Dynamic Model for the Lime Kiln in the Chemical Kraft Recovery

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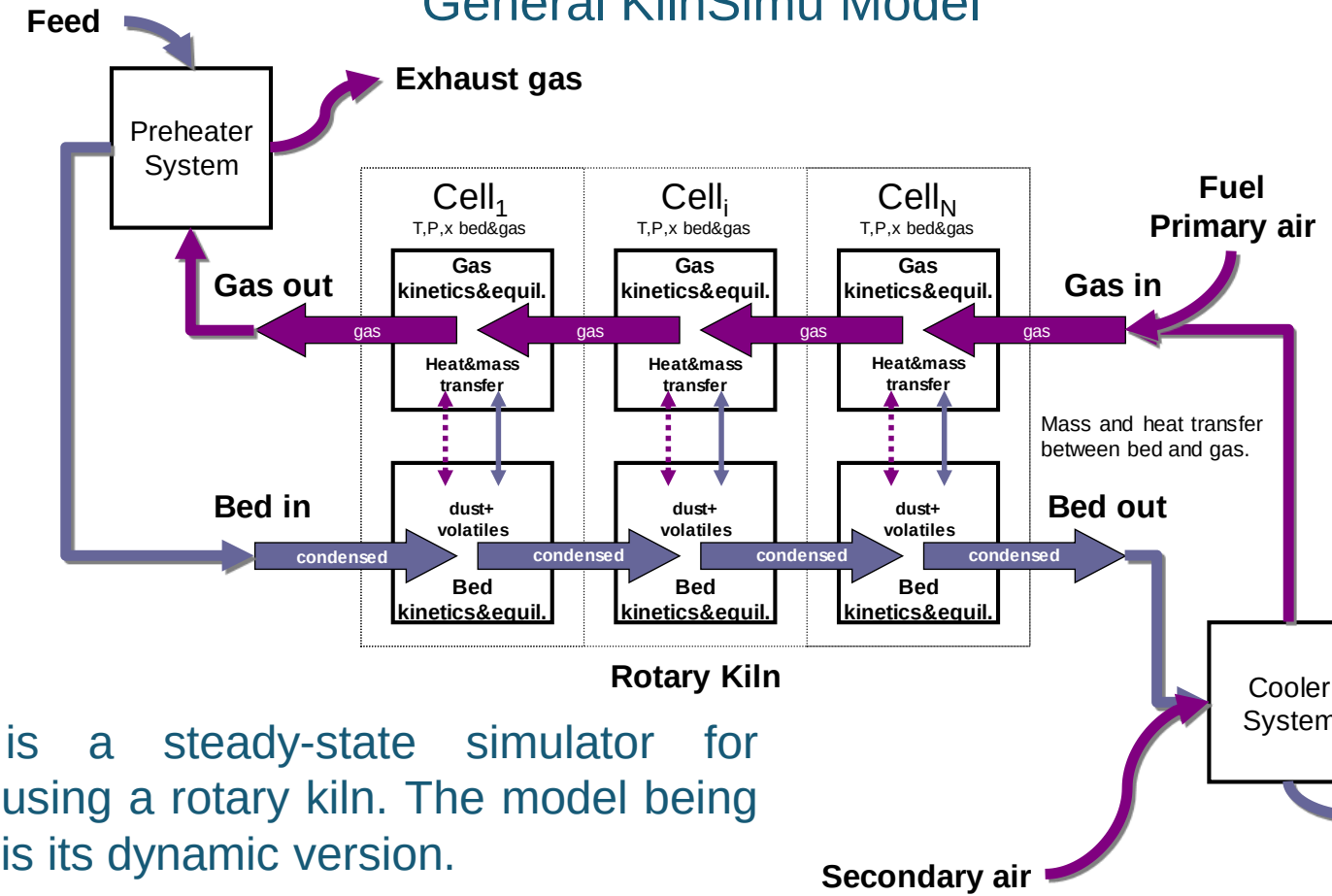
- Introduction & Background
- CROM Simulation Platform
- Dynamic Lime Kiln Model
- Simulation Results

Introduction

- Part of DeepCleanTech Project.
- Funded by Business Finland (former Tekes) and VTT.
- Task aim to develope a dynamic simulation algorithms.
- Target process: Rotary Kiln.
- Target application: lime kiln in the chemical kraft recovery.
- Interest in the behaviour of non process elements.
- Simulation model is implemented as a unit operation in CROM simulation platform.

Background

General KilnSimu Model



KilnSimu is a steady-state simulator for processes using a rotary kiln. The model being developed is its dynamic version.

CROM Simulation Platform

- CROM Introduction & Development Tools
- Kinetic Models and Combining Kinetics & Equilibrium
- Particle Model
- Calculation Node Model

CROM Introduction

- Dynamic simulation of chemical (high temperature) processes.
- Originally developed for SAF process in ferro-**chrom**ium production.
- Collection of dynamic process (Unit Operation) models.
- Sequential modular solver.
  - For handling potentially hundreds of species.
- Flowsheet tearing & partitioning & sequencing.
- Equilibrium & Kinetics & Particles.
- Uses ChemApp for thermodynamic calculations.
  - Stream equilibrium and enthalpy calculation.

CROM Development Tools

- Developed with Intel Visual Fortran in Microsoft Visual Studio.
- Uses ChemApp-library for all thermodynamic routines.
- Simple GUI in development.
- In the future parallel computing will be used when possible.
- Using Fortran Coarray extension for parallel computing (uses MPI).
  - Program is divided into number of images (per computer core).
  - Each image has its own memory and code (and thus its own copy of Chemapp).
  - Coarray extension allows syncing the data between the images with few line of source code.

