Analyzing & Testing

NETZSCH
Proven Excellence.

Ceramics Sintering: Kinetics, Simulation and Process Optimization using Kinetics Neo and Termica Neo

Elena Moukhina
10/23/2024

NETZSCH

Our three business units develop outstanding products
for nearly every industry and country around the world.

4,600+
Employees

210
Locations around the globe

3
Business units

NETZSCH Grinding & Dispersing Machines

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Rawmaterial	**Pre-grinding**	**Mass-preparation**	Forming	Pre-burn	Green-processing	Sinter-burn	Final-processing	Ceramic
Calcination	**Dry pre-grinding**	**Mixing**	Pressing	Drying	Drilling	Sintering	Grinding	Finished part
Minerals		**Wet-grinding**	Extruding	Pre-burn	Sawing		Lapping	
		Spraydrying	Casting				Polishing	

NETZSCH Dry Grinding Machines

NETZSCH Mixing and Wet Grinding Machines

Complete Solution for Customer‘s Problem: from Measurement to Simulation

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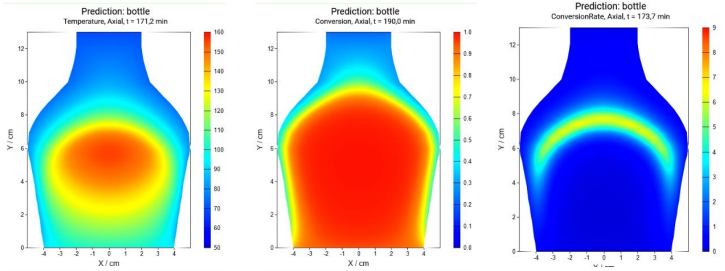
3. Simulation

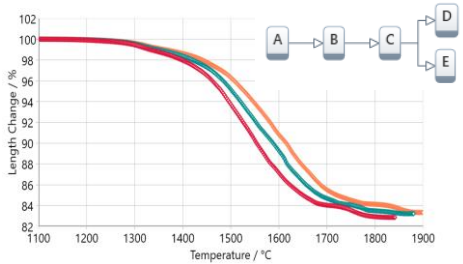
g, kg, tons, temperature gradients,



TERMICA NEO

2. Chemical Kinetics

mg, uniform known temperature, measurement impossible



KINETICS NEO

1. Laboratory measurements

mg, known temperature

STA (TG + DSC)
DIL,
LFA,
…

Complete Solution for Customer‘s Problem: from Measurement to Simulation

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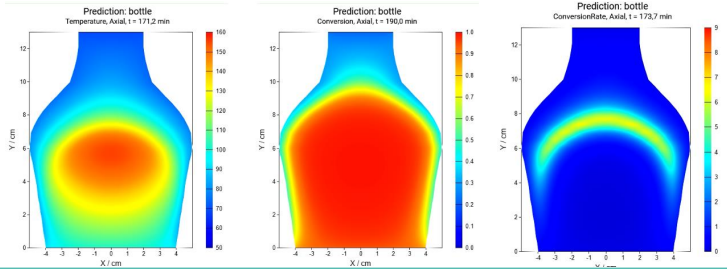
3. Simulation

g, kg, tons, temperature gradients,



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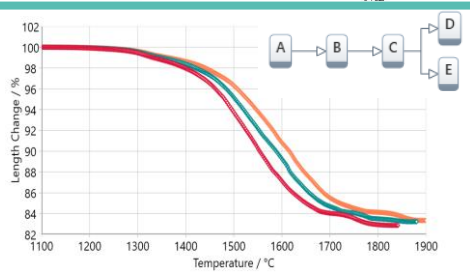


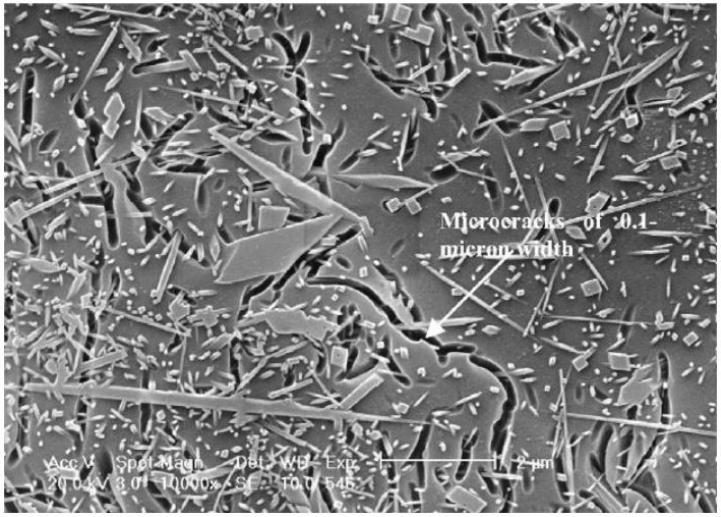
KINETICS NEO

1. Laboratory measurements

mg, known temperature

STA (TG + DSC)
DIL,
LFA,
…

High-quality ceramics



SEM image with microcracks [1]

Quality of ceramics depends on production temperature

Slow heating and cooling enhanced the quality of ceramics, but makes it more expensive

[1] Rashed Adnan Islam Y. C. Chan, January 2004 Materials Science and Engineering B 106(2):132-140 , Structure–property relationship in high-tension ceramic insulator fired at high temperature
DOI: 10.1016/j.mseb.2003.09.005
Pictures are from internet: gelenk-klinik.de, www.avonvalleydental.com.au

How to get the **best quality** in the **shortest time?**

Below 700°C:
Debinding

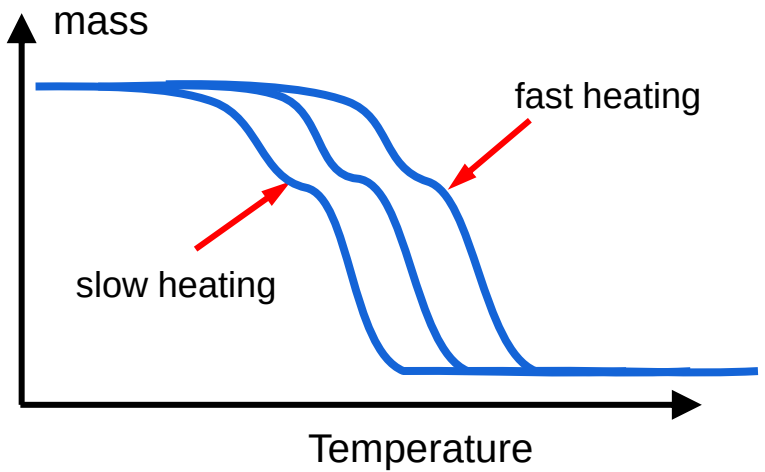
A Thermobalance gives you information about the binder burnout!

Above 700°C:

Densification

A Dilatometer gives you information about the sintering shrinkage and thermal expansion!

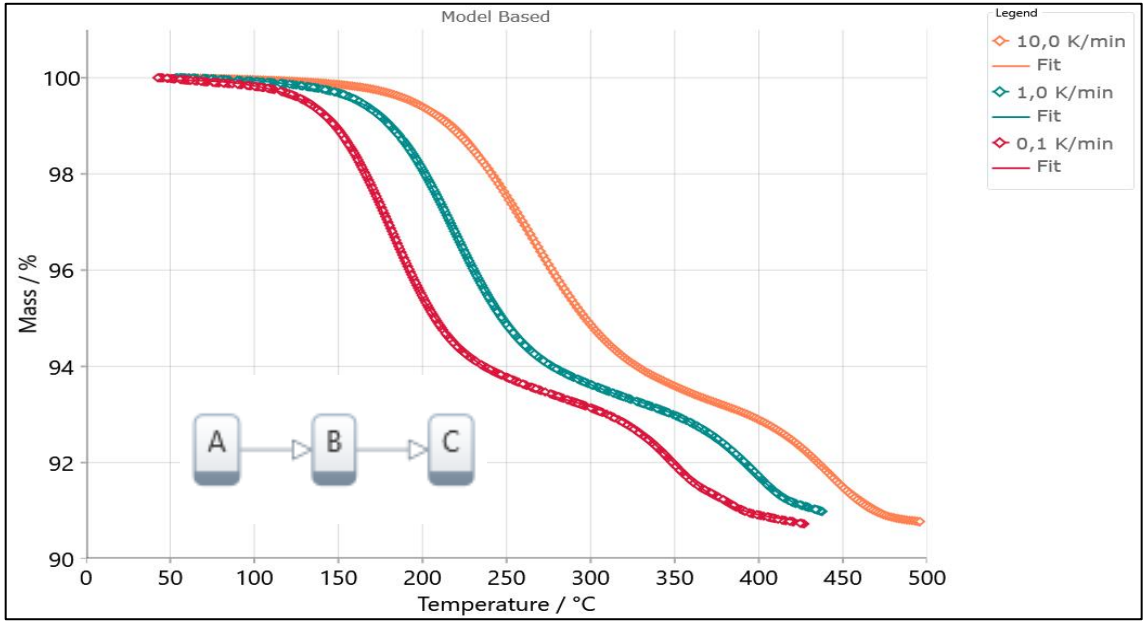
Measurements for kinetic analysis below 700°C:
Thermogravimetry method detects the mass loss



Thermogravimetry: mass change is measured during heating

Debinding below 700°C: Kinetic Analysis for TG data

STA 49 F5:
Measurement at three given temperature programs



One kinetic model with two steps can fit all measurements

This model will be used for process optimization

Theory: one Kinetic Model is used for predictions at any temperature

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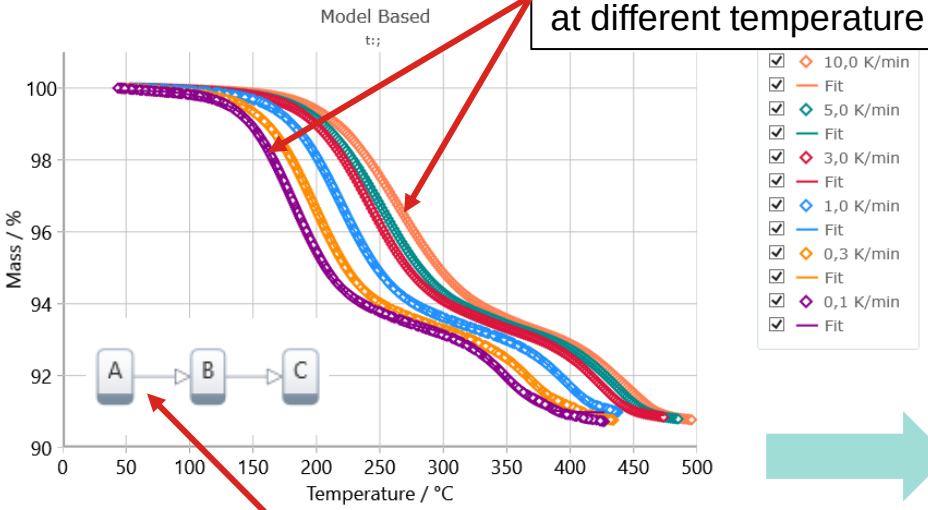
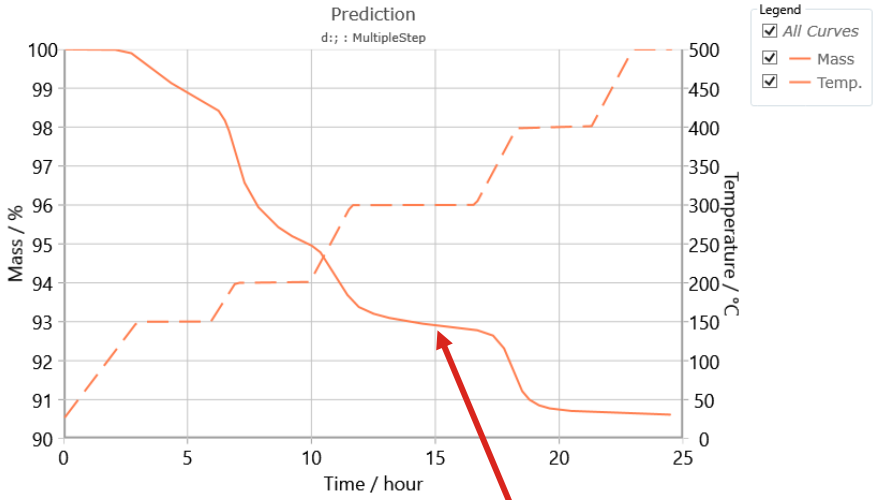
KINETICS NEO

