KilnSimu Introduction

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General

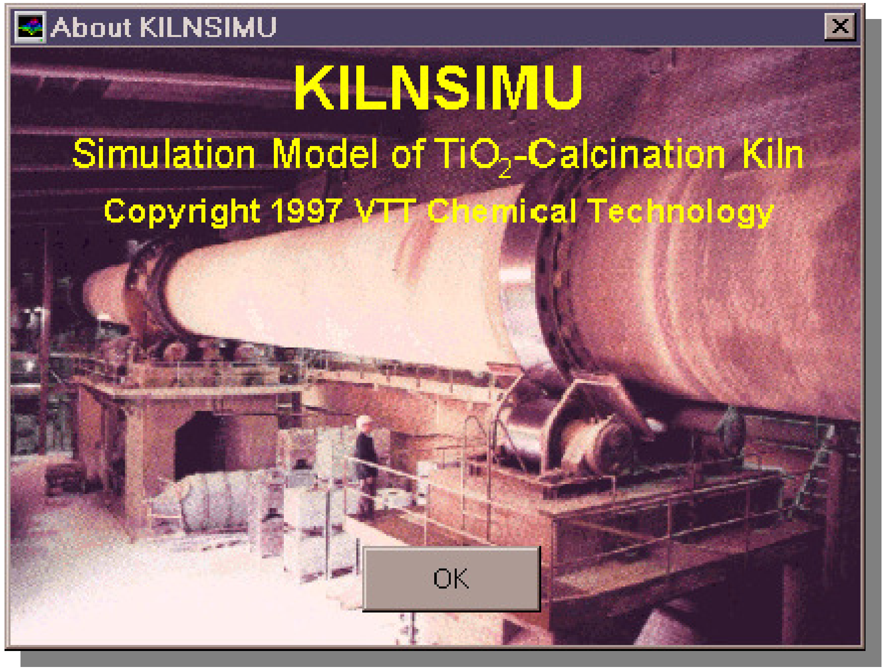
- Rotary kilns are common separator reactors in the mineral processing, metallurgical and chemical industries. The most known are pigment and cement manufacture, as well as the lime calciner in the recovery cycle of the chemicals in the pulp process.

- Most of the kilns operate in the counter-current fashion where the condensed raw material is fed into the kiln from the other end than the hot gas that is used to heat the material.

- There is increasing interest in the chemistry of the rotary kilns, as many of the raw materials as well as the fuels used as heat sources vary in their chemical composition.

Introduction

- •Simulation of multi-phase chemistry in counter-current or co-current rotary kilns.
- •Heating mechanism may be direct or indirect heating.
- •The chemical system is defined with ChemSage format thermodynamic data-file.



KILNSIMU

Simulation Model of TiO_2-Calcination Kiln

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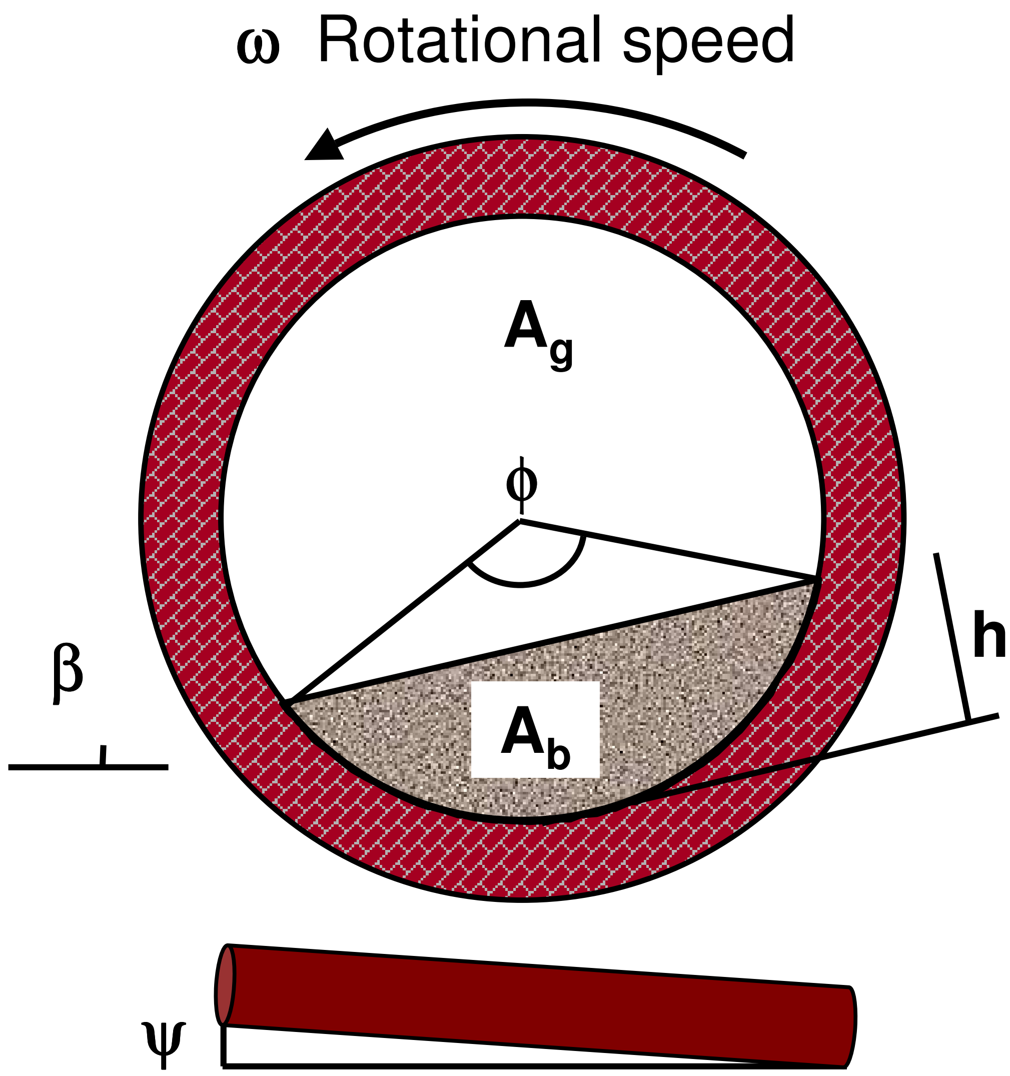
- •Uses ChemApp software to calculate the thermodynamic equilibrium of the chemical system.
- •Possibility to combine reaction kinetics with the thermodynamic calculation.
- •Uses Excel interface to define the simulation inputs and outputs.

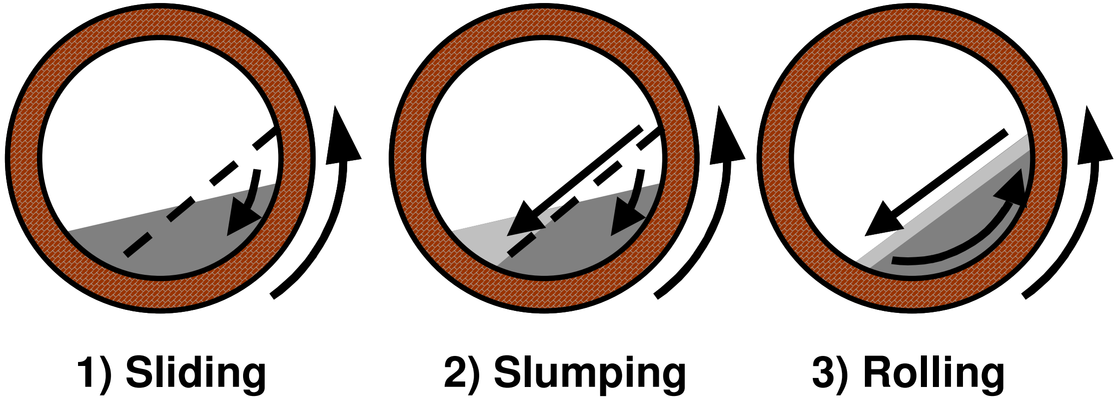
Material Bed



β	Angle of repose
ϕ	Filling angle
h	Bed height
A_b	Cross-sectional area covered by the bed
A_g	Cross-sectional area covered by the gas
ψ	Inclination of kiln