Kinetic Models

Differential form:

$$\frac{d\alpha}{dt} = kf(\alpha) = A_0 e^{-E_a/RT} f(\alpha)$$

Reaction conversion α:

$$\alpha = 1 - \frac{c_t}{c_0}$$

c_0 = Initial / max. conc.

c_t = Conc. at time *t*

Kinetic Model		$f(\alpha)$	
Power law	P2	$2\alpha^{1/2}$	
Power law	P3	$3\alpha^{2/3}$	
Power law	P4	$4\alpha^{3/4}$	
Avrami-Erofeyev	A2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	
Avrami-Erofeyev	A3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	
Avrami-Erofeyev	A4	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	
Contracting area	R2	$2(1-\alpha)^{1/2}$	$k' = k/R$
Contracting volume	R3	$3(1-\alpha)^{2/3}$	$k' = k/R$
1-D diffusion	D1	$1/2\alpha$	$k' = k/R^2$
2-D diffusion	D2	$-1/\ln(1-\alpha)$	$k' = k/R^2$
3-D diffusion	D3	$3(1-\alpha)^{2/3}/\left[2\left(1-(1-\alpha)^{2/3}\right)\right]$	$k' = k/R^2$
First-Order	F1	$(1-\alpha)$	
Second-order	F2	$(1-\alpha)^2$	
Third-order	F3	$(1-\alpha)^3$	

Combining Kinetics & Equilibrium

- Kinetics controls how fast individual phases are allowed to react to products and equilibrium calculation determines what these products are.
- At each time step kinetics is used to determine the fractions of each phase/species that are allowed to react (reactive part).
- These are then taken into equilibrim calculation to determine the reaction products.
- Other part of phases/species are inert (inert part).
- After equilibrium calculation reactive and inert parts are combined.

Particle Model

- Simulation can include one or more particles (1 to 5).
- All particles have same size classes (1 to 15).
  - Particle size distribution (PSD) (mass fractions of particle sizes).
- Each particle can have any set of phases and compositions.
- Constrained equilibrium is calculated separately for each particle including interaction with the surrounding gas.
- Particle growing and shrinking models (PSD changes).
- Sintering model for allowing particles to interact.
  - For example clinker nodules in cement production.
- Handling of melt formation included.

Calculation Node Model

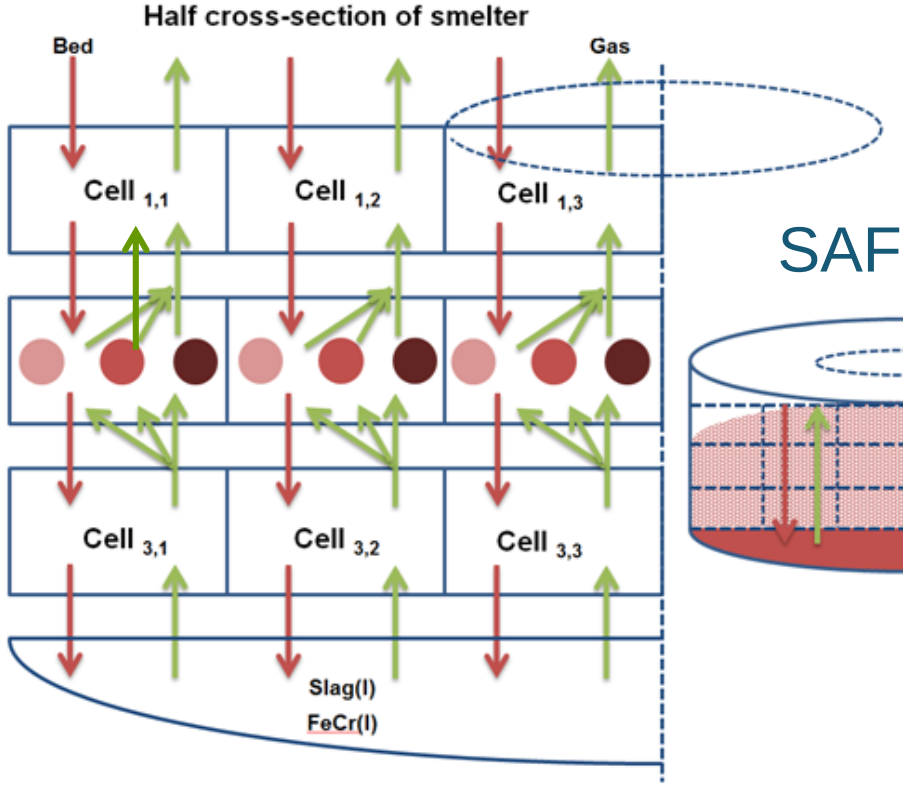
- Basic unit is a calculation node.
  - Represents a volume containing stagnant mass or mass flowing through the volume with a certain velocity (residence time = velocity * node length).
- During a time step (equivalent to residence time of the flow inside the volume) heat is added or taken from the mass and kinetically (Δt = time step) constrained equilibrium is calculated (for each particle) to solve the temperature and composition.
- Temperature is solved iteratively from the energy balance.
  - mass enthalpy change = heat change.

Example Grid (of Nodes)

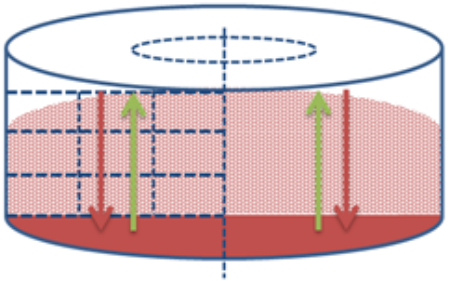
Half cross-section (3 nodes in radial direction)

Charge

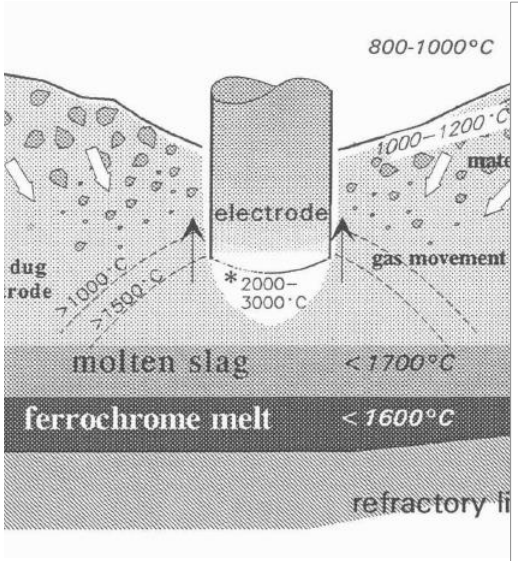
Feed (Gas)