1. Measured data for the process at different temperature conditions



2. Kinetic Model for the process
Simulated curves must fit experimental data



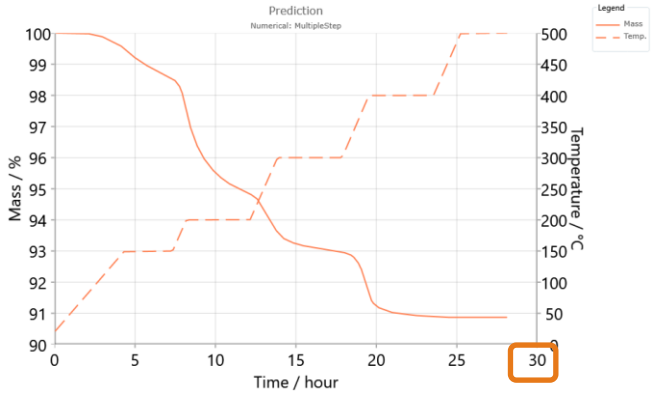
3. Simulated:
reaction for new temperatures

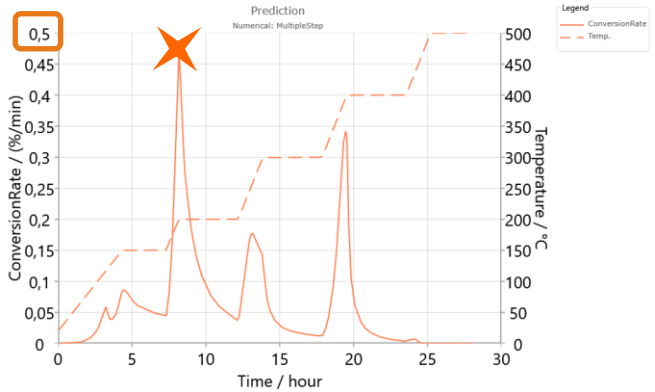
One kinetic model can fit all measurements a different temperature conditions

This model will be used for prediction at any temperature

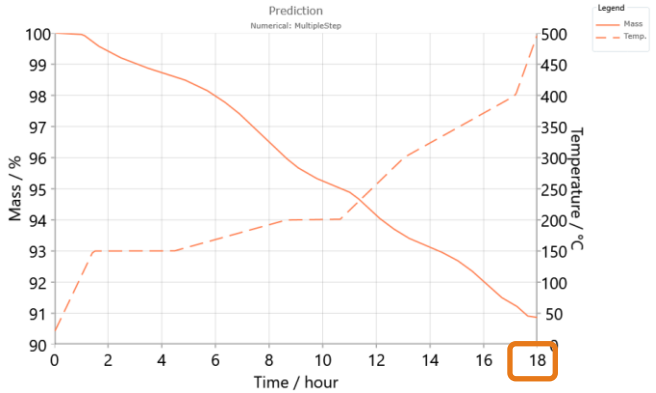
For any temperature program
the result is calculated immediately

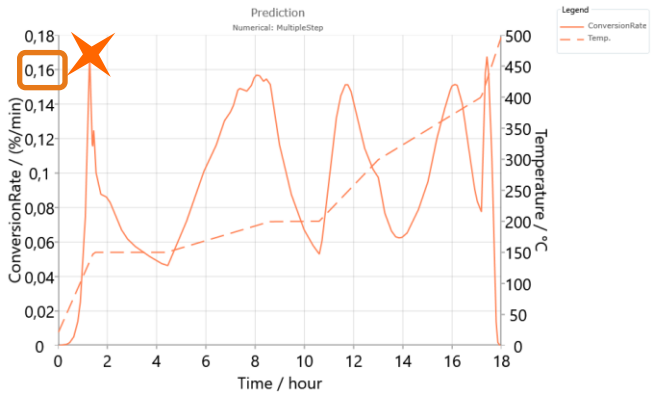
Optimization of temperature below 700°C based on TG





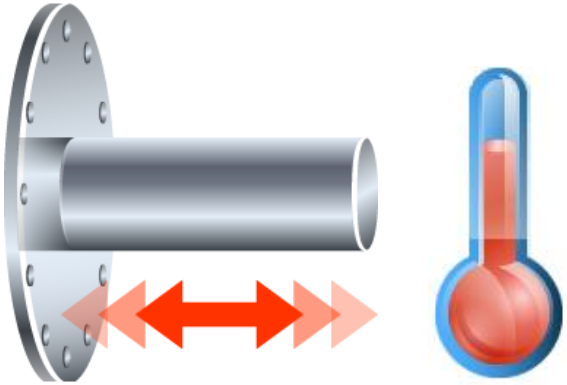
Non-optimized 29 hrs, max 0.5%/min

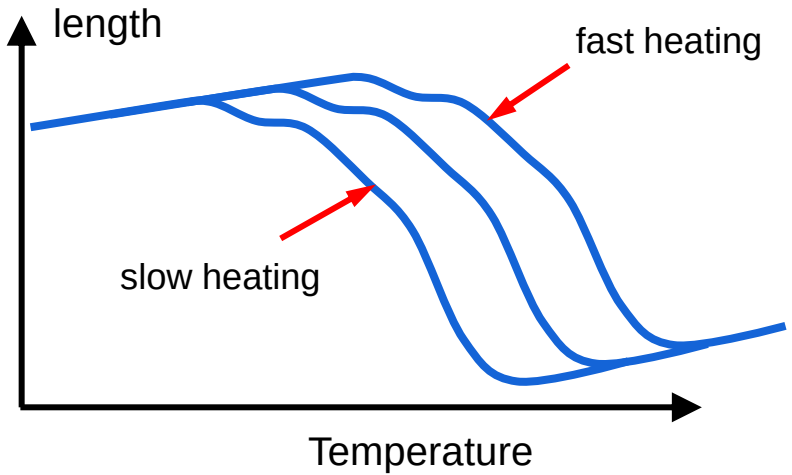




Optimized 18 hrs, max 0.16 %/min

Measurements for kinetic analysis:
Dilatometry method detects the length change

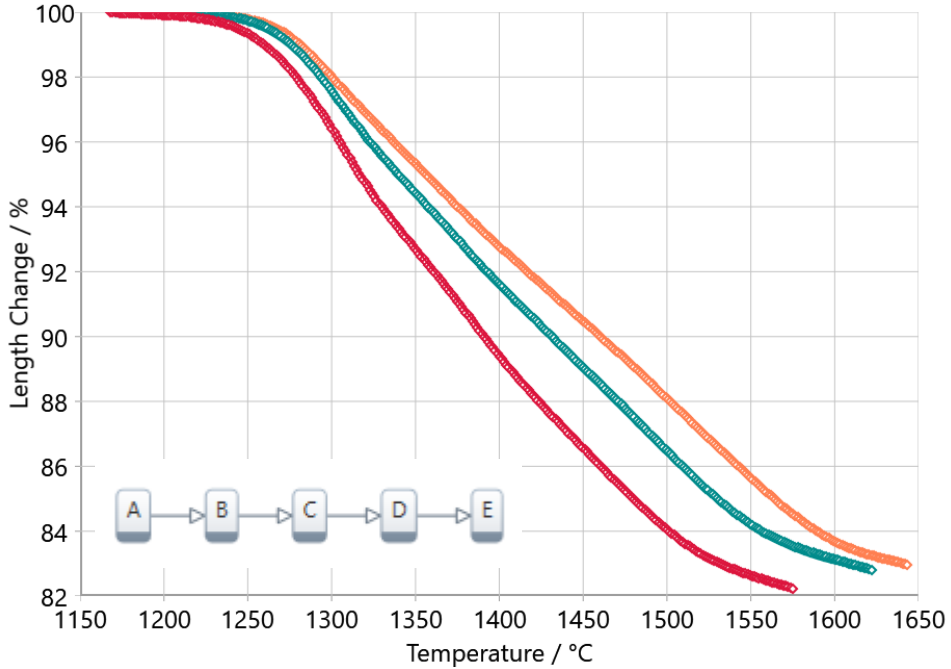




Dilatometry: length change is measured during heating

Densification above 700°C: Kinetic Analysis for DIL data

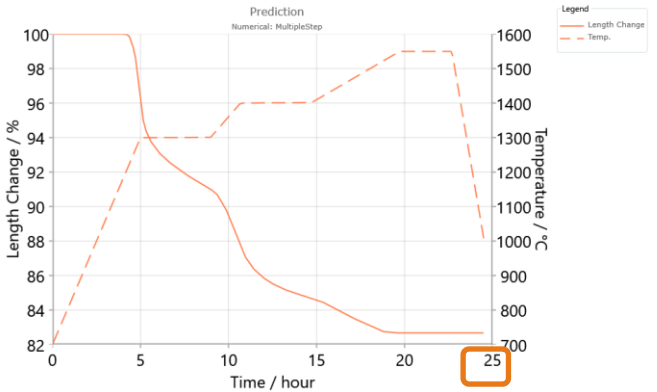
DIL 402:
Measurement of porcelain at four given temperature programs

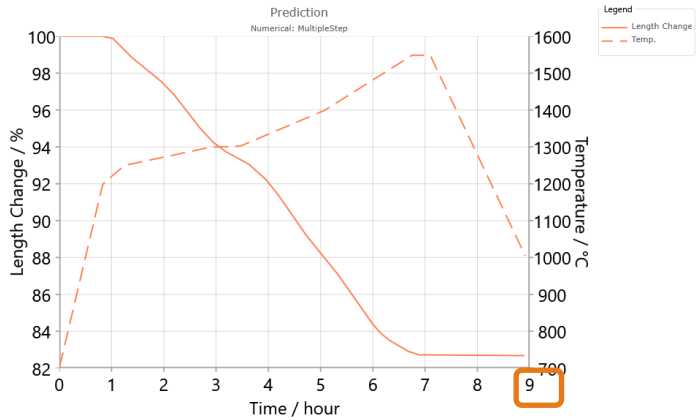


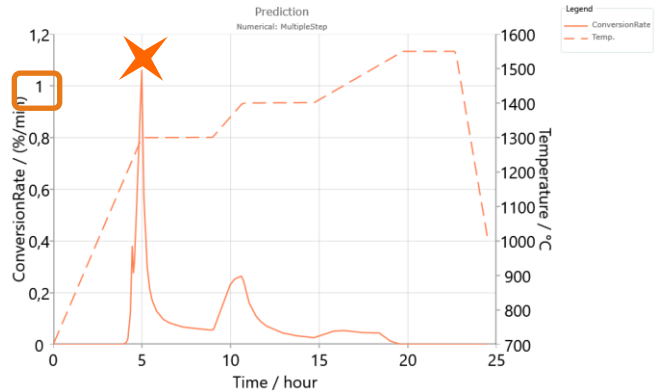
One kinetic model can fit all measurements

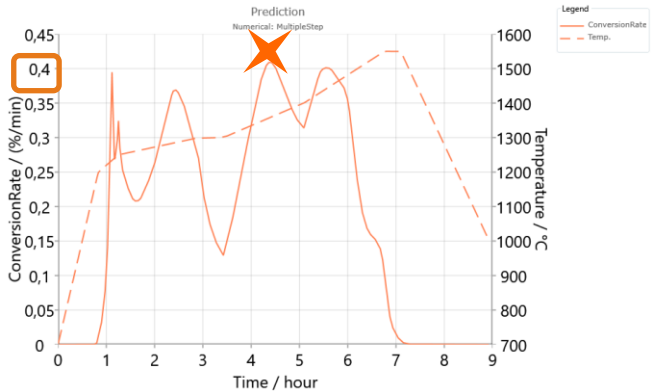
This model will be used for process optimization