Bed Movement

There are three different radial movement types for the bed in industrial kilns (slower rotational speed):

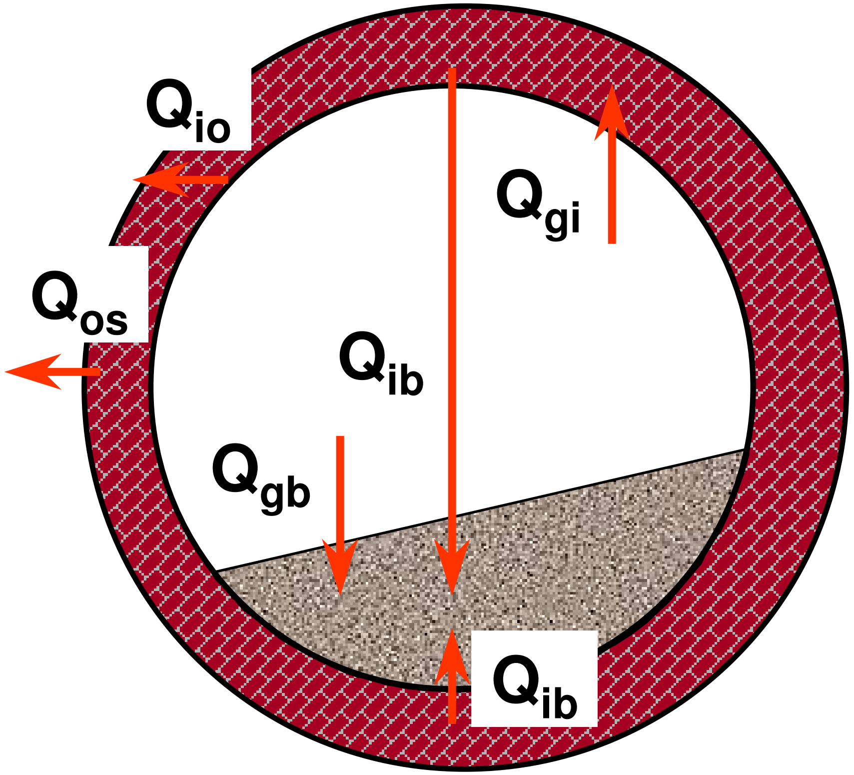


The type of the movement depends on the properties of the bed and the rotational speed of the kiln.

The bed velocity is proportional to inner diameter, rotational speed and inclination of the kiln and is inversely proportional to dynamic angle of repose of bed. In addition the bed velocity is inversely proportional to the height of the bed or the holdup of the kiln.

$$v_b = k\frac{D_i \cdot \omega \cdot f(\psi)}{f(\beta)}$$

Radial Heat Transfer



Q_{gb} Convection and radiation from gas to bed

Q_{gi} Convection and radiation from gas to inner wall

Q_{ib} Conduction and radiation from inner wall to bed

Q_{io} Conduction from inner wall to outer wall

Q_{os} Convection and radiation from outer wall to surroundings

Heat Transfer Mechanism

The heat transfer model contains **convection** heat transfer from gas to a surface. Surface may be the kiln wall or the surface of the bed. The convection is given as:

$$q = hA\left(T_g - T_s\right)$$

There is also **conduction** heat transfer from wall to bed surface that is in contact for certain time with the wall. The conduction heat transfer coefficient may be derived from *penetration* theory and is given as:

where λ_b is the heat conductivity of bed, ρ_b is the density of bed, c_b is the heat capacity of bed and t_c is the contact time between bed and wall (function of bed sliding).

Radiation model takes into accaunt the radiation between two gray surfaces (inner wall and bed) and gray gas.

The radiation between surfaces depends on the view factor between them. View factor is a function of geometry and emissivities of surfaces.

Emissivity of gas is calculated using combustion products like CO, CO_2, H_2O and for other polyatomic molecules like SO_2. Also small particles like soot and ash emit heat.

KilnSimu

The heat transfer from gas to bed is:

$$q_{gb} = h_{gb} A_{gb} \left(T_g - T_b\right) + \overline{GS_b}\,\sigma\left(T_g^4 - T_b^4\right)$$

The heat transfer from gas to inner wall is:

$$q_{gi} = h_{gi} A_{gi} \left(T_g - T_i\right) + \overline{GS_i}\,\sigma\left(T_g^4 - T_i^4\right)$$

The heat transfer from inner wall to bed is:

$$q_{ib} = h_{ib} A_{ib} \left(T_i - T_b\right) + \overline{S_i S_b}\,\sigma\left(T_i^4 - T_b^4\right)$$

The heat transfer from inner to outer wall and from outer wall to surroundings:

$$q_{io} = \frac{2\pi L\left(T_i - T_o\right)}{\sum_{j}^{n} \frac{1}{\lambda_j} \ln \frac{r_{j+1}}{r_j}} \qquad q_{os} = h_{os} A_{os} \left(T_o - T_s\right) + \overline{S_o S_s}\,\sigma\left(T_o^4 - T_s^4\right)$$

Where r is the radius, A is the heat transfer area, h is the heat transfer coefficient, T is the temperature, $\overline{GS}$ is the total exchange area between gas and surface, and $\overline{S_1 S_2}$ is the total exchange area between two surfaces (bed and wall).

Gibbs Energy

The thermodynamic state of a closed system can be defined with the Gibbs energy function:

$$G = G(T, P, n_1, \ldots, n_m)$$

In constant temperature and pressure the equilibrium state of the system is obtained by finding the minimum value of Gibbs energy:

$$G(T, P, n_1', \ldots, n_m') \leq G(T, P, n_1, \ldots, n_m)$$

The Gibbs energy of the system of phases is given as:

$$G = \sum_{\alpha} \sum_{j} n_j^{\alpha} \left(\mu_j^{\circ\alpha}(T) + RT \ln a_j^{\alpha} + RT \ln P \right)$$

Thermodynamic Properties

The chemical potential of *j*th phase constituent in temperature *T* is: given as:

$$\mu_j^\circ(T) = H_j^\circ(T) - TS_j^\circ(T)$$

The enthalpy and entropy of *j*th phase constituent in temperature *T* is given as:

$$H_j^\circ(T) = H_j^\circ(T_\circ) + \int_{T_\circ}^{T} C_{pj}(T)dT$$

$$S_j^\circ(T) = S_j^\circ(T_\circ) + \int_{T_\circ}^{T} \frac{C_{pj}(T)}{T} dT$$

The heat capacity of *j*th phase constituent in temperature *T* is given as:

$$C_{pj}(T) = C_{1j} + C_{2j}T + C_{3j}T^2 + \frac{C_{4j}}{T^2}$$

Stoichiometric Matrix

Phase constituents have compositions expressed as amounts of a number of components (which usually are elements). The mass balance constraints for the elements are thus given as:

$\sum_{j=1}^{m} a_{ij} n_j = b_i \qquad i = 1,...,l$ or in matrix form:

$$\begin{bmatrix} a_{11} & a_{12} & \cdots & a_{1m} \\ a_{21} & a_{22} & \cdots & a_{2m} \\ \vdots & \vdots & \ddots & \vdots \\ a_{l1} & a_{l2} & \cdots & a_{lm} \end{bmatrix} \begin{bmatrix} n_1 \\ n_2 \\ \vdots \\ n_m \end{bmatrix} = \begin{bmatrix} b_1 \\ b_2 \\ \vdots \\ b_l \end{bmatrix}$$

where a_{ij} is the amount of component i in constituent j.