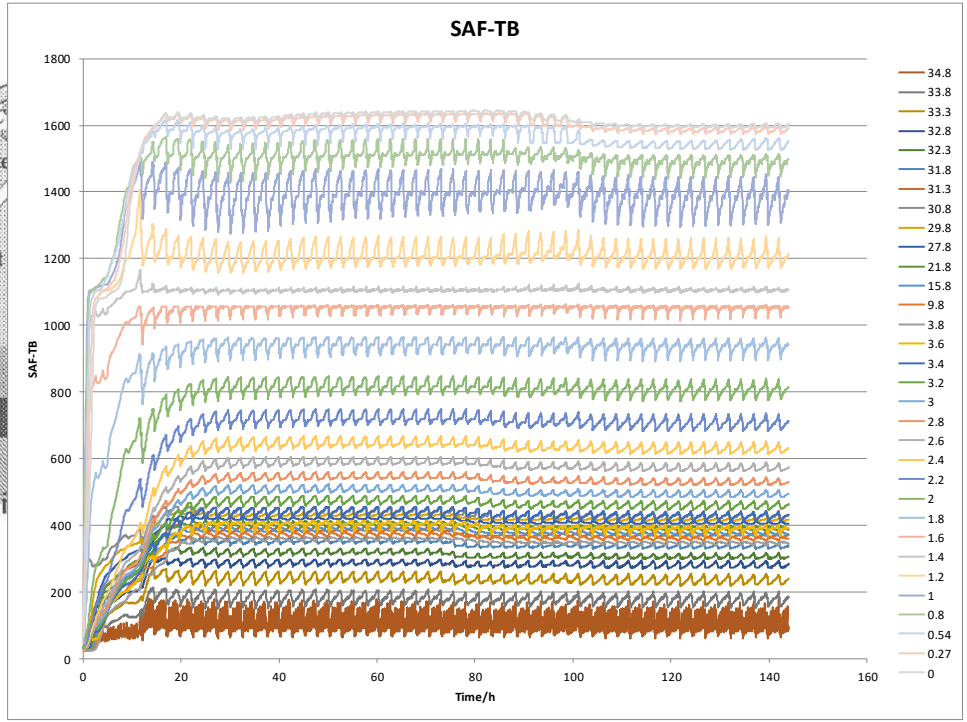


SAF / BF



Example of SAF Model



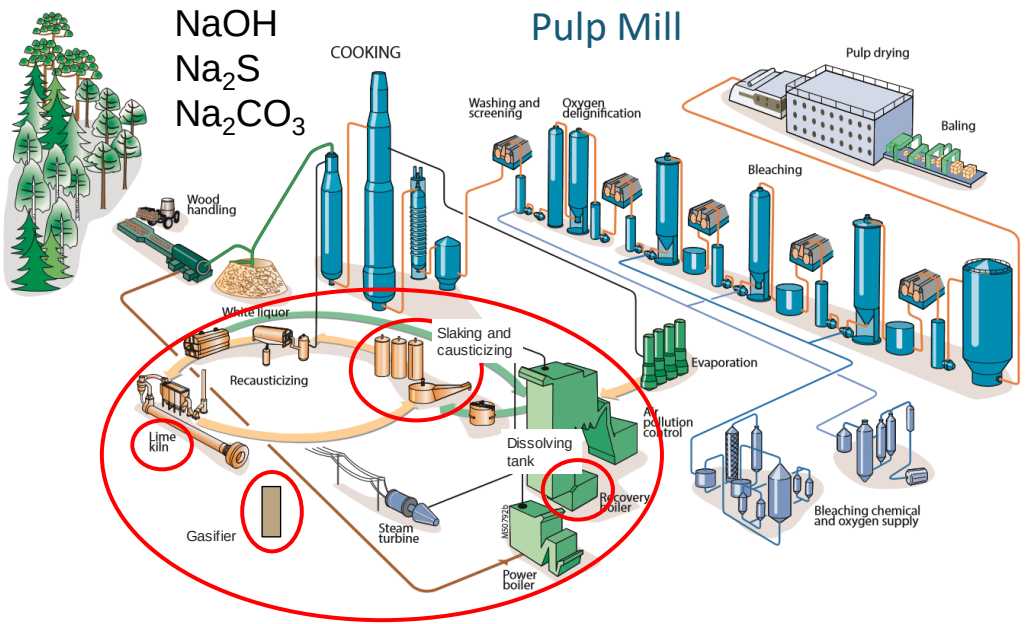


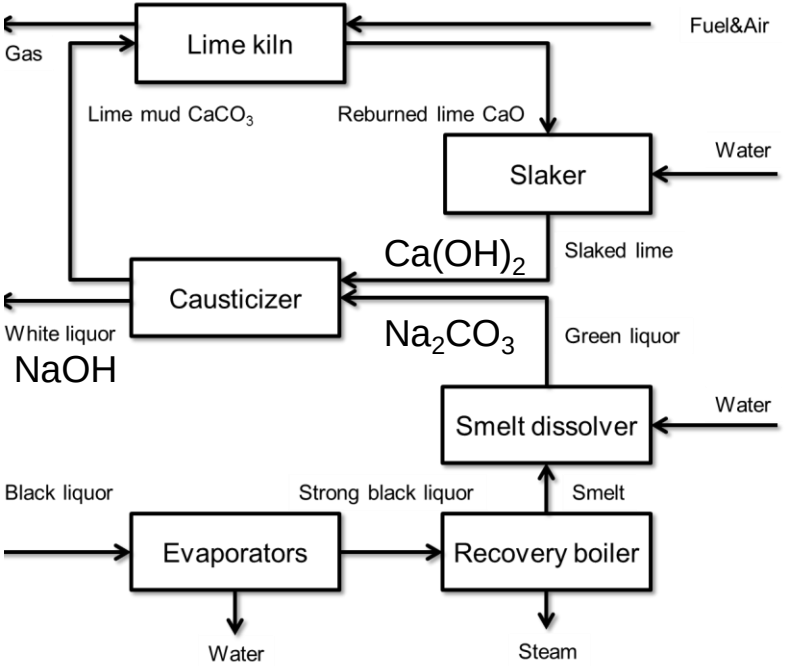
Simulated temperature profiles as function of time at diffrent heights in preheater, feeding tubes and smelter.