Optimization of temperature above 700°C based on DIL









Non-optimized 25 hrs, max 1%/min

Optimized 9 hrs, max 0.4%/min

New material

HALFOAM ALUMINA ™

by

Morgan Advanced Materials
HALDENWANGER

Production time was reduced more than by 50%

By applying of process optimization in kinetics

Ceramitec, Munich, 2018, NATAS conference 2019

Additional information is on *kinetics.netzsch.com*

Additive manufacturing of ceramic components

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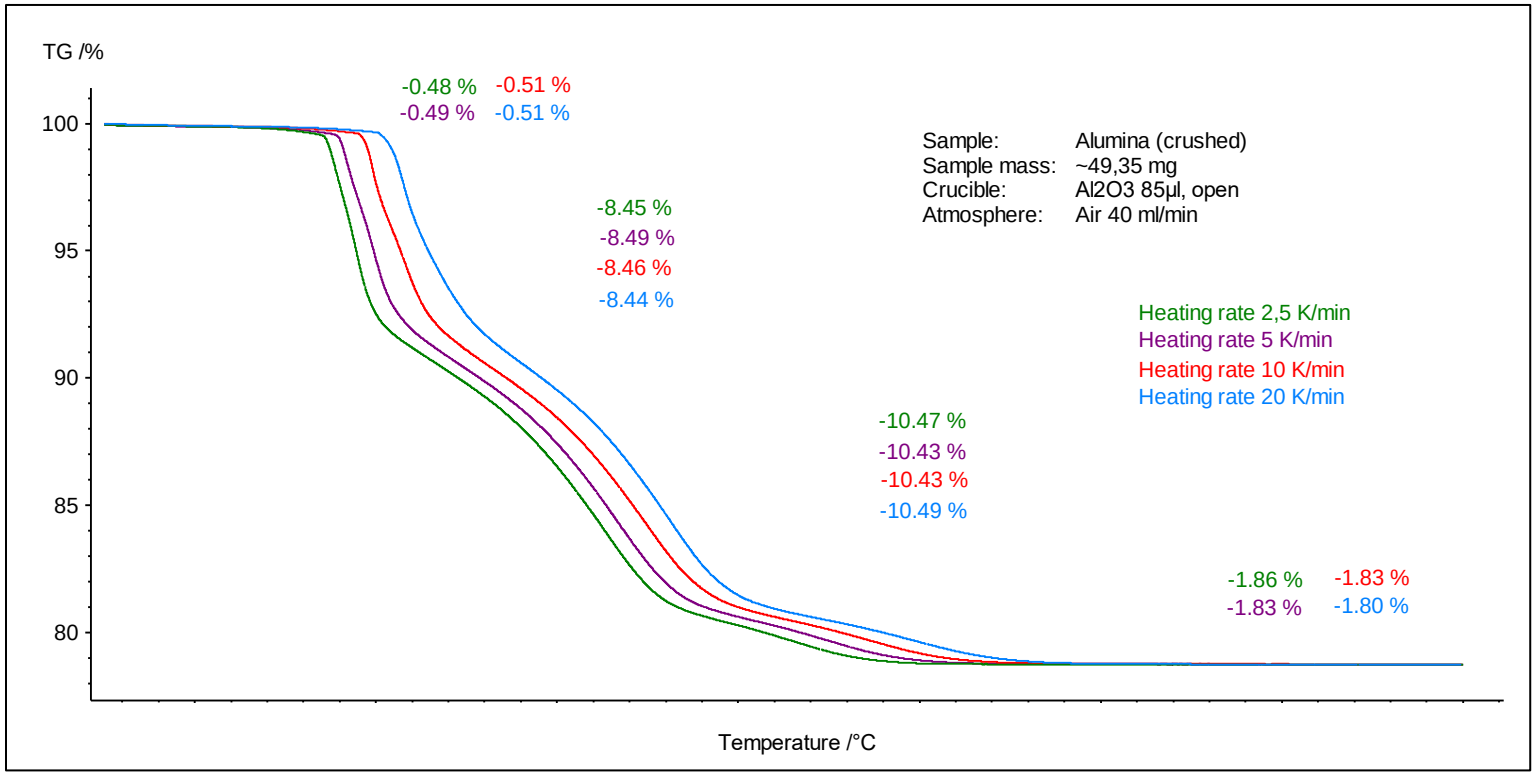
Lithography-based ceramic 3D manufacturing (LCM)

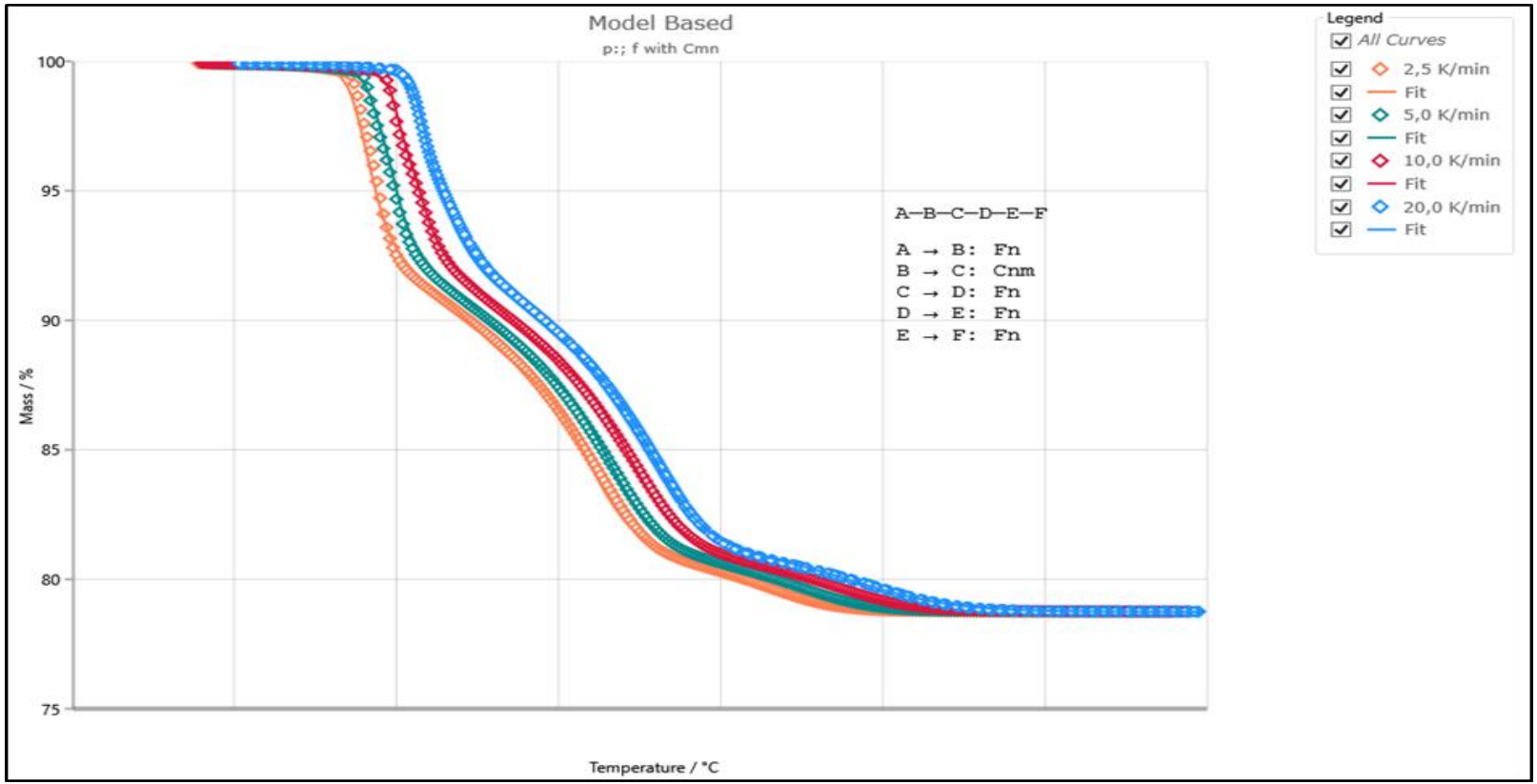
Source: Lithoz

Analysis and Optimization of the Binder Burnout of 3D-Printed Ceramic Components| C. Strunz, Thermal conductivity conference ITCC, 2021

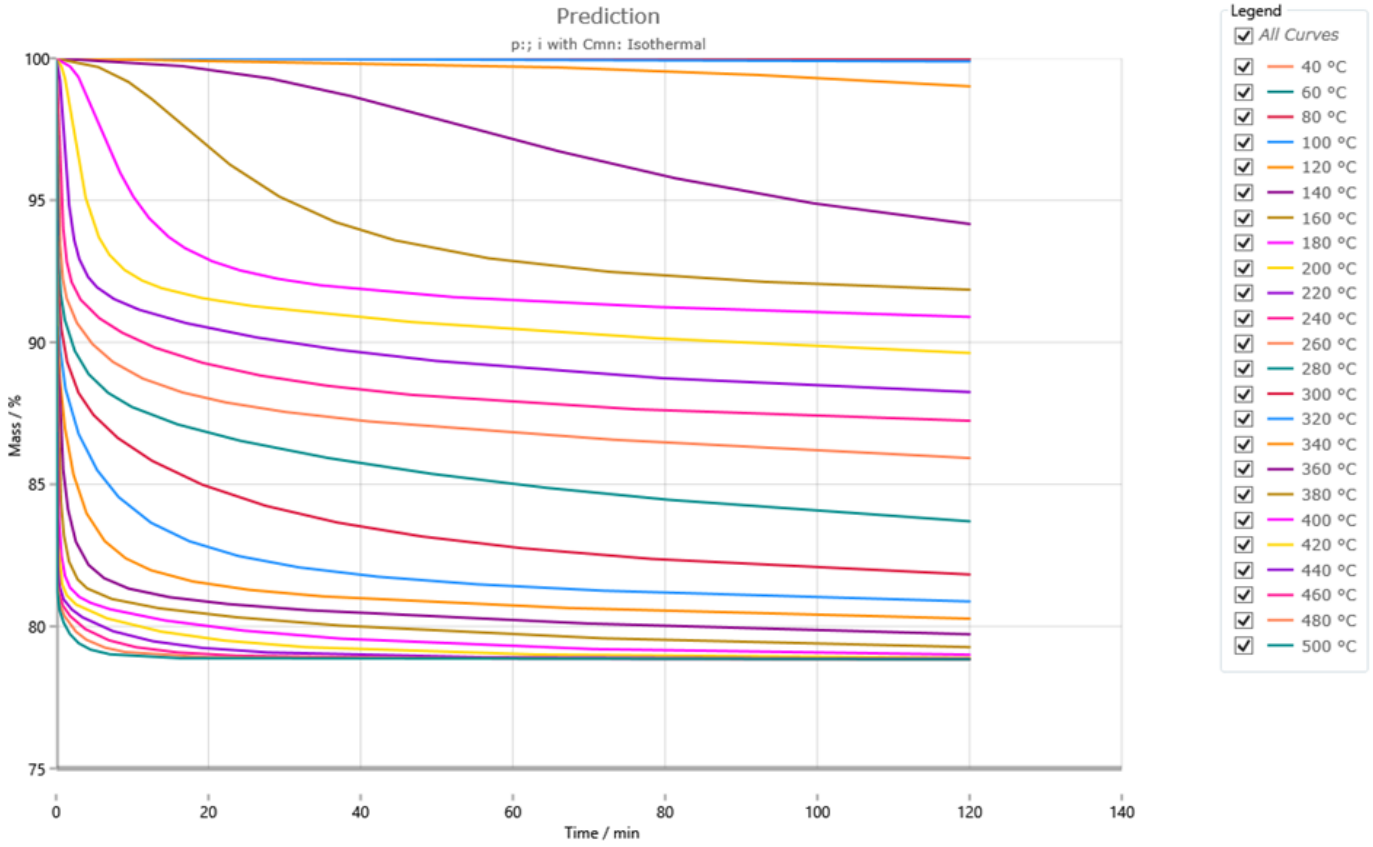
TG on crushed Alumina sample at different heating rates



Binder burnout –TGA Results (kinetic analysis)