Example System

Phase	Constituent	N	O	H	C	S	Ti
Gas	N_2	2	0	0	0	0	0
	O_2	0	2	0	0	0	0
	H_2O	0	1	2	0	0	0
	C_3H_8	0	0	8	3	0	0
	CO	0	1	0	1	0	0
	CO_2	0	2	0	1	0	0
	SO_2	0	2	0	0	1	0
	SO_3	0	3	0	0	1	0
	H_2SO_4	0	4	2	0	1	0
H_2O	H_2O	0	1	2	0	0	0
H_2SO_4	H_2SO_4	0	4	2	0	1	0
$TiO_2(A)$	$TiO_2(A)$	0	2	0	0	0	1
$TiO(OH)_2$	$TiO(OH)_2$	0	3	2	0	0	1
$TiOSO_4$	$TiOSO_4$	0	5	0	0	1	1
$TiO_2(R)$	$TiO_2(R)$	0	2	0	0	0	1

Thermodynamic system of TiO_2-calcination and its stoichiometric matrix. TiO_2-system contains one mixture phase (the gas phase) and six condensed phases.

Reaction Zones

Schematically the rotary kiln can be divided into three zones according to reactions in the bed:

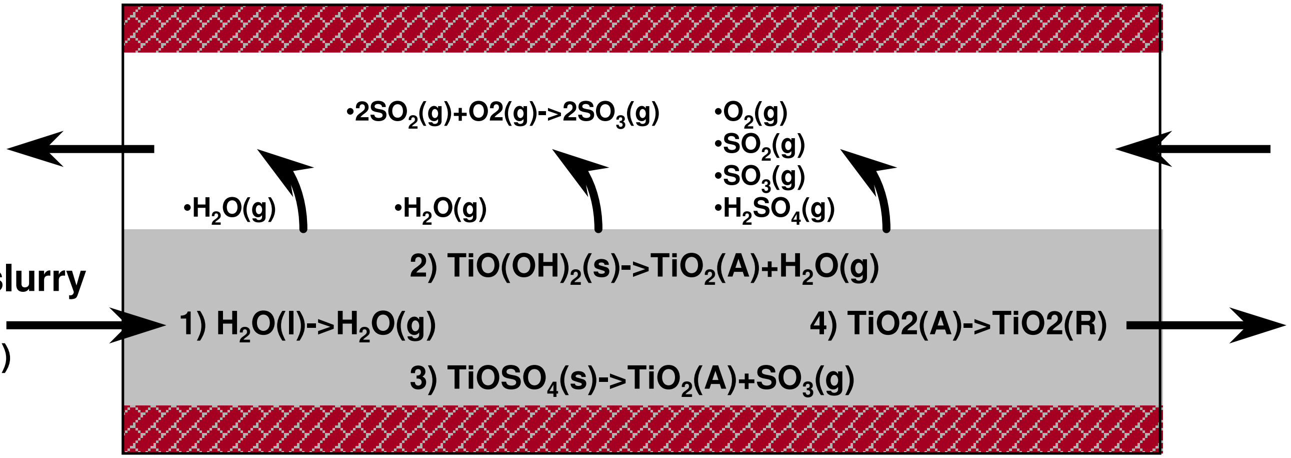
- Drying zone
- Heating zone
- Reaction zone

If there is moisture in the bed then it is removed in the drying zone. While drying the temperature of bed stays close to 100 degrees celsius or increases slowly as the heat is used to vaporize the water.

After all the water has been removed the temperature of the bed increases quickly until it reaches the reaction temperature.

Kiln may contain several reaction zones depending on the thermodynamic characteristics of the bed.

Reaction Zones in TiO_2-Calcination



Exit gas
- $N_2(g)$
- $O_2(g)$
- $H_2O(g)$
- $CO_2(g)$
- $CO (g)$
- $SO_2(g)$

Titanium slurry
- $H_2O(l)$
- $TiO(OH)_2(s)$
- $TiOSO_4(s)$

- $H_2O(g)$
- $H_2O(g)$
- $2SO_2(g)+O2(g)\rightarrow 2SO_3(g)$
- $O_2(g)$
- $SO_2(g)$
- $SO_3(g)$
- $H_2SO_4(g)$