Lime Kiln Model

- Chemical Kraft recovery Process
- Lime Kiln
- Lime Kiln Model

Chemical Kraft Recovery

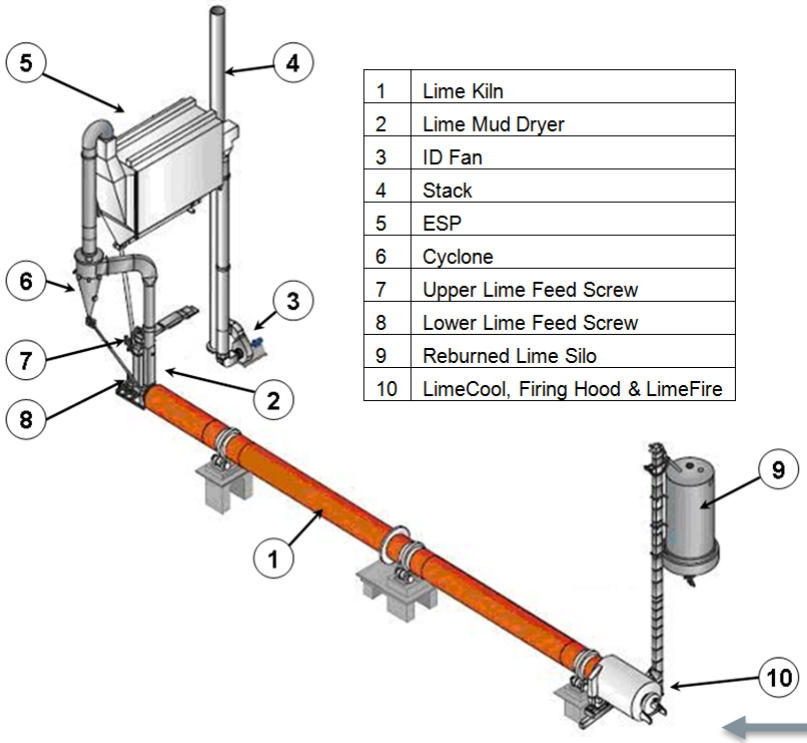




- In chemical pulping cooking chemicals are used to remove the lignin from the wood and thereby releasing the fibers. The chemical pulping process commonly used in the world is Kraft cooking.
- Sodium carbonate in green liquor is transformed to sodium hydroxide in the causticizer by allowing it to react with calsium hydroxide. Sodium hydroxide is reused as a cooking chemical but the other product, calcium carbonate is transformed back to calcium hydroxide in lime kiln and slaker.