Binder burnout –TGA Results (kinetic predictions, isothermal)



Cracks because of temperature gradients in big volume

Simulation for big volume is necessary

Complete Solution for Customer‘s Problem: from Measurement to Simulation

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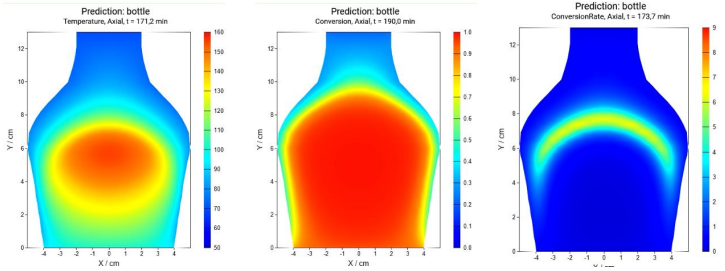
3. Simulation

g, kg, tons, temperature gradients,



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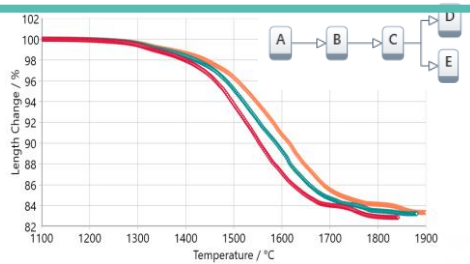

KINETICS NEO

1. Laboratory measurements

mg, known temperature

STA (TG + DSC)
DIL,
LFA,
…

Finite elements are used in Termica Neo software
Heat balance for small element with reaction heat as the heat source

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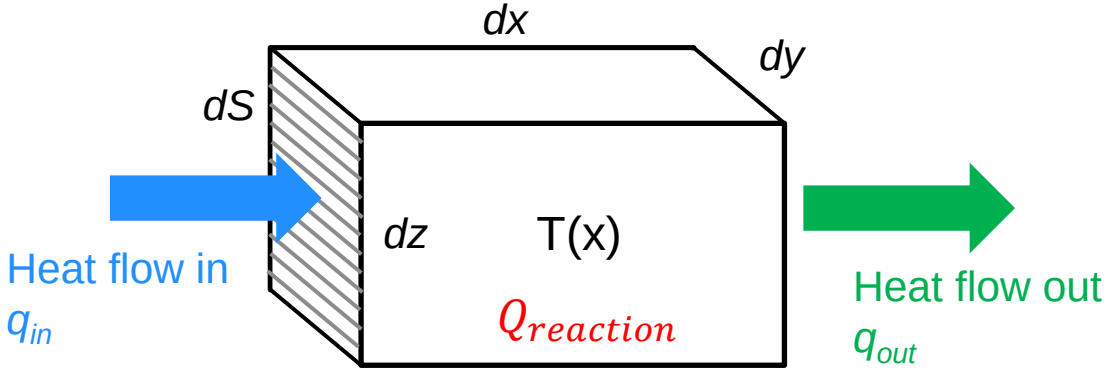


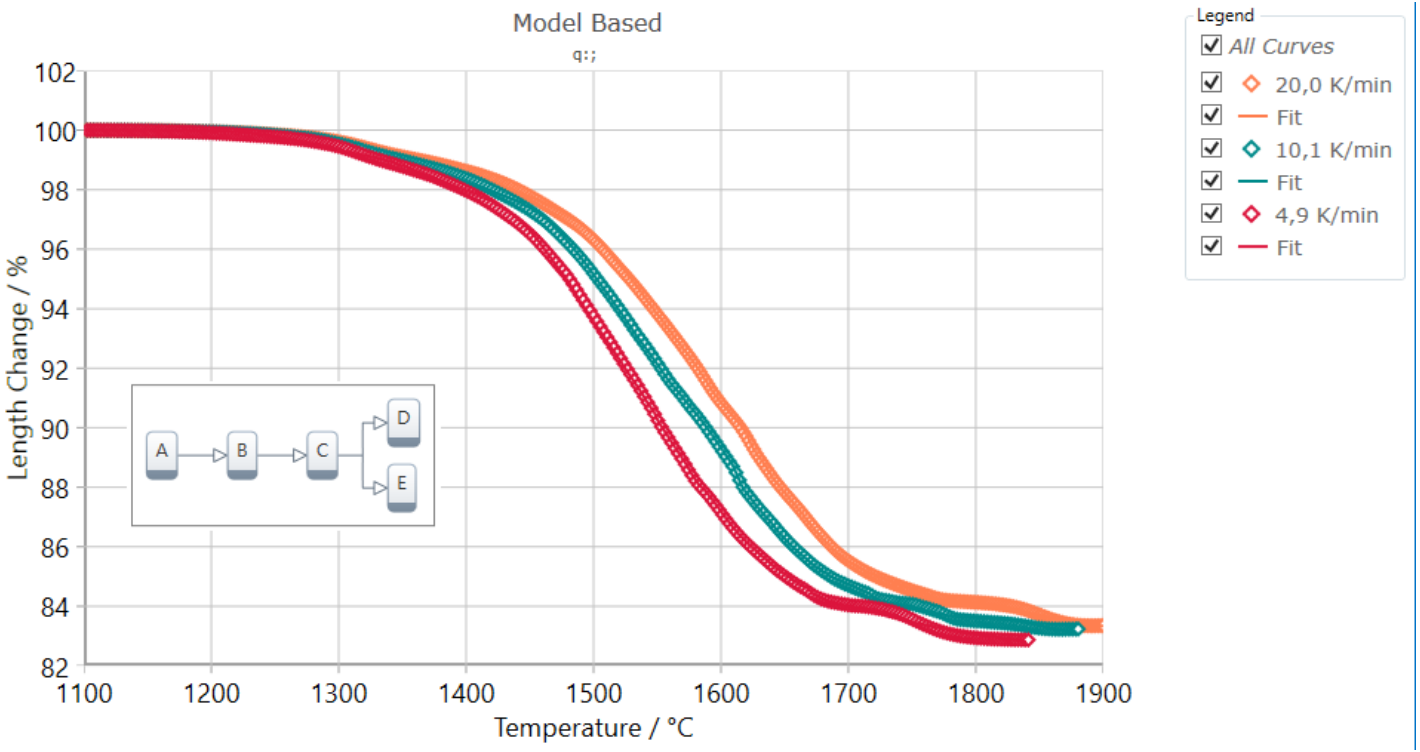
$$Cp \cdot dm \cdot \frac{dT}{dt} = q_{in} - q_{out} + Q_{reaction}$$

$$\frac{\partial T}{\partial t} = a\frac{\partial^2 T}{\partial^2 x} + \Delta T_{ad}\frac{d\alpha}{dt}$$

$$\frac{\partial T}{\partial t} = a\left[\frac{\partial^2 T}{\partial^2 x} + \frac{\partial^2 T}{\partial^2 y} + \frac{\partial^2 T}{\partial^2 z}\right] + \Delta T_{ad}\frac{d\alpha}{dt}$$

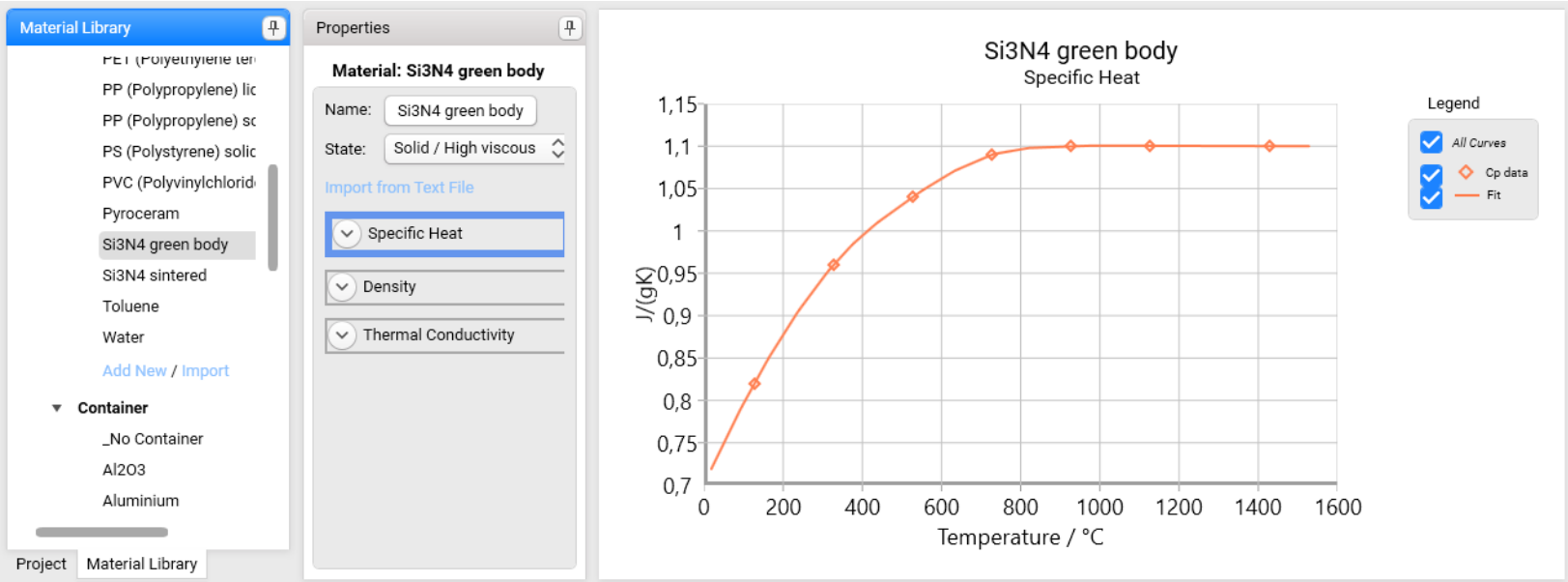
$dS = dy\,dz$ $dV = dx\,dy\,dz$ $dm = \rho\,dV$	Area Volume Mass
$q_{in} = dS\,\lambda \left.\frac{\partial T}{\partial x}\right\|_{x-\frac{dx}{2}}$	Heat flow *in* at point x-dx/2
$q_{out} = dS\,\lambda \left.\frac{\partial T}{\partial x}\right\|_{x+\frac{dx}{2}}$	Heat flow *out* at point x+dx/2
$Q_{reaction} = \Delta H \cdot dm \cdot \frac{d\alpha}{dt}$	Reaction Heat
$Cp \cdot dm \cdot \frac{dT}{dt}$	Self-heating
$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot \exp\left[\frac{-E}{RT}\right]$	Reaction rate
$q_{in} - q_{out} = dS\,\lambda \frac{\partial^2 T}{\partial^2 x}$	Heat flow difference
$a = \lambda\,/(Cp \cdot \rho)$	Thermal diffusivity
$\Delta T_{ad} = \Delta H/Cp$	Adiabatic Temperature increase

Technical ceramics:
Data: Dilatometer measurements for sintering of Si_3N_4



Kinetic model contains 4 individual reaction steps, two last of them are competing