2) $TiO(OH)_2(s)\rightarrow TiO_2(A)+H_2O(g)$

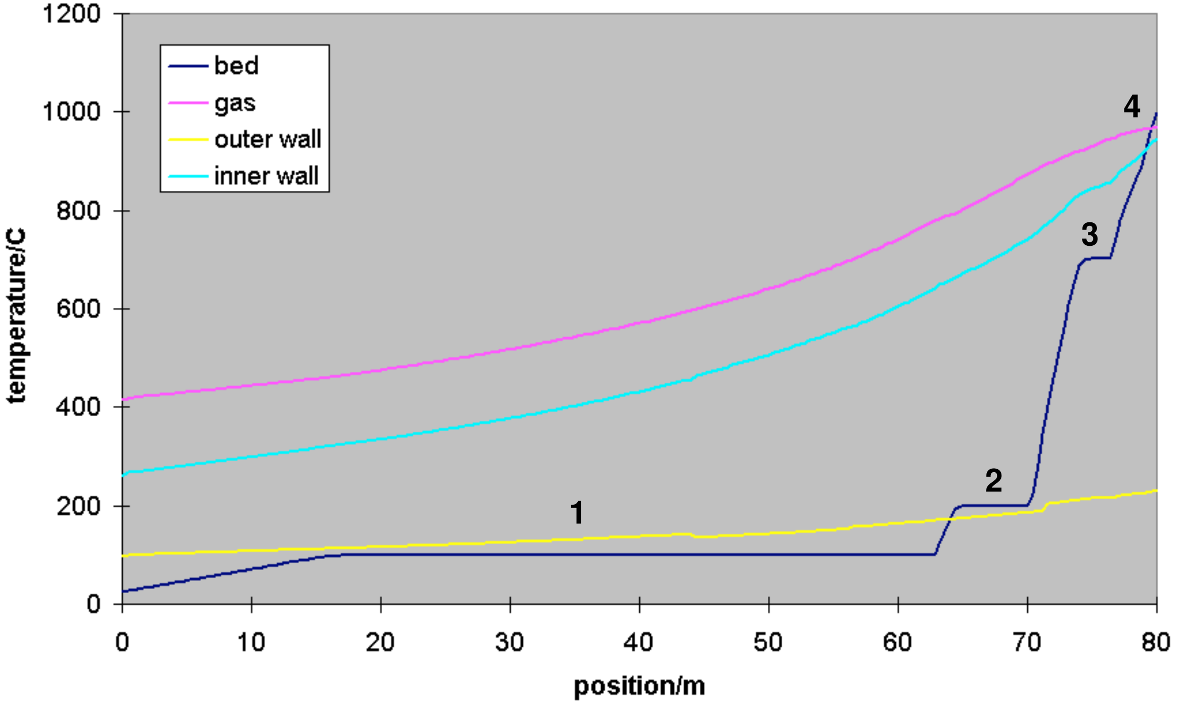
1) $H_2O(l)\rightarrow H_2O(g)$

4) $TiO2(A)\rightarrow TiO2(R)$

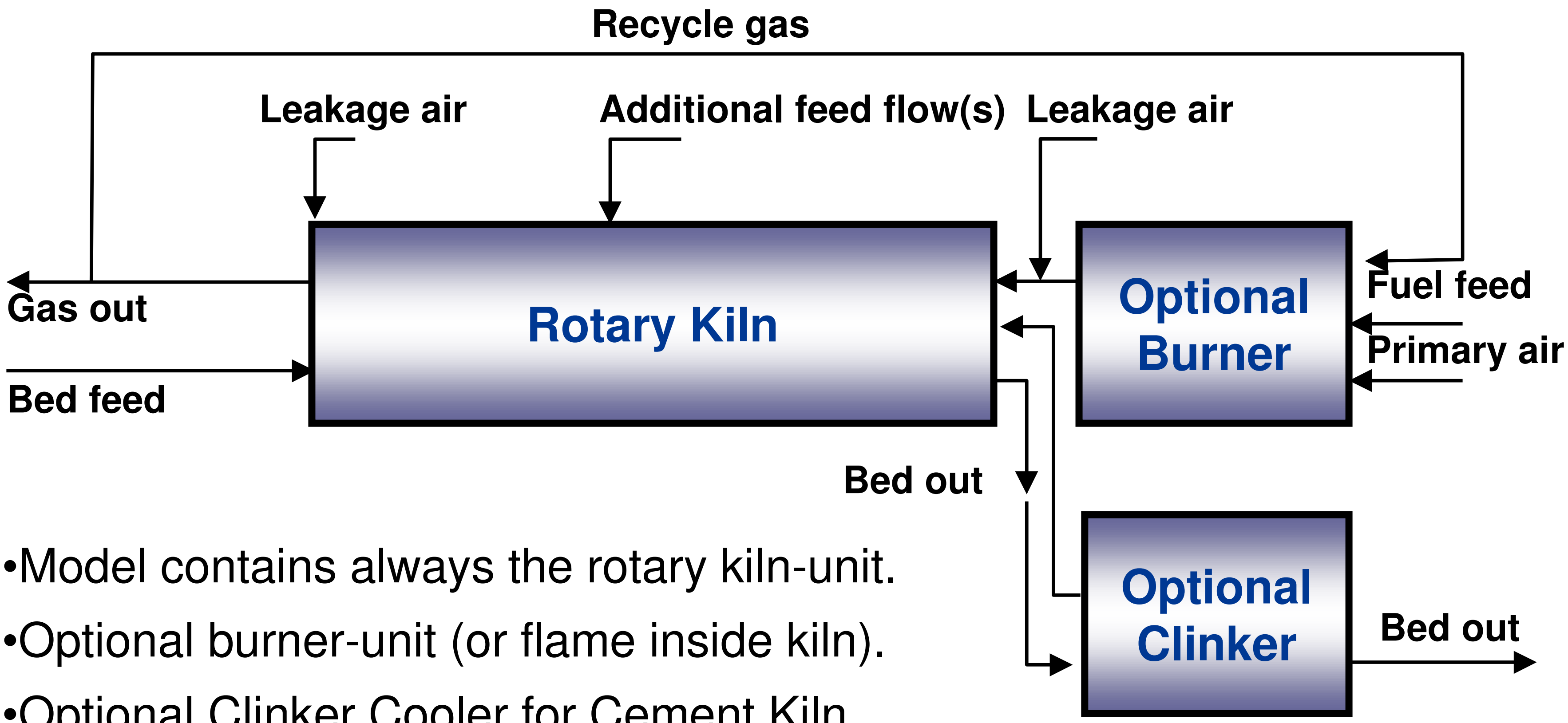
3) $TiOSO_4(s)\rightarrow TiO_2(A)+SO_3(g)$

Burner gas (+recycle)
- $N_2(g)$
- $O_2(g)$
- $H_2O(g)$
- $CO_2(g)$
- $CO (g)$
- $SO_2(g$

Pigment product
- TiO_2(Rutile)
- TiO_2(Anatase)

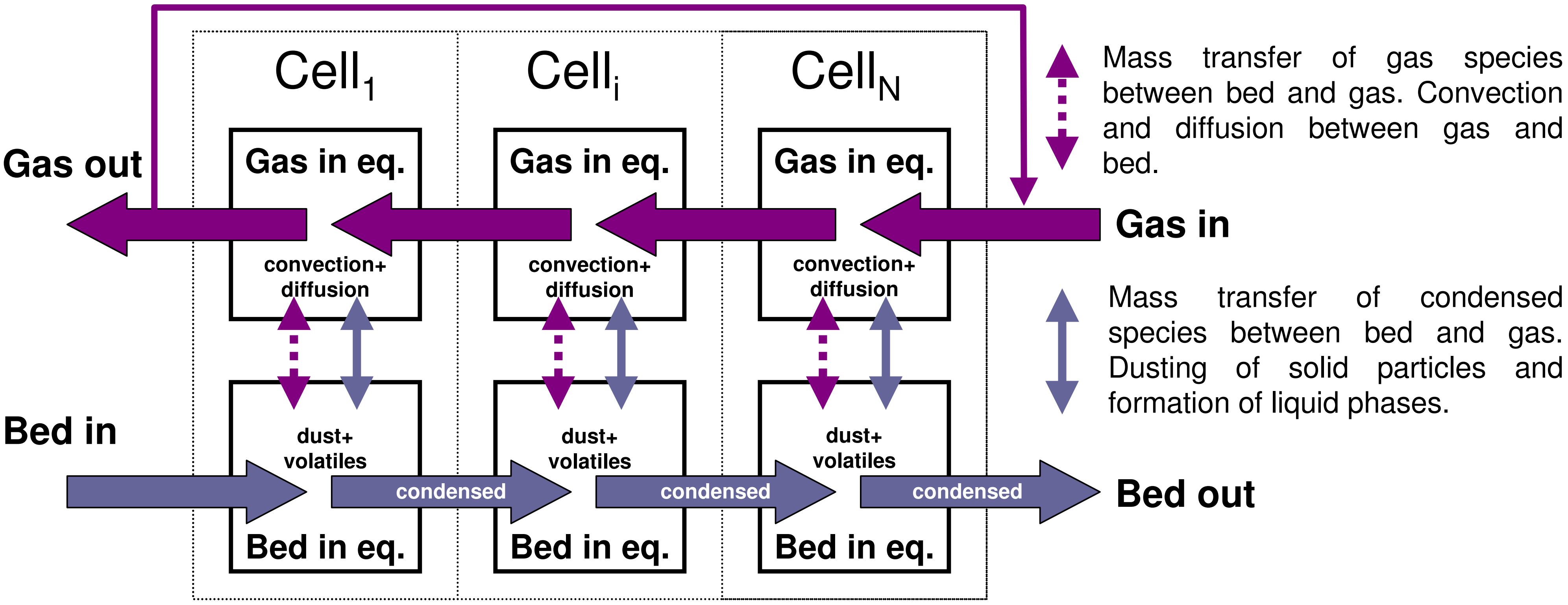


Kiln Flowsheet



- Model contains always the rotary kiln-unit.
- Optional burner-unit (or flame inside kiln).
- Optional Clinker Cooler for Cement Kiln.
- Units may contain any number of feed flows.
- Feed flows may contain any number of gaseous and condensed species.
- Optional gas recycle back to burner or rotary kiln.

Rotary Kiln Model



Mass transfer of gas species between bed and gas. Convection and diffusion between gas and bed.

Mass transfer of condensed species between bed and gas. Dusting of solid particles and formation of liquid phases.

Rotary Kiln

- Axial plug flow model is used for both the bed and the gas in each cell.
- The variables in each cell are the temperature of bed, gas, inner and outer wall and the mass flows of species in bed and gas.
- The bed and gas output from each cell is in thermodynamic equilibrium but they may contain non-reactive parts that are calculated with kinetics.