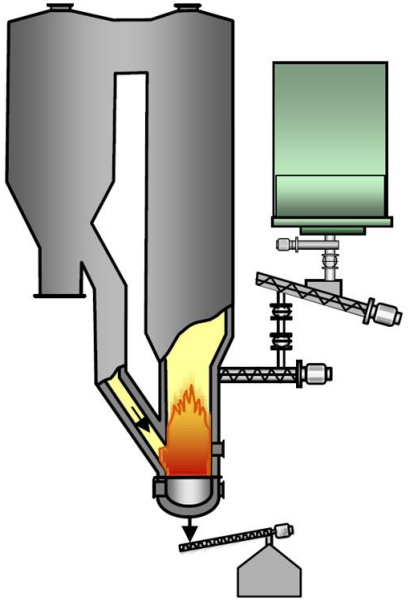
Lime Kiln

LMD-Kiln-Cooler System

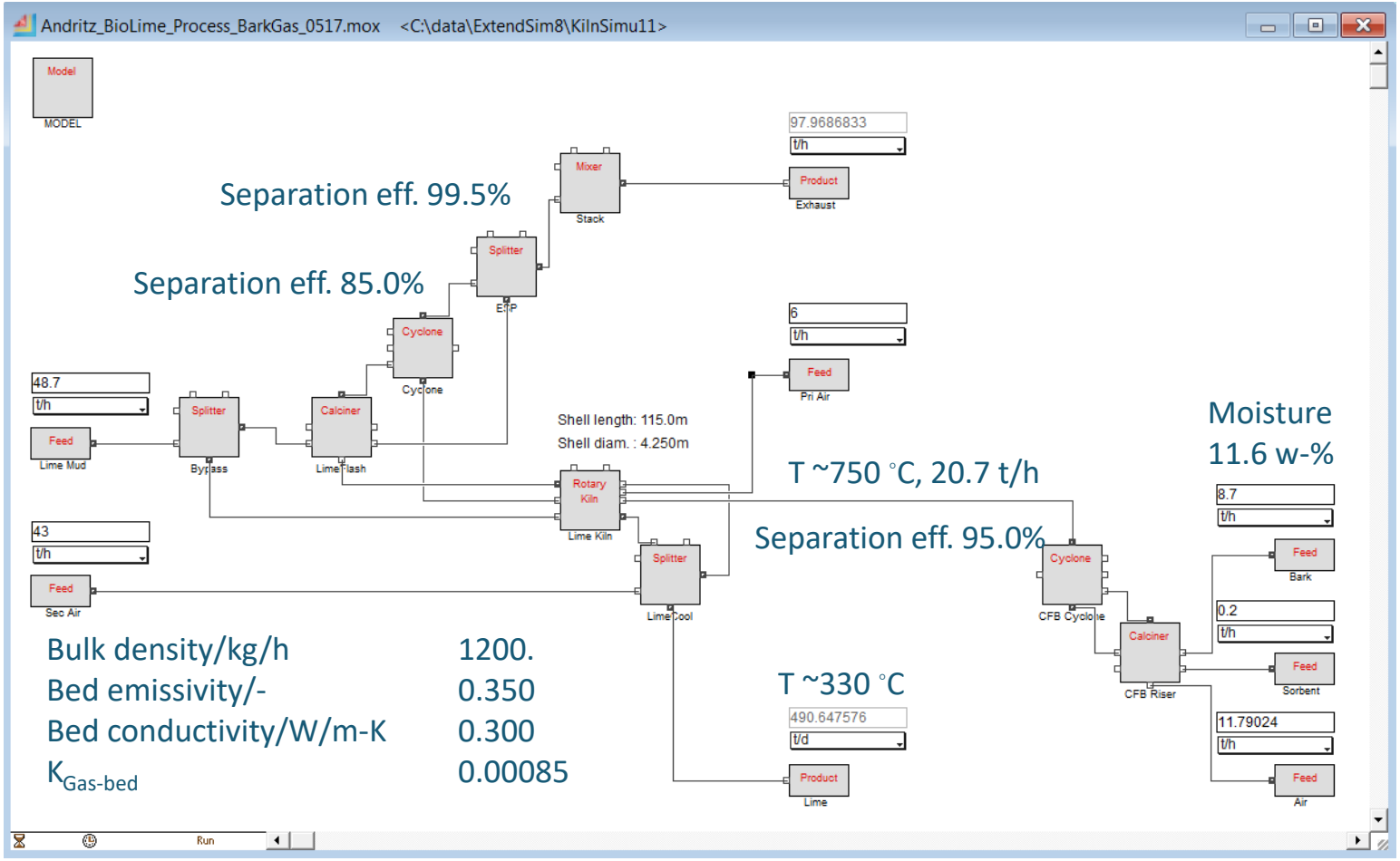


1	Lime Kiln
2	Lime Mud Dryer
3	ID Fan
4	Stack
5	ESP
6	Cyclone
7	Upper Lime Feed Screw
8	Lower Lime Feed Screw
9	Reburned Lime Silo
10	LimeCool, Firing Hood & LimeFire

Bark Gasifier



Example of KilnSimu Lime Kiln Model



Lime Kiln Model

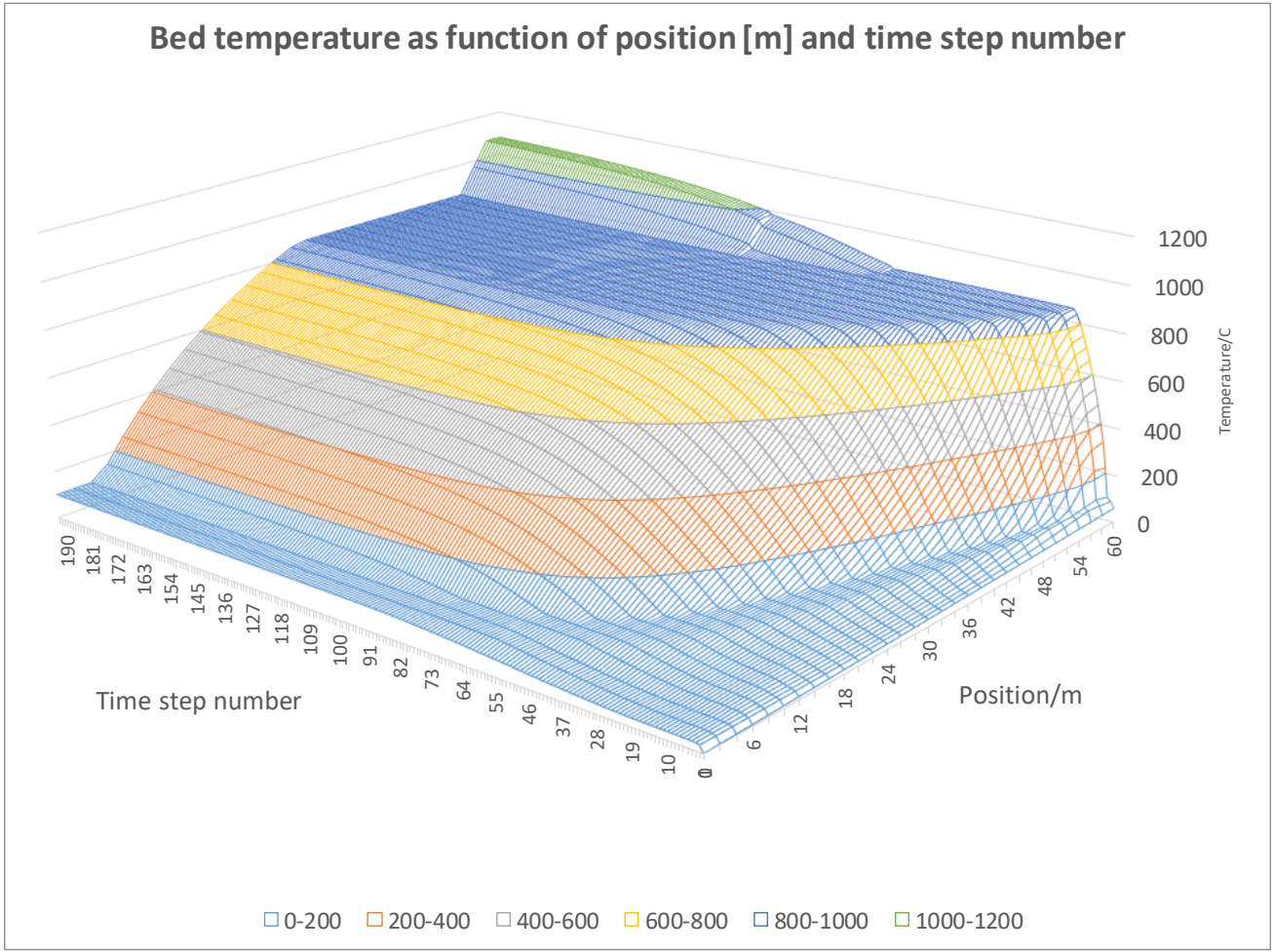
- Kiln is divided axially into calculation nodes for the bed and gas sides.
  - Only one node for bed and gas in any axial position.
  - In the future bed can be divided into surface and bottom regions.
- At start kiln is filled with charge of given composition.
- For each time step (bed residence time in node, gas semi-continuous):
  1. Bed, gas and wall temperatures and bed and gas compositions are solved iteratively starting from gas feed end.
  2. After all nodes solved, bed moves forward by one node.
  3. Go to next time step.