Library of mostly used reactive and container materials



Physical properties of mostly used materials are in the material library

Physical properties of green body and sintered ceramics for Si_3N_4

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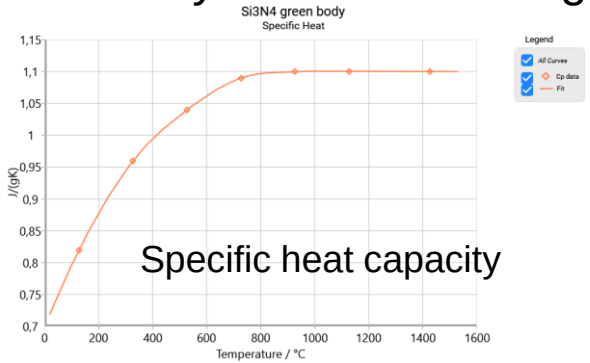
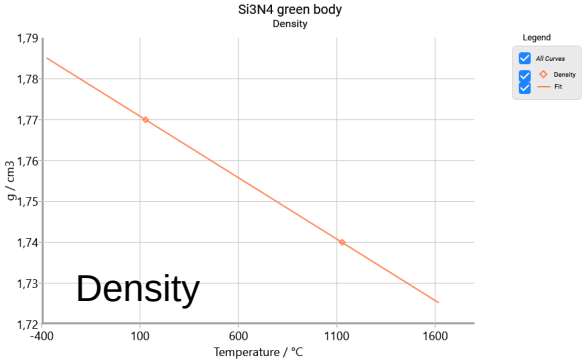
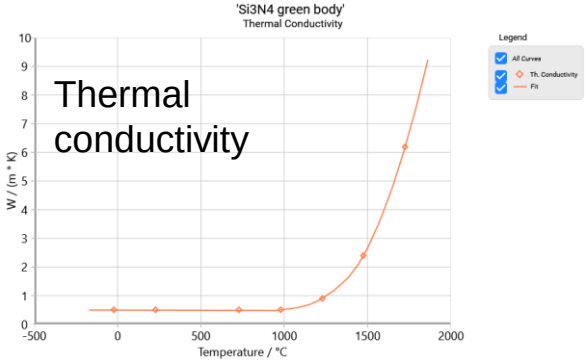
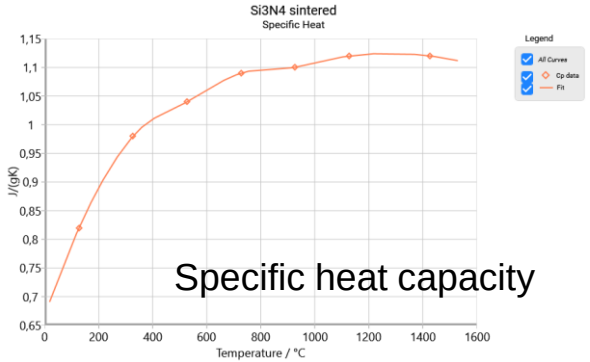
Green body: before sitntering

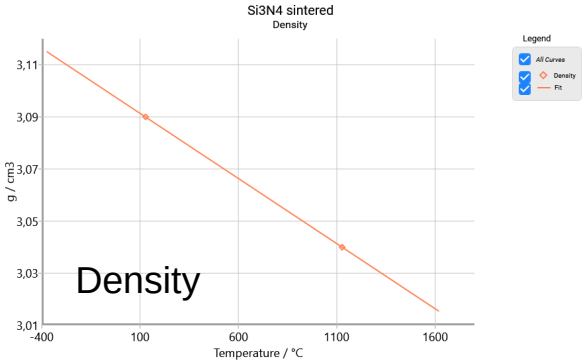


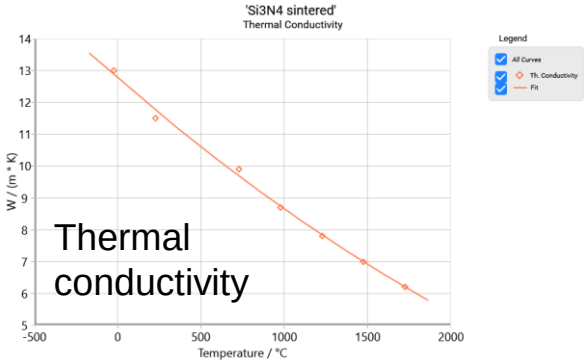




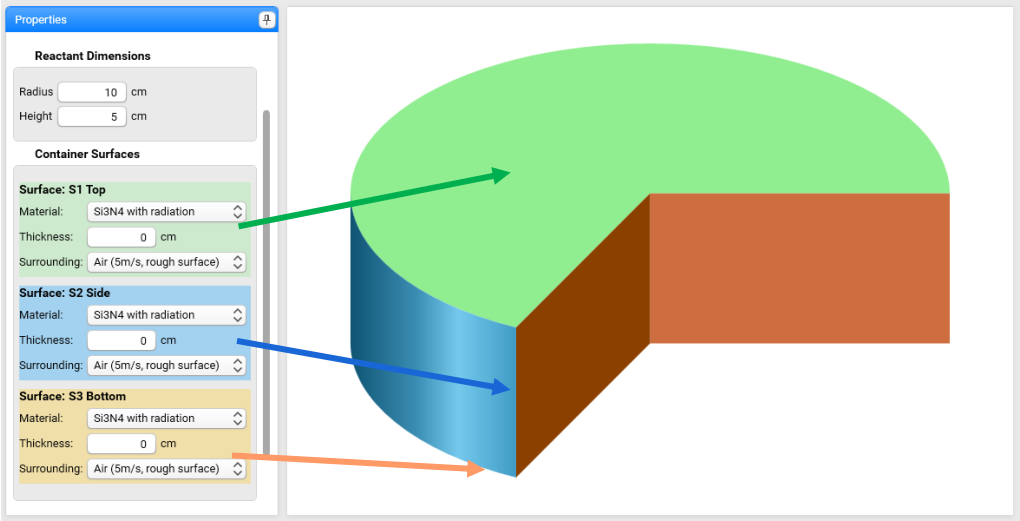
Ceramics: after sintering







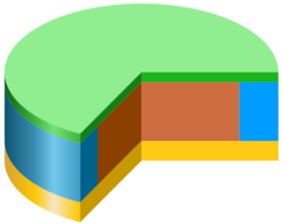
Physical data for simulation: reacting media and containers



Surface properties:
Heat transfer coefficient and emissivity

All physical properties are temperature-dependent

Material library
contains mostly used materials like polymers, metals, alloys



If necessary, then containers of different materials can be added

Results: Temperature vs time at any point of the reacting volume: Vertical or horizontal

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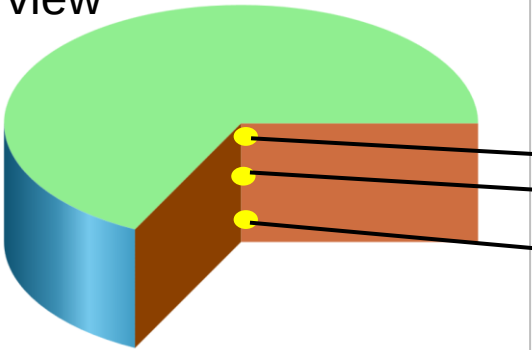
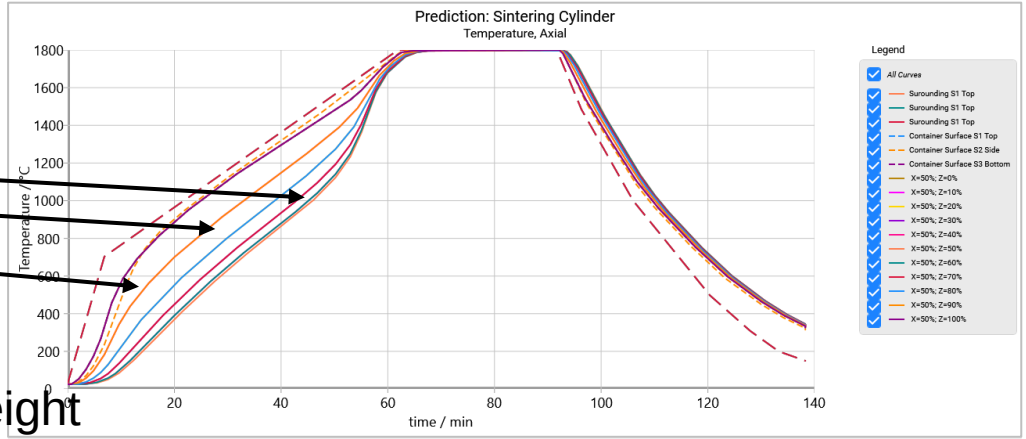
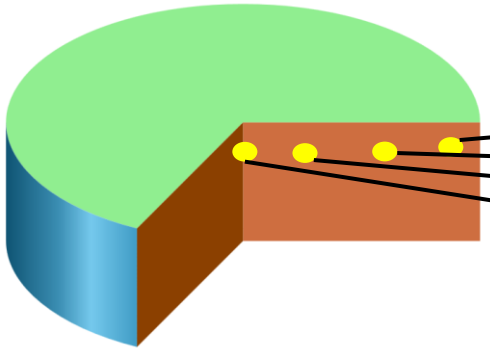
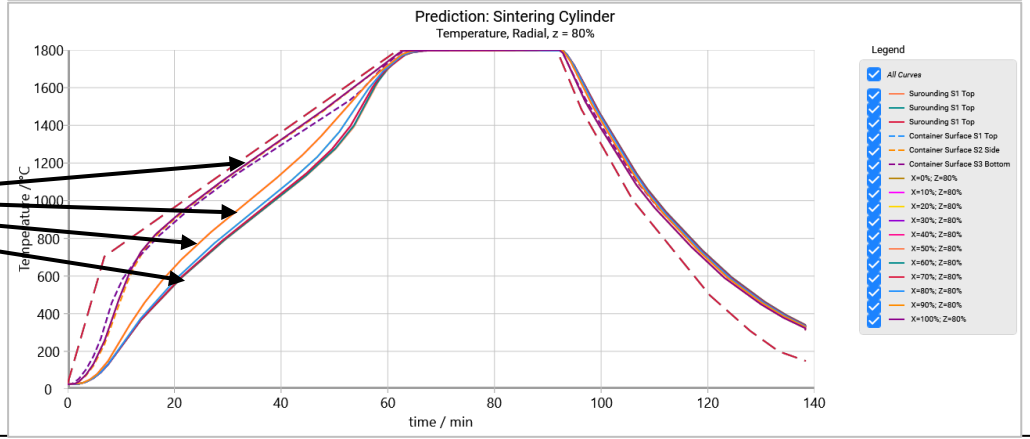
Axial view





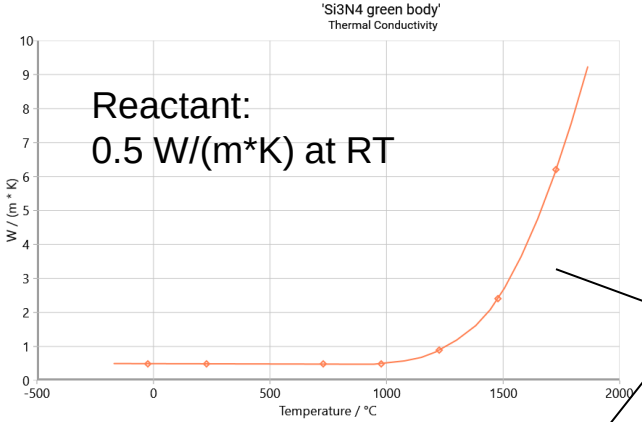
Radial view at the selected height



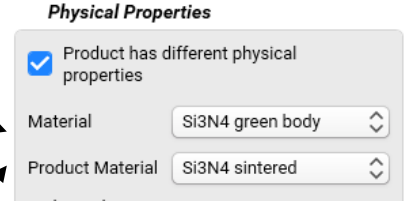


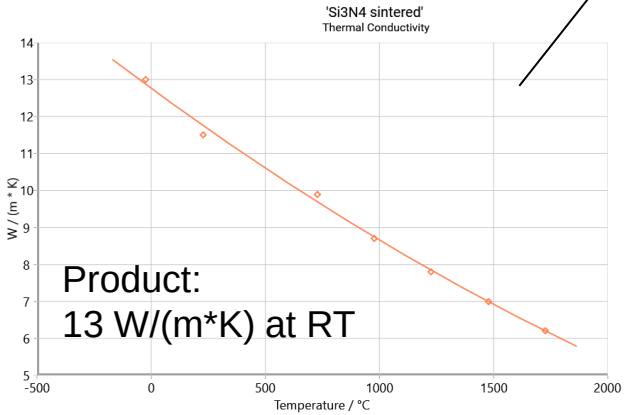
Possible to show: Temperature, conversion, conversion rate, concentrations vs time