Kinetic Restrictions

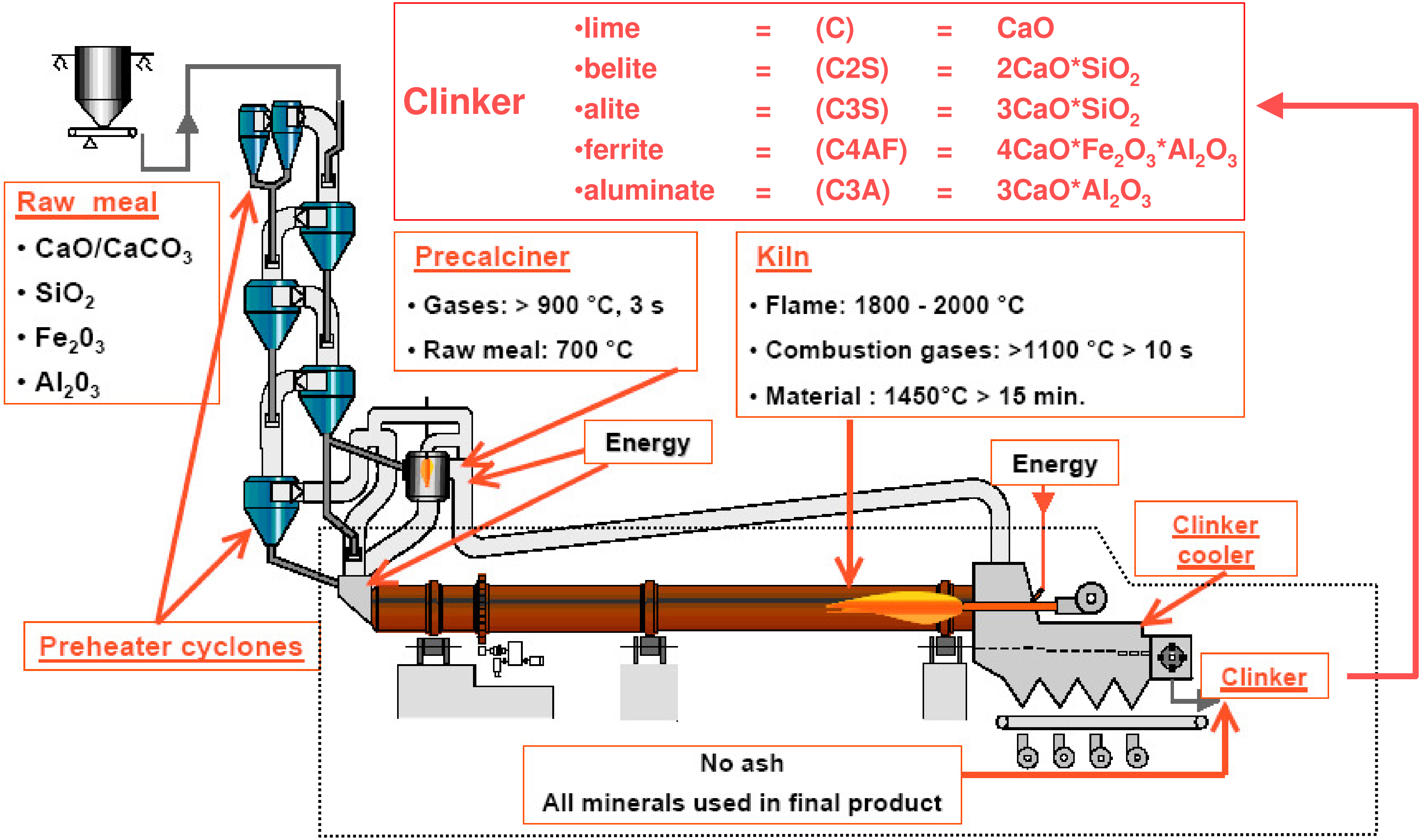
- Kinetic restrictions can be defined for each phase with Arrhenius type first order reaction rate:

$$\frac{dm}{dt} = km = A_0 e^{-E_a/RT} m$$

A_0	frequency factor of Arrhenius equation, () 1/s
E_a	activation energy of Arrhenius equation, () J/mol
T	temperature of bed or gas, () K
m	mass, () kg

- Kinetic restrictions give the reactive and inert parts of phases in bed and gas flows. Thermodynamic equilibrium is calculated between phases in reactive parts and inert parts are considered only in energy balances:

Cement System (Preheater+Kiln+Cooler)



Clinker

- lime = (C) = CaO
- belite = (C2S) = $2CaO*SiO_2$
- alite = (C3S) = $3CaO*SiO_2$
- ferrite = (C4AF) = $4CaO*Fe_2O_3*Al_2O_3$
- aluminate = (C3A) = $3CaO*Al_2O_3$

Raw meal

- $CaO/CaCO_3$
- SiO_2
- Fe_2O_3
- Al_2O_3

Precalciner

- Gases: > 900 °C, 3 s
- Raw meal: 700 °C

Kiln

- Flame: 1800 - 2000 °C
- Combustion gases: >1100 °C > 10 s
- Material : 1450°C > 15 min.