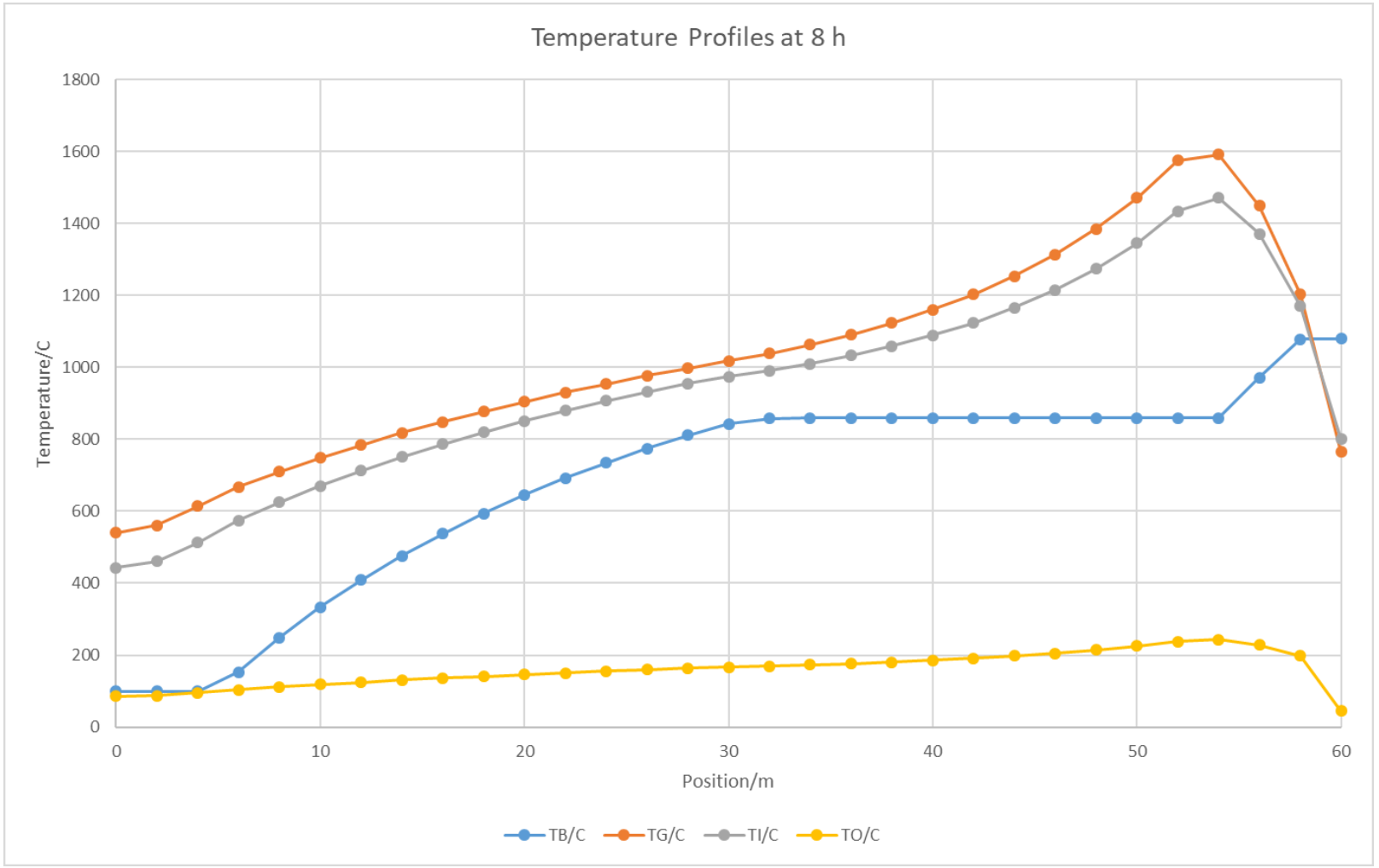
Results

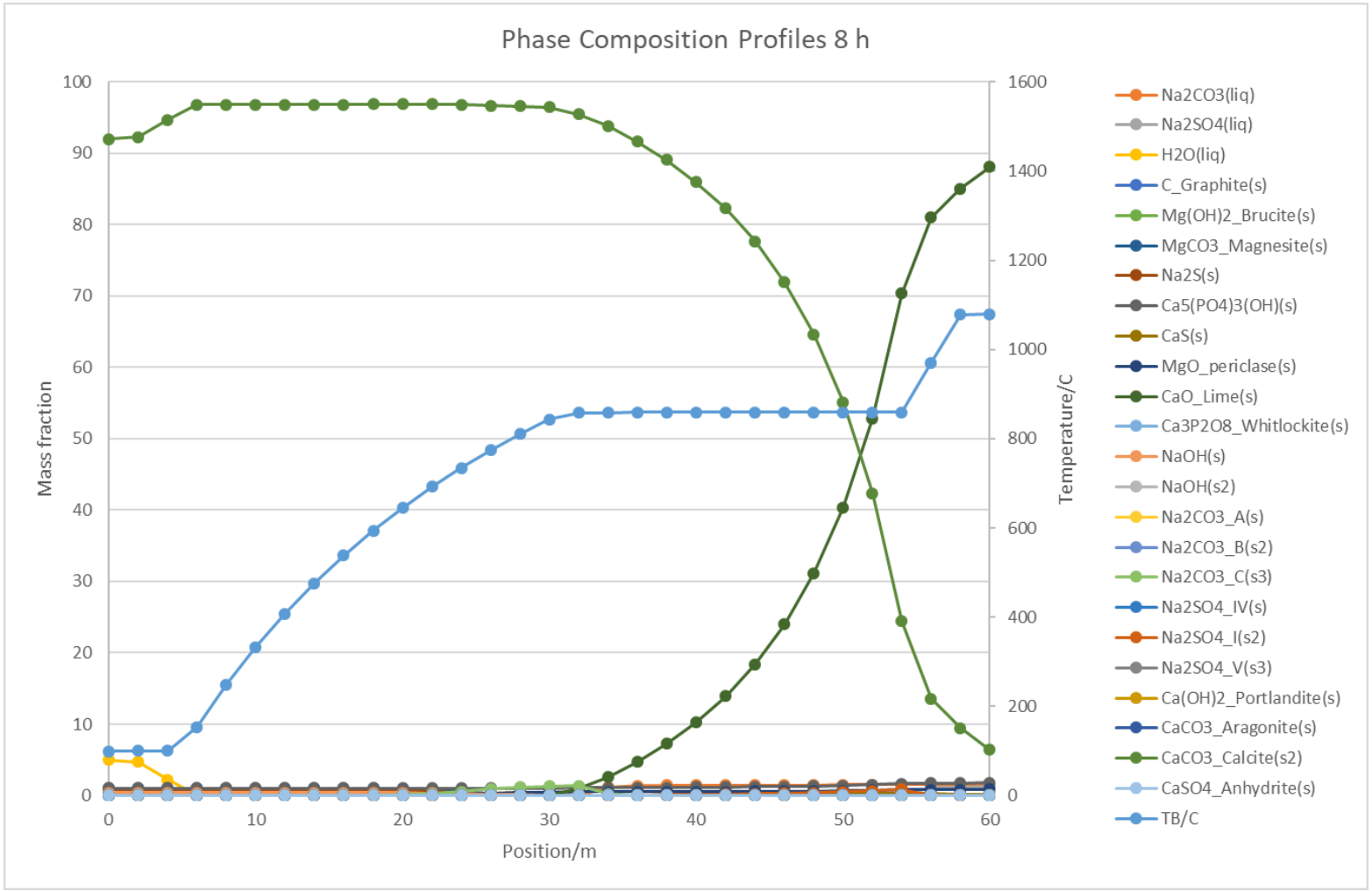
- Process settings
- Temperature profiles
- Phase composition profiles