Different thermal conductivity before and after reaction

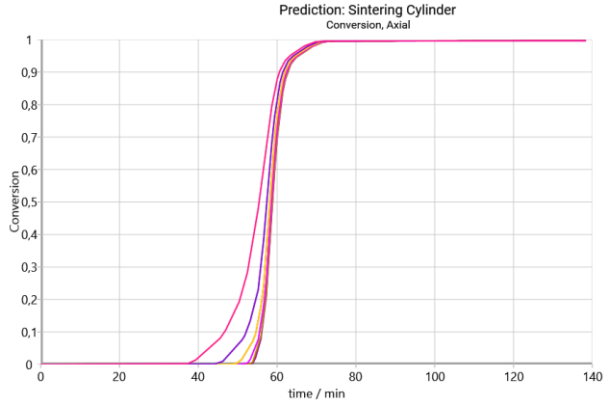


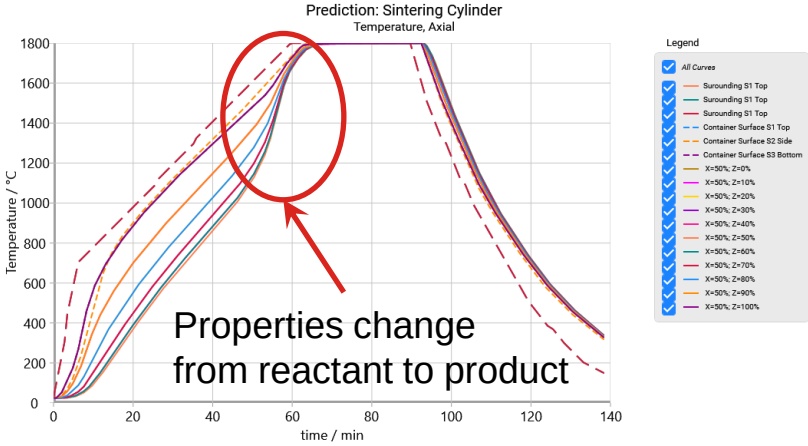
Reactant:
0.5 W/(m*K) at RT





Product:
13 W/(m*K) at RT





Changing of density during sintering

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Reactant

Name: Si3N4

Physical Properties

Product has different physical properties

Material: Si3N4 green body

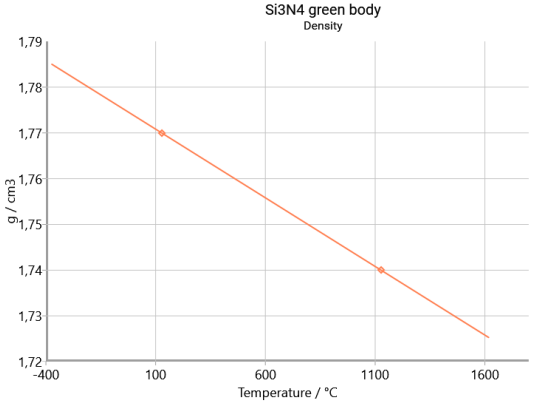
Product Material: Si3N4 sintered

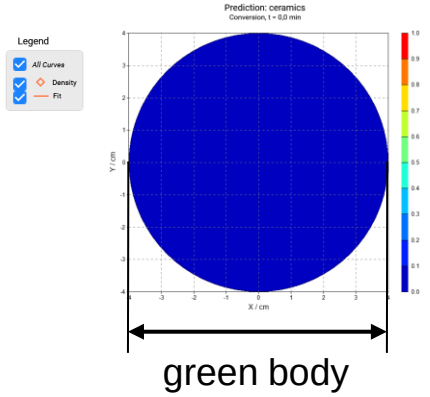
before sintering

ρ(20°C)=1.77 g/cm³

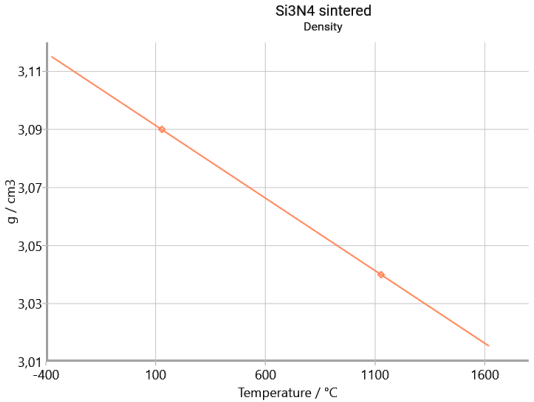
after sintering

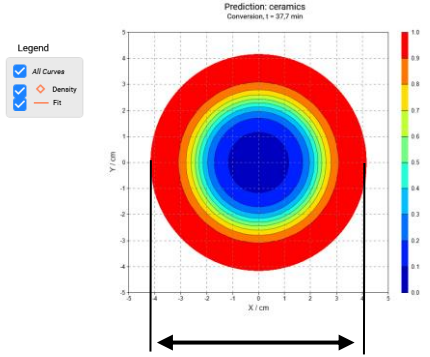
ρ(20°C)=3,10 g/cm³





green body

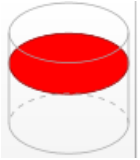




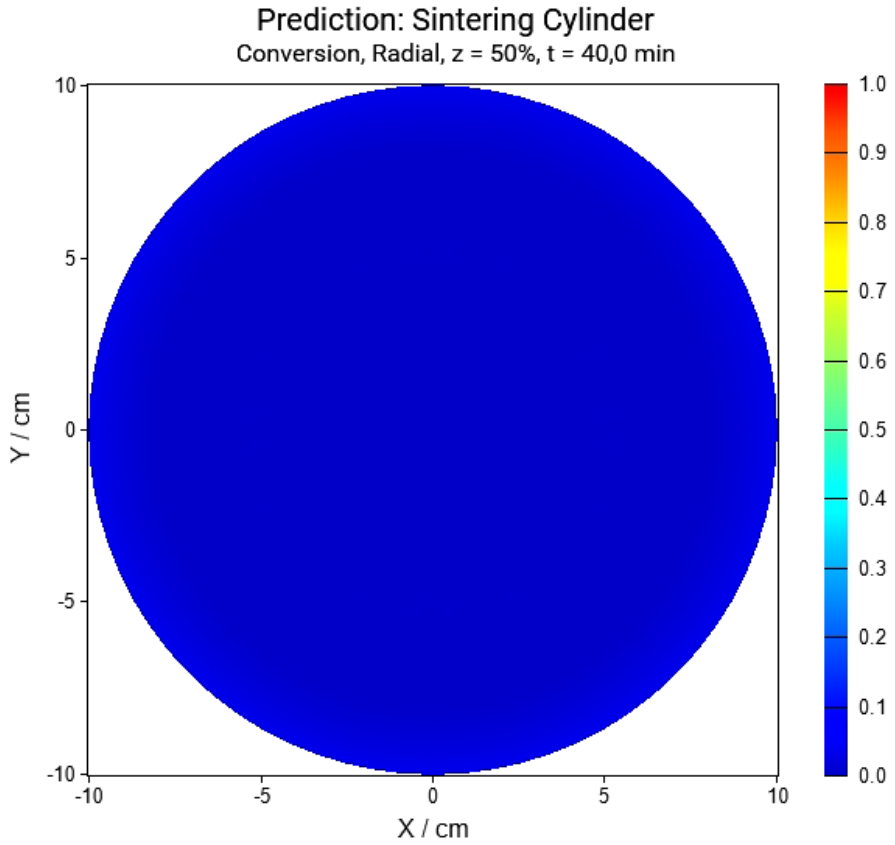
sintered

Reasons for linear changes:
1. thermal expansion
2. different density properties for reactant and final product (here)

Material has different density before and after reaction

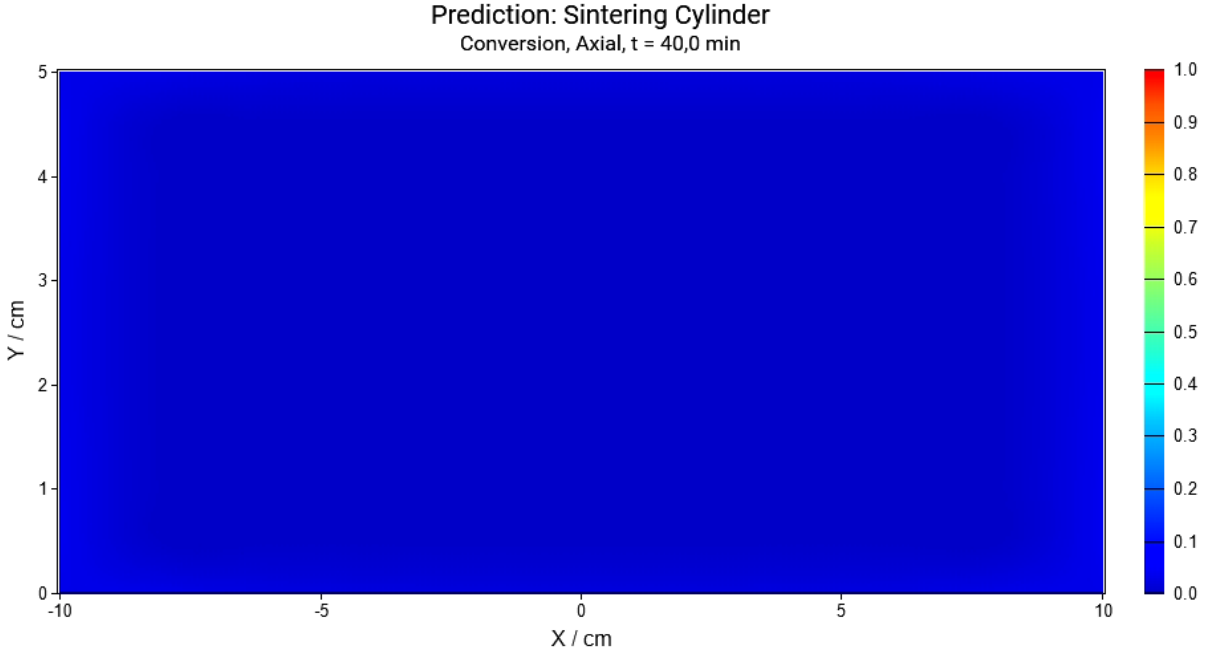


Horizontal Section

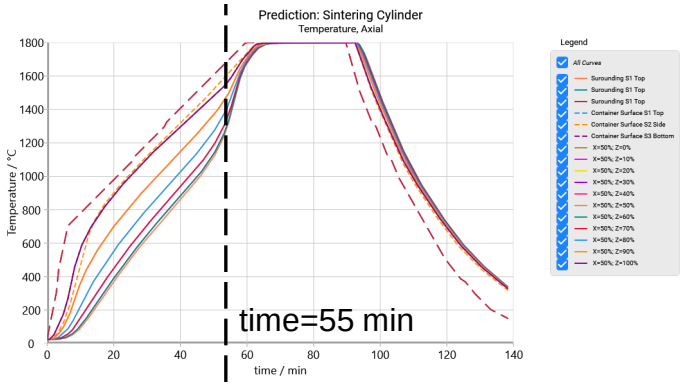


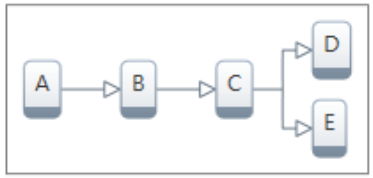
Material has different density before and after reaction

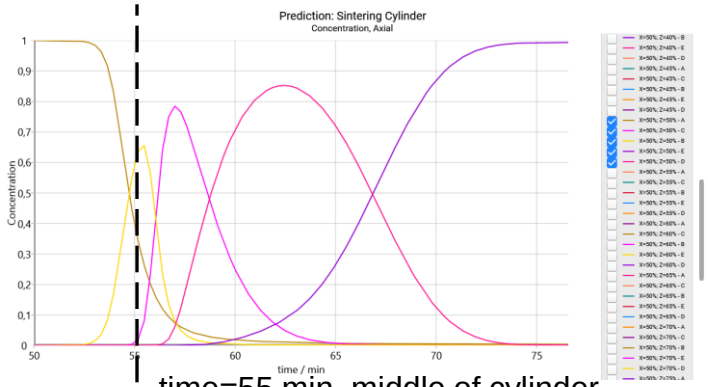
Vertical Section



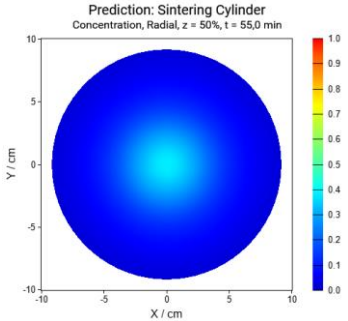
Concentration of each component during sintering