Energy

Energy

Clinker cooler

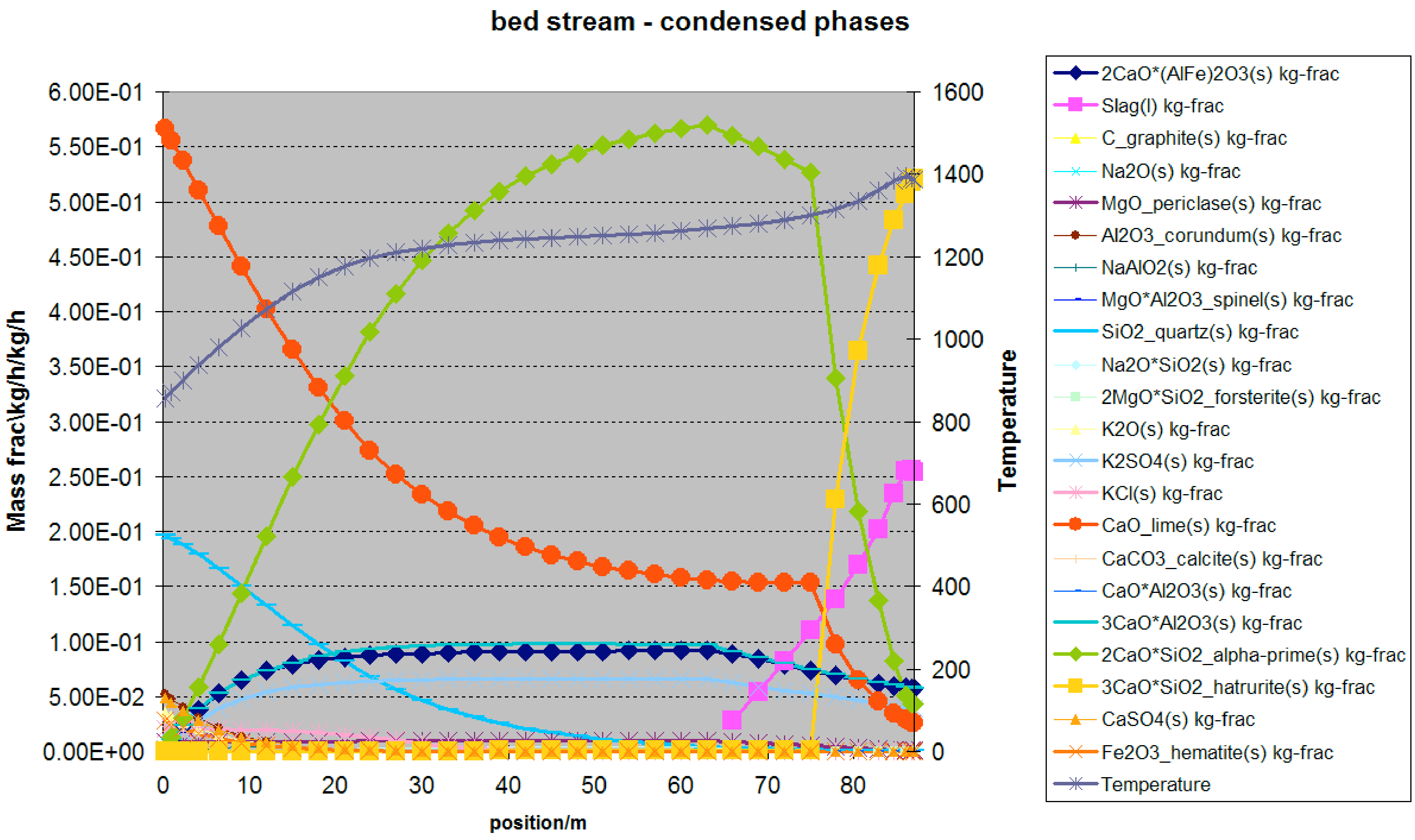
Clinker

Preheater cyclones

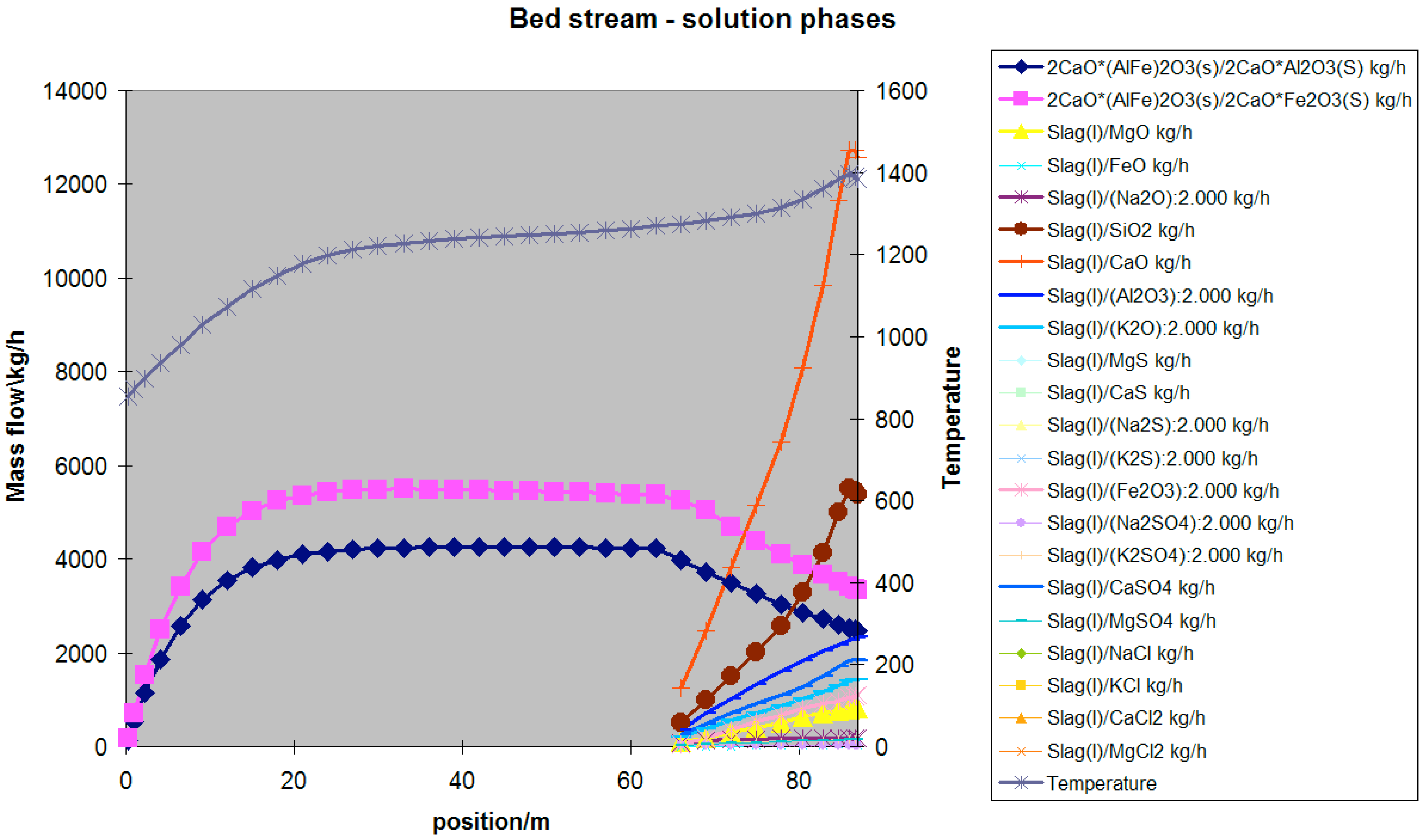
No ash

All minerals used in final product

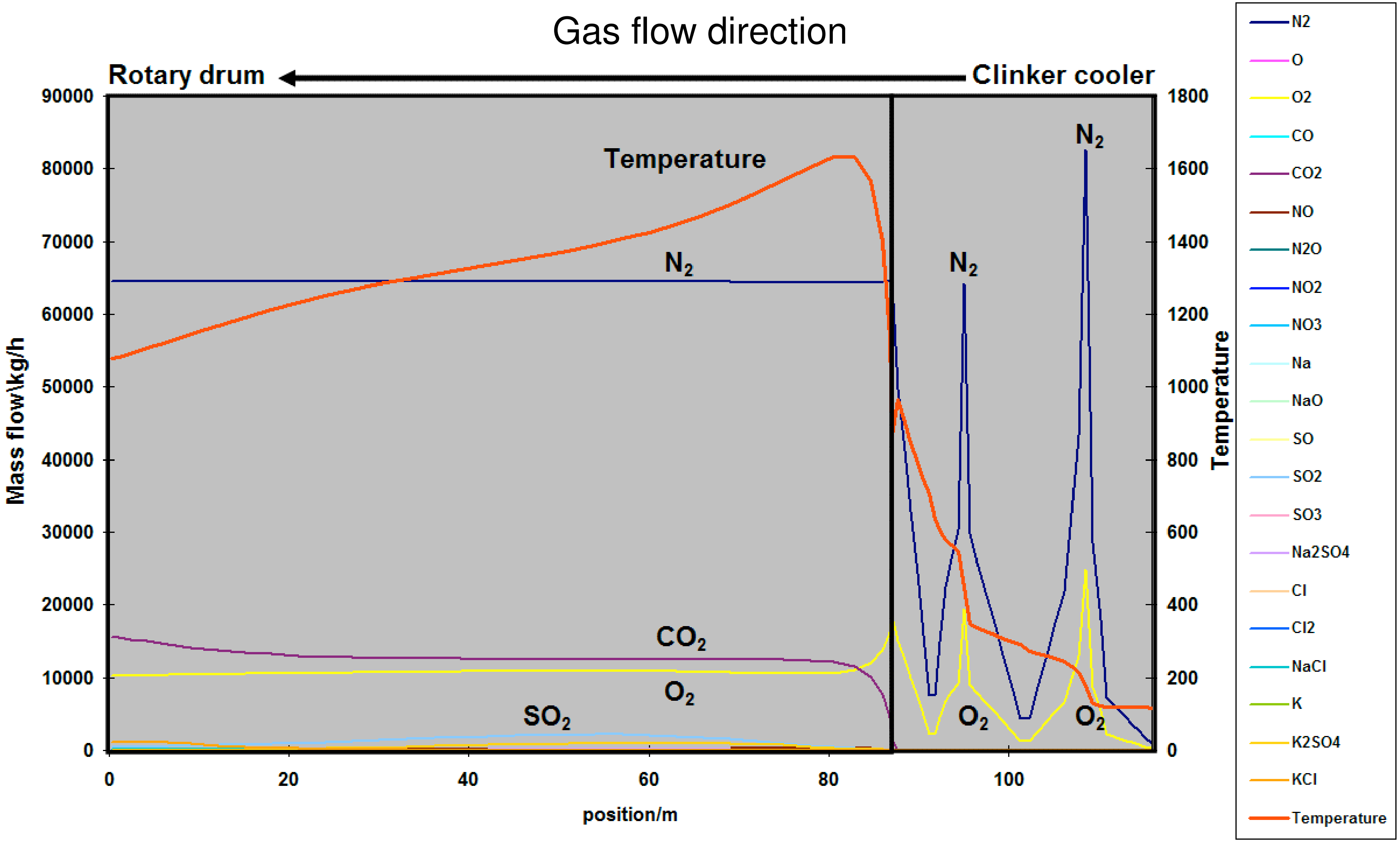
Bed Composition in Rotary Kiln



Composition of Solution Phases



Gas Flow from Clinker Cooler to Rotary Kiln



Gas to rotary kiln is preheated in clinker cooler.