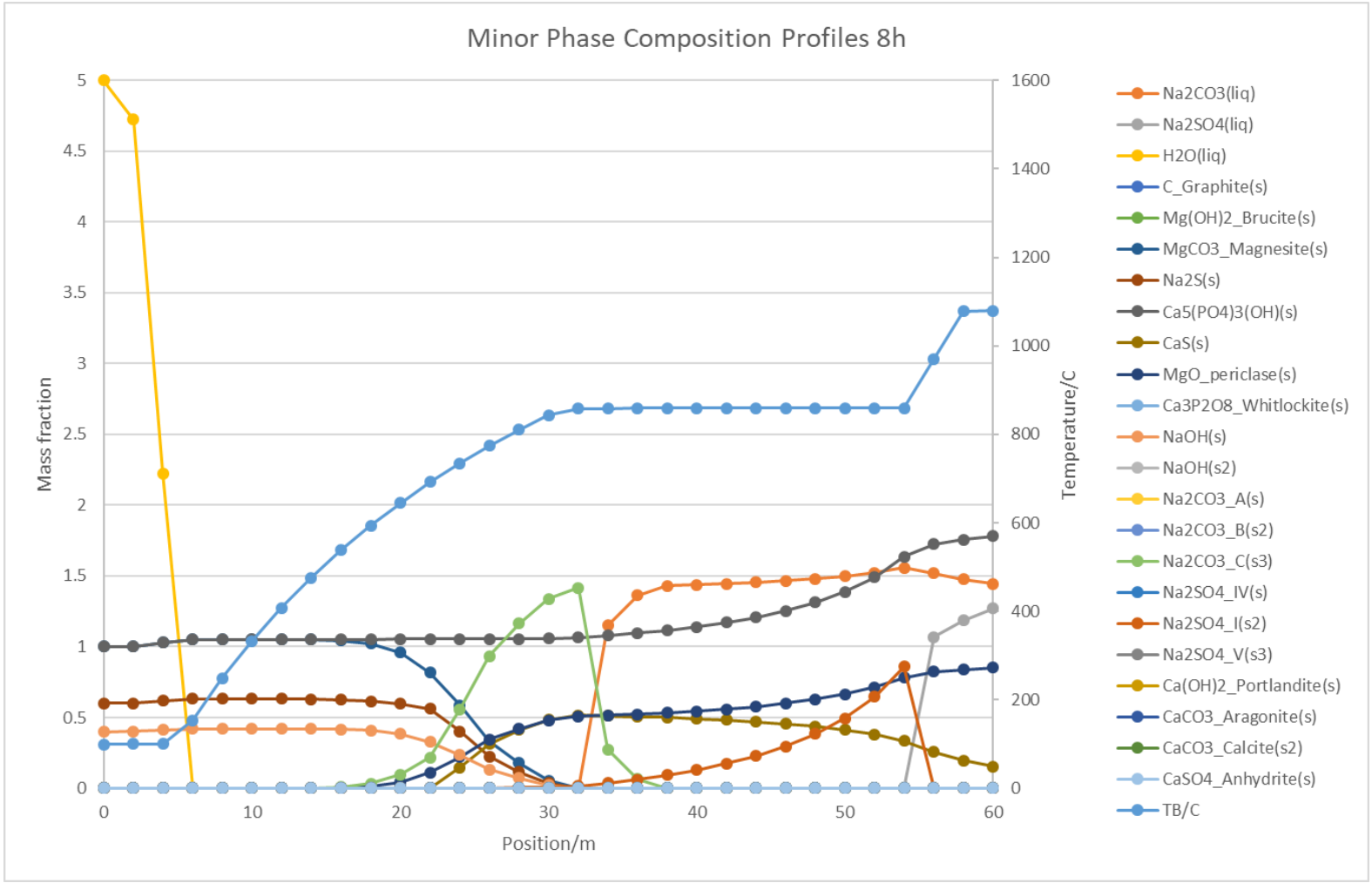
Process Parameters

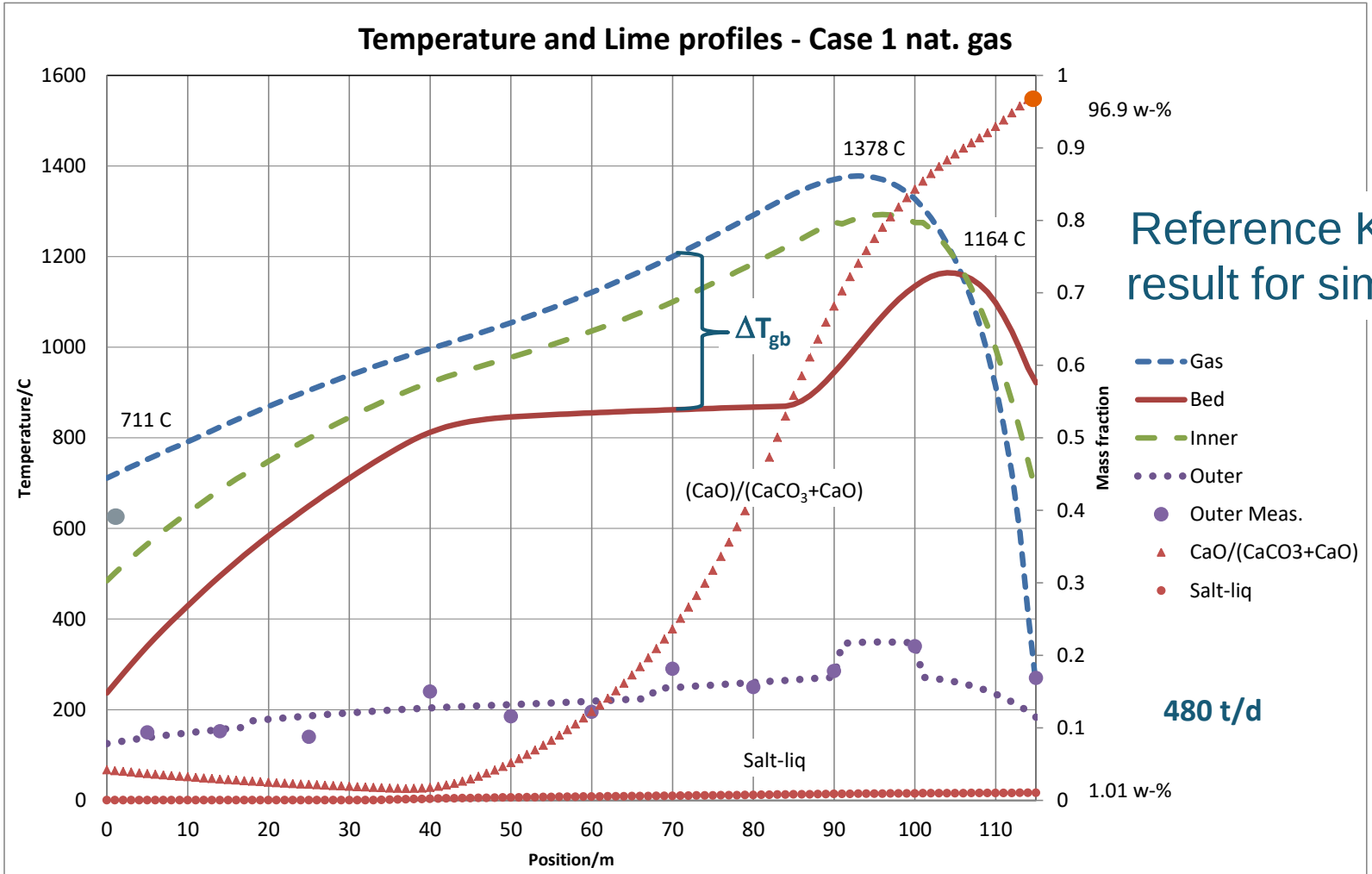
- Lime kiln: 60 meters in length, 4 meters in diameter (inner)
- Feed: $CaCO_3$ (92%) $MgCO_3$ (1%) $Ca_5(PO_4)_3(OH)$(s) (1%)
- Na_2S(s) (0.6%) NaOH(s) (0.4%) H_2O(l) (5 m-%)
- One particle with four size classes.
- Initially same composition inside kiln at 25 C (Bed&Wall)
- Main reactions (from equilibrium calculations):
- $CaCO_3$(s) -> CaO(s) + CO_2(g) MgCO3(s) -> MgO + CO_2(g)
- H_2O(l) -> H_2O(g)
- Simulation for 8 hours after process startup, time step ~150 seconds.
- Number of calculation nodes 31(for bed and gas sides).


Bed temperature as function of position [m] and time step number
1200
1000
800
600
400
200
0
Temperature/C
190
181
172
163
154
145
136
127
118
109
100
91
82
73
64
55
46
37
28
19
10
0
Time step number
0
6
12
18
24
30
36
42
48
54
60
Position/m
0-200
200-400
400-600
600-800
800-1000
1000-1200


Temperature Profiles at 8 h
Temperature/C
1800
1600
1400
1200
1000
800
600
400
200
0
0
10
20
30
40
50
60
Position/m
TB/C
TG/C
TI/C
TO/C