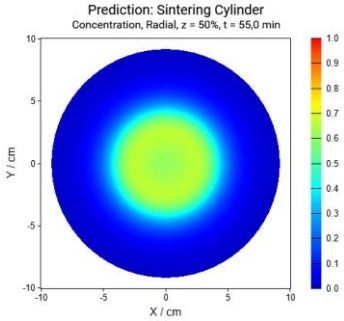




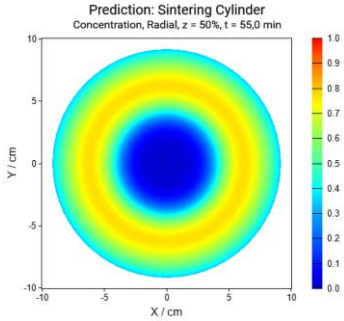
time=55 min, middle of cylinder



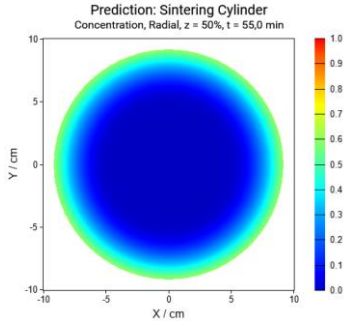
Concentration A



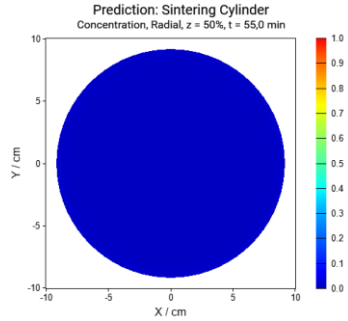
Concentration B



Concentration C

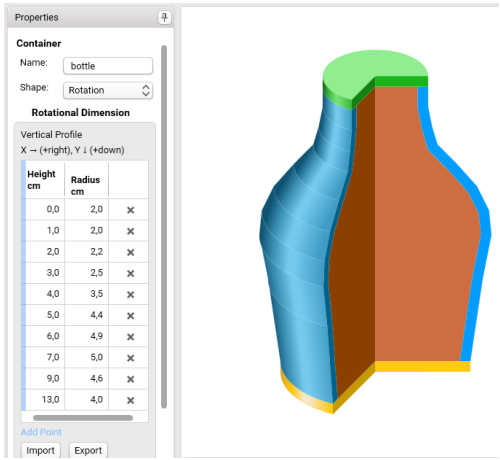


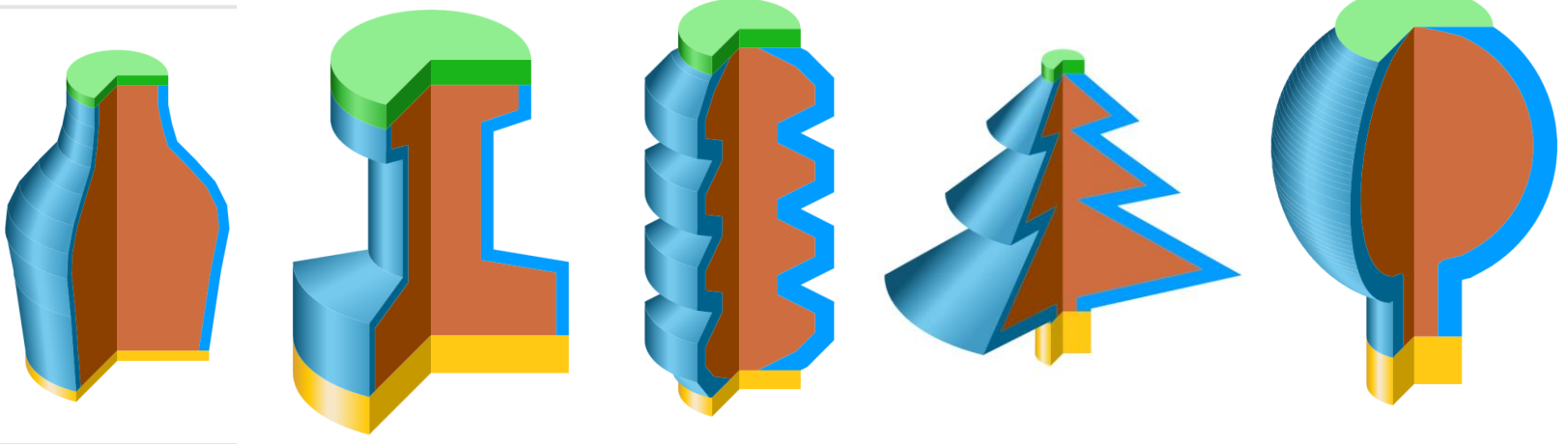
Concentration D



Concentration E

Rotation geometry of arbitrary profile



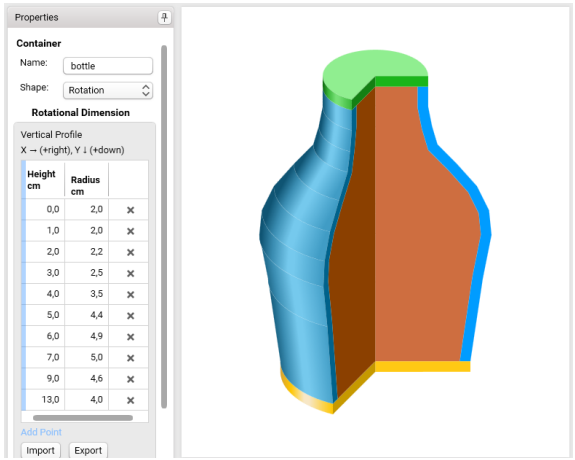


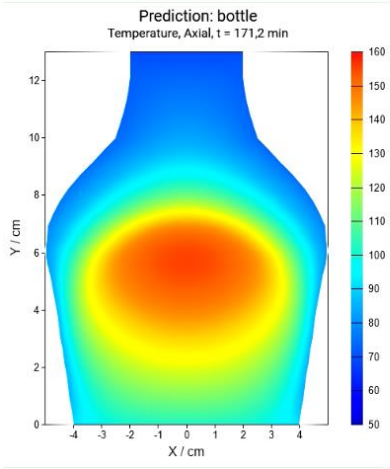
Rotation geometry of arbitrary profile

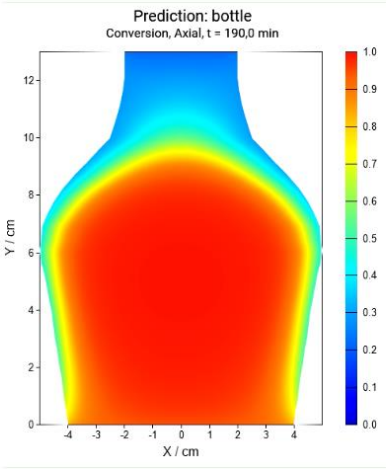
Temperature

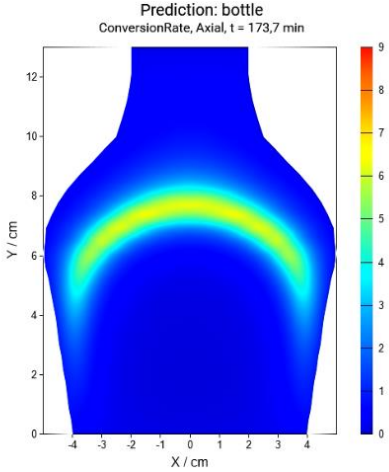
Conversion

Conversion rate









Surface: S1 Top

Isothermal

Temperature	60,00	°C
Time	250,00	min

Surface: S2 Side

Isothermal

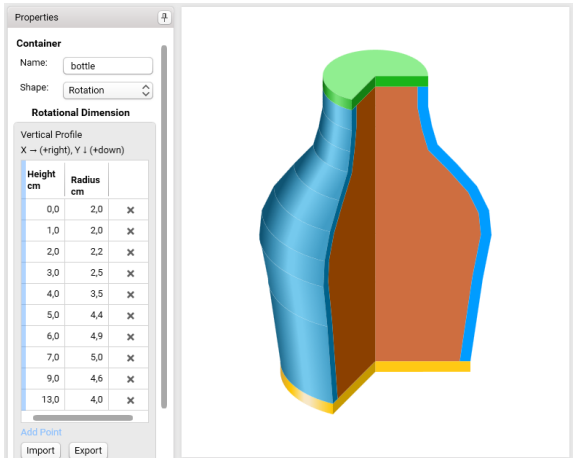
Temperature	60,00	°C
Time	250,00	min

Surface: S3 Bottom

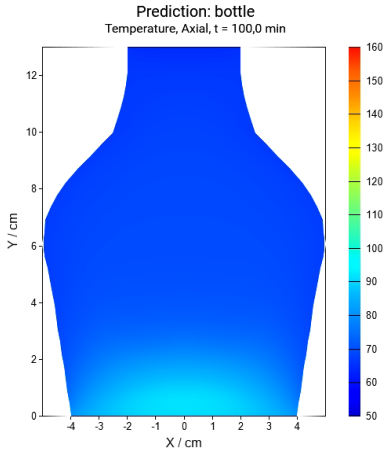
Isothermal

Temperature	100,00	°C
Time	250,00	min

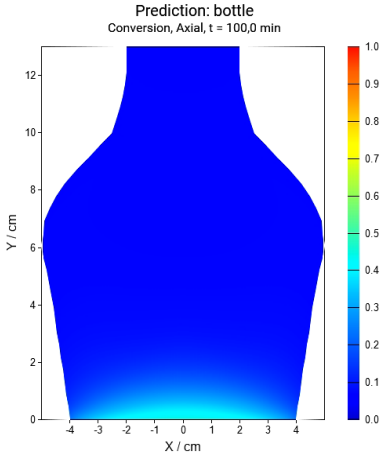
Rotation geometry of arbitrary profile



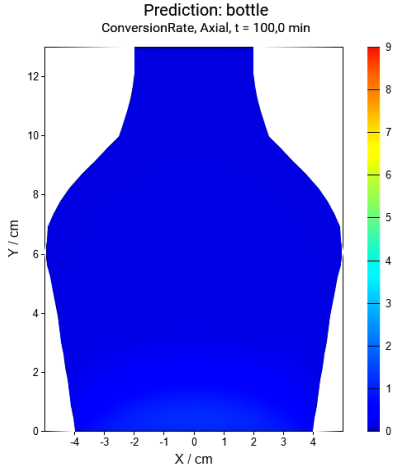
Temperature



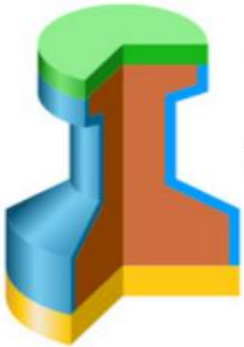
Conversion



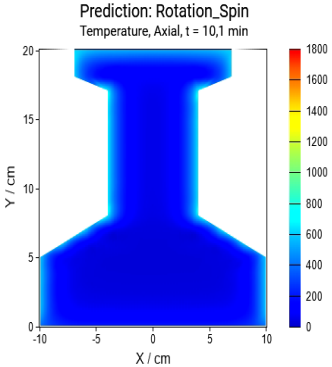
Conversion rate



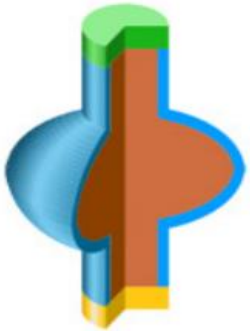
Simulation results for rotation shape



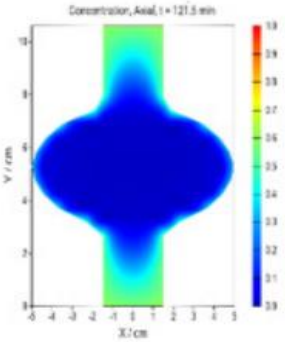
Shape



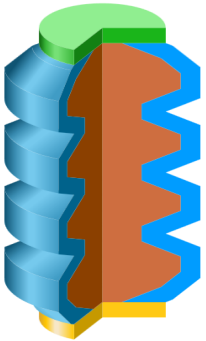
Temperature



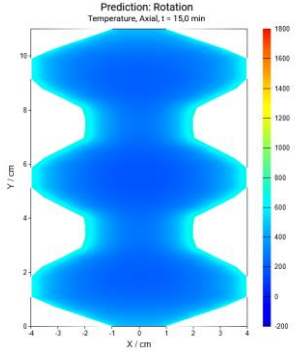
Shape



Concentrations



Shape



Temperature

General functionality of Termica Neo

1. Simulation of the chemical reactions in big volumes
2. Calculation of the following properties at each point of volume as the function of time
    1. Temperature
    2. Degree of conversion
    3. Conversion rate
    4. Concentrations