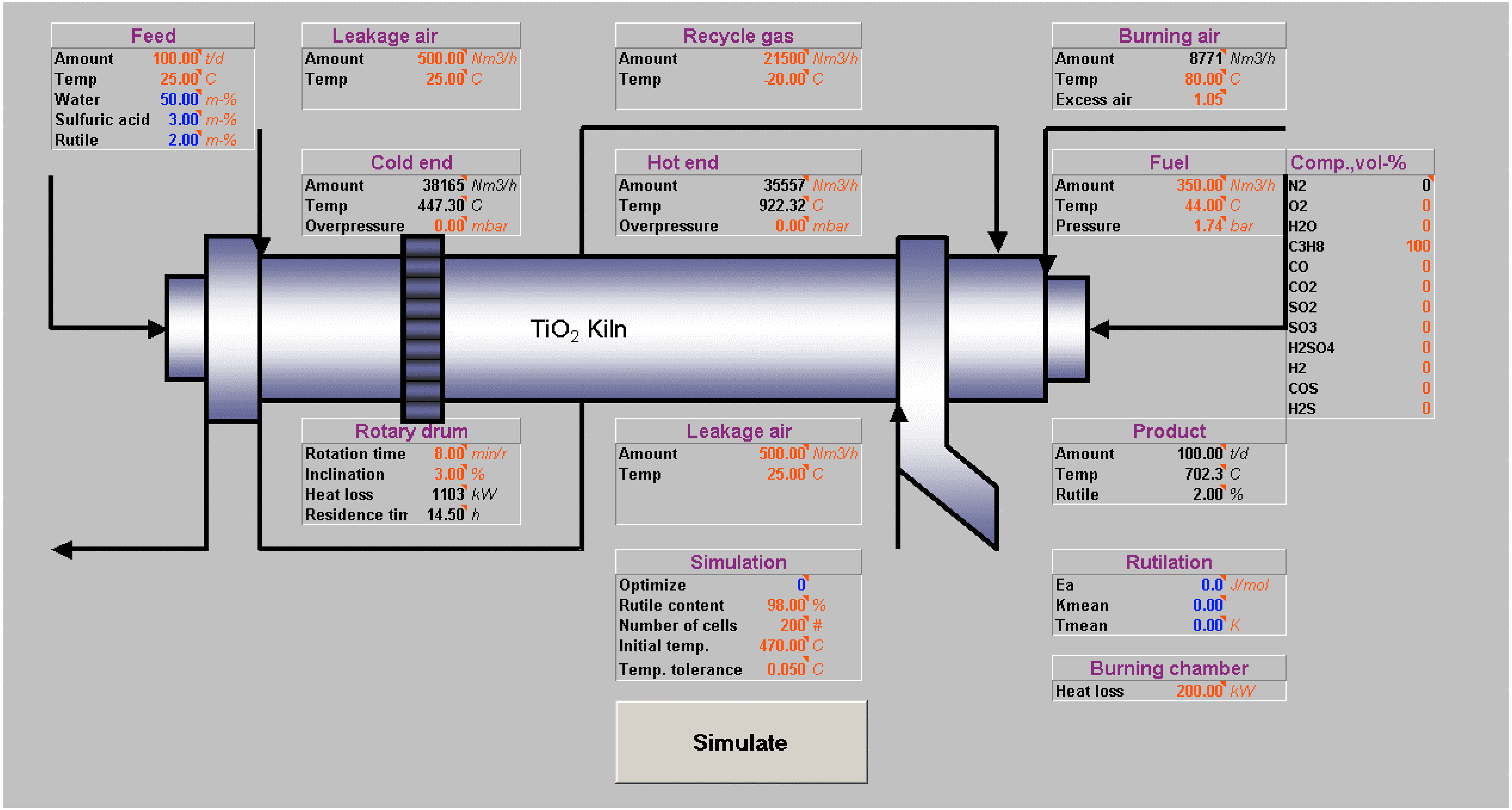
Model Inputs

- Rotary kiln parameters:
  - rotational speed
  - inclination
- Material bed properties:
  - static and dynamic angle of repose
  - density
  - emissivity
  - conductivity
- Geometry of rotary kiln. Geometry data may contain one ore more wall sections and each section contains:
  - length
  - outer diameter of wall
  - steel layer and one or more refractory layers of given thickness and conductivity
- Feed flow parameters :
  - temperature and pressure
  - amounts of one or more feed species
- Simulation parameters:
  - number of iterations
  - convergence criterion
- Kinetic parameters:
  - Reaction rate coefficients for each phase in material bed and gas.
    - frequency factor
    - activation energy
    - particle diameter
- Dusting parameters:
  - dusting coefficient for each condensed phase
- ChemSage data-file containing the definitions and thermodynamic properties of system phases and phase constituents.
- Physical properties of the gas phase:
  - conductivity parameters
  - viscosity paramaters

Model Outputs

- The thermodynamic model provides a great amount of numerical data for the user. In principle, from the Gibbs energy functions, all extensive and intensive (locally measurable) thermochemical quantities can be calculated.
- The axial variable profiles for which Excel charts are generated include:
  - wall geometry
  - temperatures
  - heat flows
  - convection coefficients
  - residence time
  - gas velocity
  - condensed phases in material bed
  - composition of solution phases in material bed
  - vaporized gaseous species in material bed
  - gaseous species in gas
  - condensed phases in gas

Example of Customer "Tailored" Interface



Feed

Amount	100.00	t/d
Temp	25.00	C
Water	50.00	m-%
Sulfuric acid	3.00	m-%
Rutile	2.00	m-%

Leakage air

Amount	500.00	Nm3/h
Temp	25.00	C

Recycle gas

Amount	21500	Nm3/h
Temp	-20.00	C

Burning air

Amount	8771	Nm3/h
Temp	80.00	C
Excess air	1.05	

Cold end

Amount	38165	Nm3/h
Temp	447.30	C
Overpressure	0.00	mbar

Hot end

Amount	35557	Nm3/h
Temp	922.32	C
Overpressure	0.00	mbar

Fuel

Amount	350.00	Nm3/h
Temp	44.00	C
Pressure	1.74	bar

Comp.,vol-%

N2	0
O2	0
H2O	0
C3H8	100
CO	0
CO2	0
SO2	0
SO3	0
H2SO4	0
H2	0
COS	0
H2S	0

Rotary drum

Rotation time	8.00	min/r
Inclination	3.00	%
Heat loss	1103	kW
Residence tir	14.50	h

Leakage air

Amount	500.00	Nm3/h
Temp	25.00	C

Product

Amount	100.00	t/d
Temp	702.3	C
Rutile	2.00	%

Simulation

Optimize	0	
Rutile content	98.00	%
Number of cells	200	#
Initial temp.	470.00	C
Temp. tolerance	0.050	C