Phase Composition Profiles 8 h
Mass fraction
Temperature/C
Position/m
0
10
20
30
40
50
60
70
80
90
100
200
400
600
800
1000
1200
1400
1600
Na2CO3(liq)
Na2SO4(liq)
H2O(liq)
C_Graphite(s)
Mg(OH)2_Brucite(s)
MgCO3_Magnesite(s)
Na2S(s)
Ca5(PO4)3(OH)(s)
CaS(s)
MgO_periclase(s)
CaO_Lime(s)
Ca3P2O8_Whitlockite(s)
NaOH(s)
NaOH(s2)
Na2CO3_A(s)
Na2CO3_B(s2)
Na2CO3_C(s3)
Na2SO4_IV(s)
Na2SO4_I(s2)
Na2SO4_V(s3)
Ca(OH)2_Portlandite(s)
CaCO3_Aragonite(s)
CaCO3_Calcite(s2)
CaSO4_Anhydrite(s)
TB/C


Minor Phase Composition Profiles 8h
Mass fraction
Temperature/C
Position/m
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
0
200
400
600
800
1000
1200
1400
1600
0
10
20
30
40
50
60
Na2CO3(liq)
Na2SO4(liq)
H2O(liq)
C_Graphite(s)
Mg(OH)2_Brucite(s)
MgCO3_Magnesite(s)
Na2S(s)
Ca5(PO4)3(OH)(s)
CaS(s)
MgO_periclase(s)
Ca3P2O8_Whitlockite(s)
NaOH(s)
NaOH(s2)
Na2CO3_A(s)
Na2CO3_B(s2)
Na2CO3_C(s3)
Na2SO4_IV(s)
Na2SO4_I(s2)
Na2SO4_V(s3)
Ca(OH)2_Portlandite(s)
CaCO3_Aragonite(s)
CaCO3_Calcite(s2)
CaSO4_Anhydrite(s)
TB/C



Reference KilnSimu result for similar Kiln

480 t/d

Thank You
For Your Attention!