used to estimate relative density, which is an important parameter for quality control of sintering.

Conclusions and Future Work

For the grain growth model

1. More complicated velocity, hard to get analytical solution.

2. To validate the model, we can use asymptotic steady-state solution in some special cases.

For the combination model

1. It's a grain growth model coupled with densification. We introduce the relative density, which could be calculated from the result of pore shrinkage model, to be an input parameter of the grain growth model.

2. To better control the sintering result, grain growth distribution at the end of sintering should be considered together with relative density.

Conclusions and Future Work

Future Work:

1. To simulate the relative density, more accurate initial values and parameters are needed. The following things should be reconsidered thoroughly:

   - model error (e.g. assumptions in ideal situation)
   - measurement error
   - numerical error
   - etc.

2 . How can we get the initial values and parameters in the grain growth model and the combination model?

3. When we get temperature cycle from combustion model, is it possible to combine all these things together?

TU Delft


Dank u wel