NETZSCH

ICTAC: *International Confederation for Thermal Analysis and Calorimetry*

KINETICS NEO

- Model free analysis
- Multi-step model-fitting (model based)
- Diffusion control for curing
- Crystallization kinetics
- Kamal model for curing
- Deconvolution analysis (sum of peaks)

ELSEVIER

Thermochimica Acta
Volume 689, July 2020, 178597

Review

ICTAC Kinetics Committee recommendations for analysis of multi-step kinetics

Sergey Vyazovkin [a], Alan K. Burnham [b], Loic Favergeon [c], Nobuyoshi Koga [d], Elena Moukhina [e], Luis A. Pérez-Maqueda [f], Nicolas Sbirrazzuoli [g]

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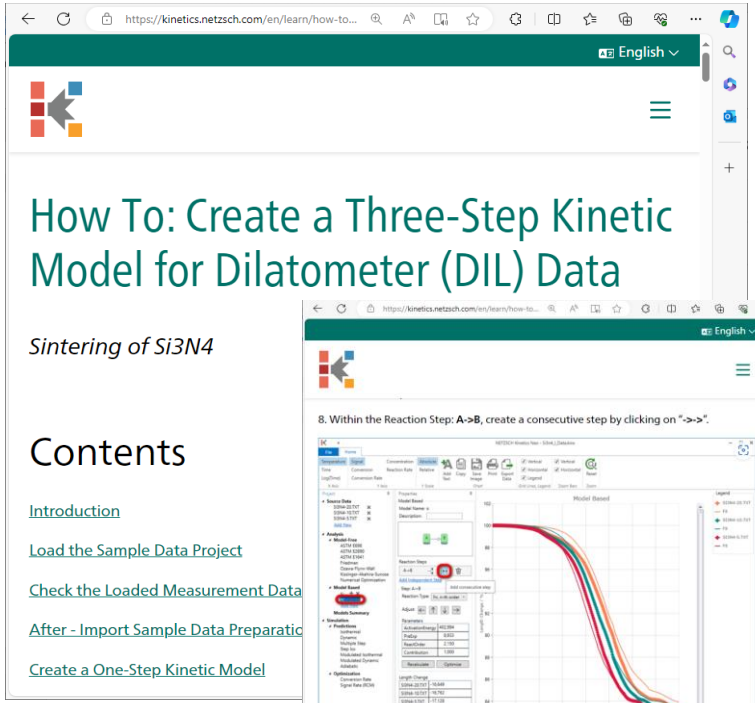
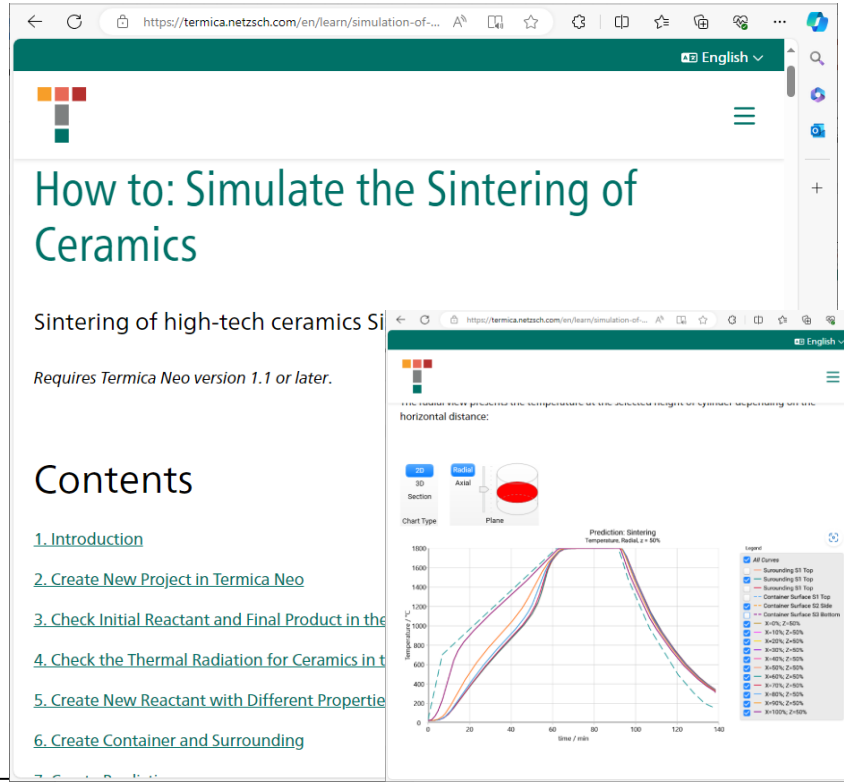
NETZSCH Kinetics Neo Web Site, NETZSCH Termica Neo Web Site

NETZSCH

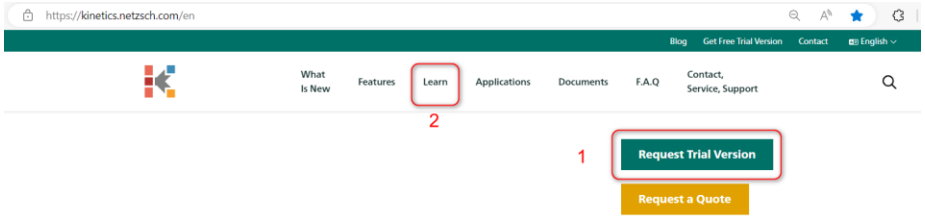
Users Guide, Training examples,
Webinars: Thermokinetics (pdf and video):





kinetics.netzsch.com *Trial Version 30 days* termica.netzsch.com

- Go to: https://kinetics.netzsch.com
- *Trial Version 30 days*



KINETICS NEO

Kinetics Neo

Software for Kinetic Analysis and Simulation of Thermoanalytical Data for Chemical Processes

Kinetics Neo software fully supports "ICTAC Kinetics Committee recommendations for analysis of multi-step kinetics" .

News

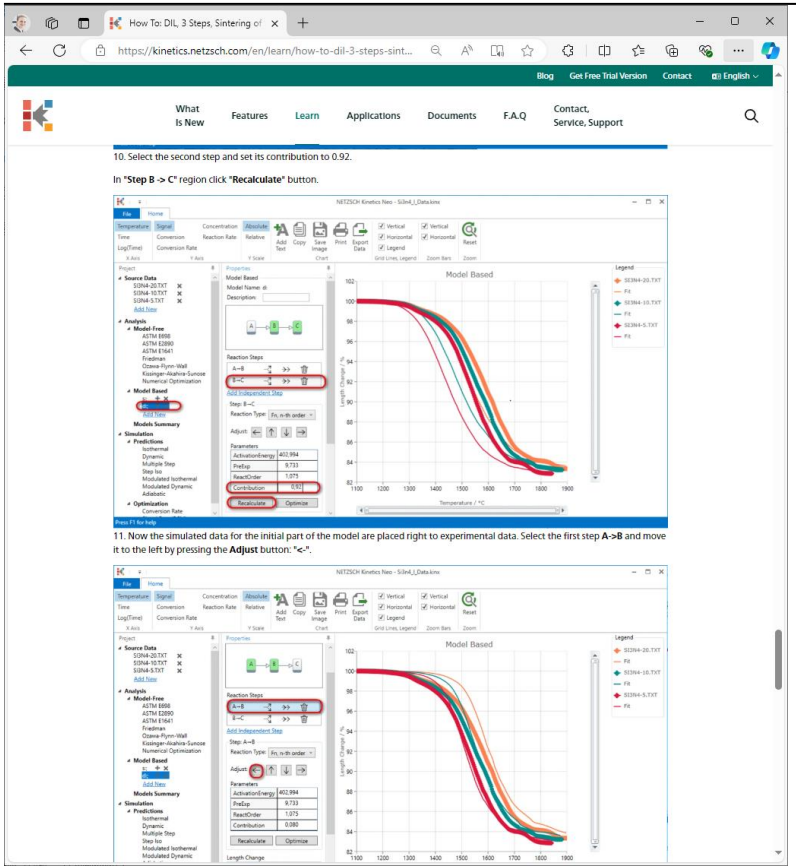
October, 23, 2024 Webinar Ceramics Sintering: Kinetics, Simulation and Process Optimization Using the Kinetics Neo and Termica Neo Software.

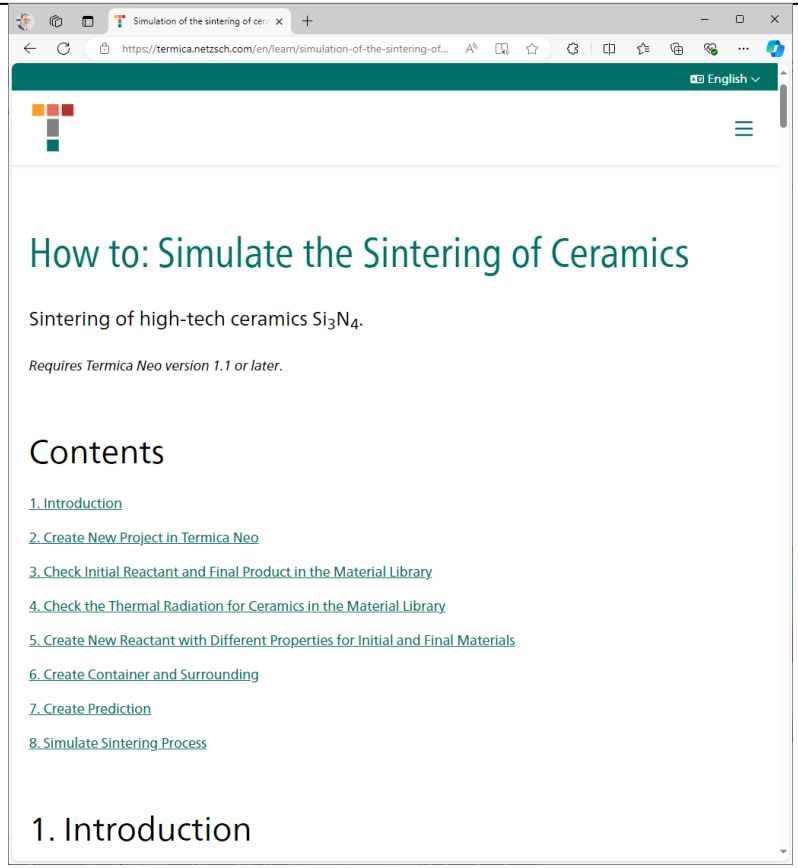
In this webinar, we will present the typical solution steps sintering optimization of different ceramic materials in order to get the highest quality at lowest costs. They include kinetic modelling of the process by the NETZSCH Kinetics Neo software and then the simulation of this process for the user's geometry by the Termica Neo software. This helps understand your process and saves a lot of time and efforts compared to the way of trial-and-error.
Register for Webinar

September 25-27, 2024. Kinetics Neo and Termica Neo will be presented on 50th GEFTA annual conference 2024 in Gießen, Germany is 2 talks:

- Elena Moukhina, Jan Hanss. Kinetic Modeling of Metal Reduction at Different Temperature Conditions and Hydrogen Concentrations

Training examples for sintering





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Proven Excellence.

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