Rutilation

Ea	0.0	J/mol
Kmean	0.00	
Tmean	0.00	K

Burning chamber

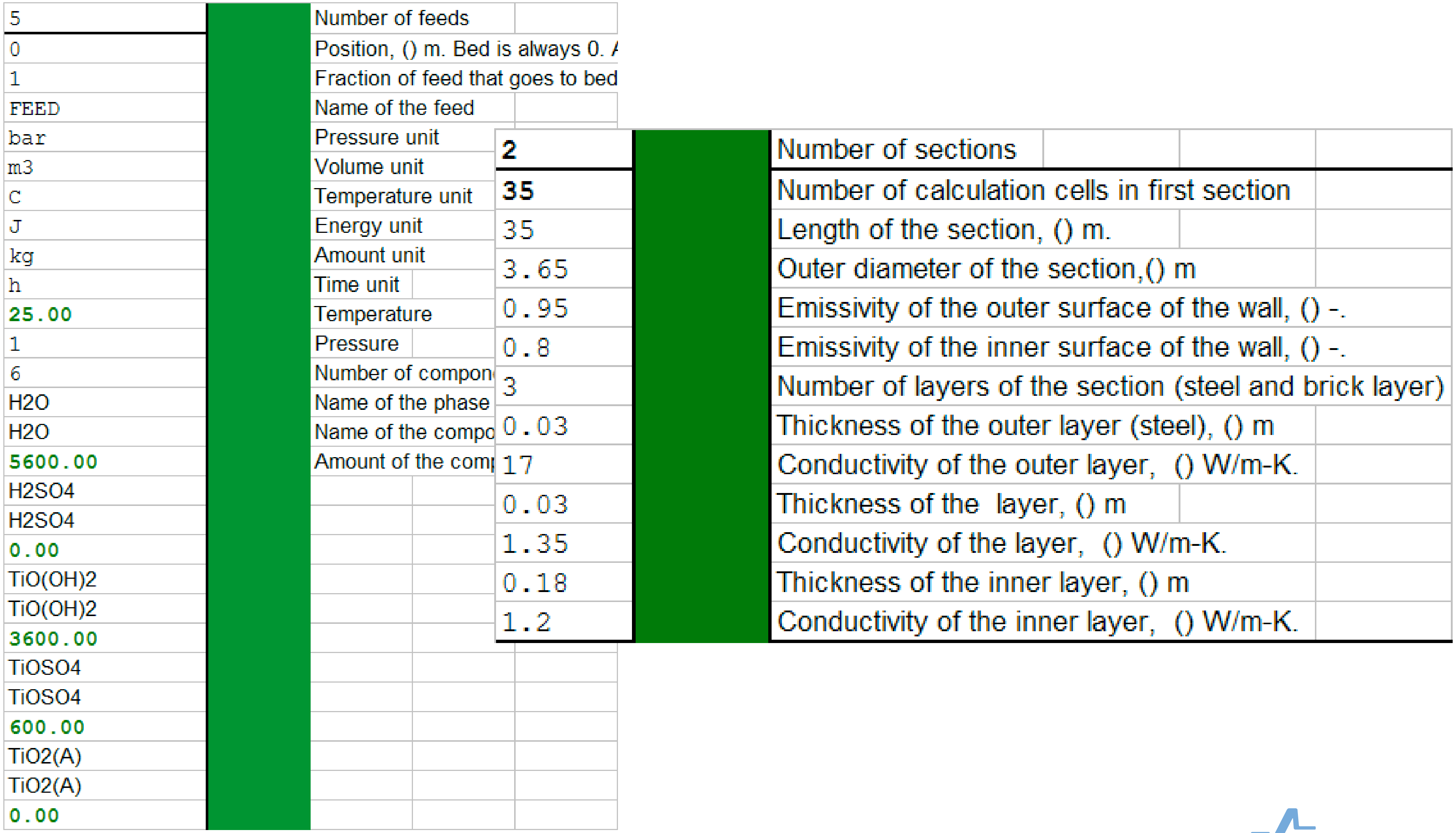
Heat loss	200.00	kW

General Interface

Excel workbook that contains following worksheets:

- FeedDat-sheet – feed flow parameters.
- KilnDat-sheet – general kiln and simulation parameters.
- WallDat-sheet – kiln geometry parameters.
- RateDat-sheet – phase status and reaction rate parameters.

Examples of FeedDat and WallDat



5	Number of feeds
0	Position, () m. Bed is always 0.
1	Fraction of feed that goes to bed
FEED	Name of the feed
bar	Pressure unit
m3	Volume unit
C	Temperature unit
J	Energy unit
kg	Amount unit
h	Time unit
25.00	Temperature
1	Pressure
6	Number of compon
H2O	Name of the phase
H2O	Name of the compo
5600.00	Amount of the comp
H2SO4	
H2SO4	
0.00	
TiO(OH)2	
TiO(OH)2	
3600.00	
TiOSO4	
TiOSO4	
600.00	
TiO2(A)	
TiO2(A)	
0.00	

2	Number of sections
35	Number of calculation cells in first section
35	Length of the section, () m.
3.65	Outer diameter of the section,() m
0.95	Emissivity of the outer surface of the wall, () -.
0.8	Emissivity of the inner surface of the wall, () -.
3	Number of layers of the section (steel and brick layer)
0.03	Thickness of the outer layer (steel), () m
17	Conductivity of the outer layer, () W/m-K.
0.03	Thickness of the layer, () m
1.35	Conductivity of the layer, () W/m-K.
0.18	Thickness of the inner layer, () m
1.2	Conductivity of the inner layer, () W/m-K.

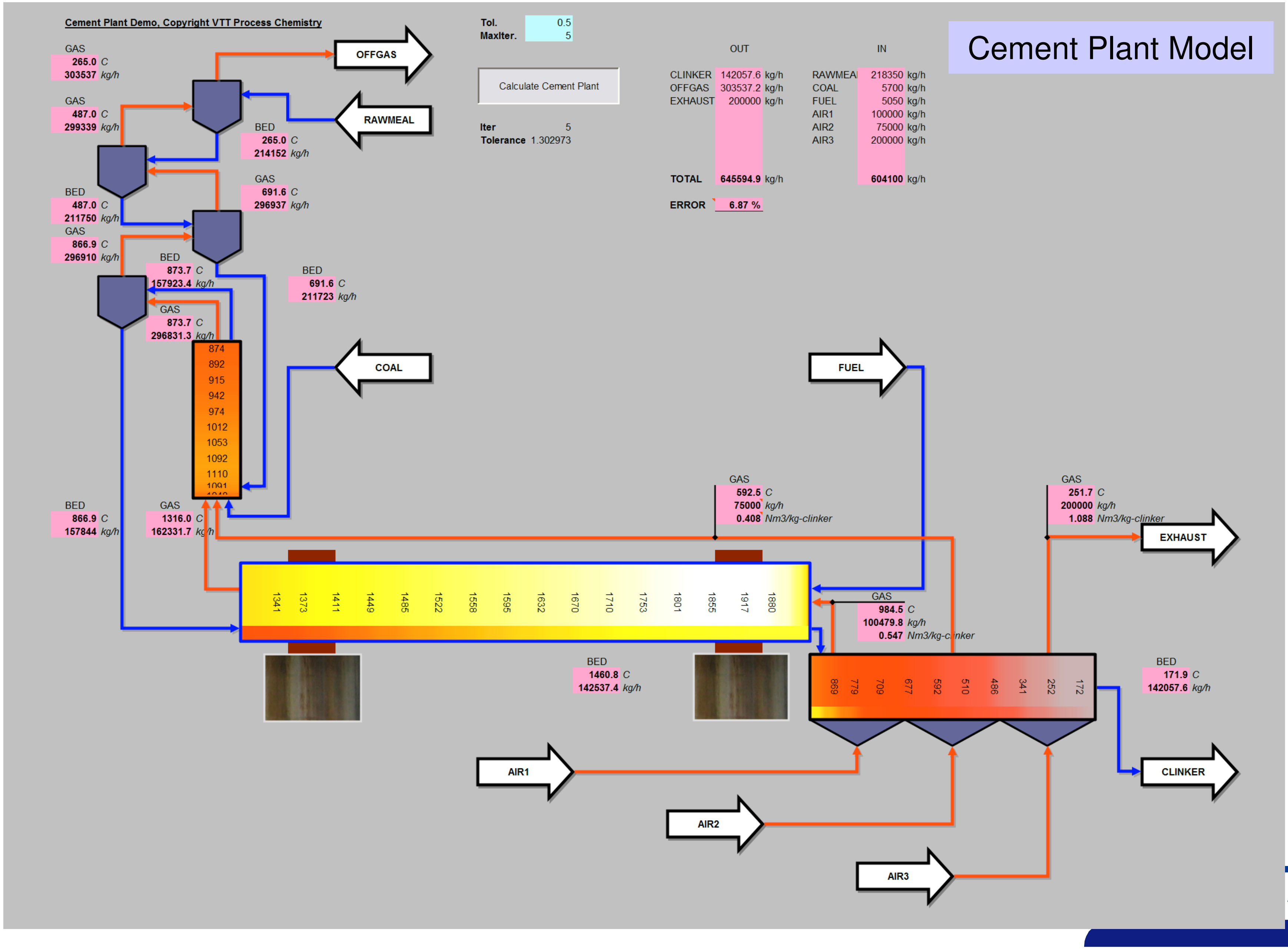
Use of Kilnsimu

- Demand of combustion air
- Study of various fuels
- Optimization of fuel consumption
- Optimization of gas circulation
- Optimization of energy efficiency
- Phase formation studies (material bed and gas composition)
- Exit bed composition
- Exit gas composition
- Kiln scale-up

Use of Kilnsimu

- Calcination of TiO2 (production of pigment)
- Calcination of $CaCO_3$ (lime kiln in pulp industry)
- Cement production
- Reduction of ores (ilmenite)
- Zinc oxide fuming (Waelz kiln in zinc production)
- Industrial Waste incineration
- Carburization of organic waste

Current Development – New Excel Based Simulation Tool



Cement Plant Demo, Copyright VTT Process Chemistry

Cement Plant Model

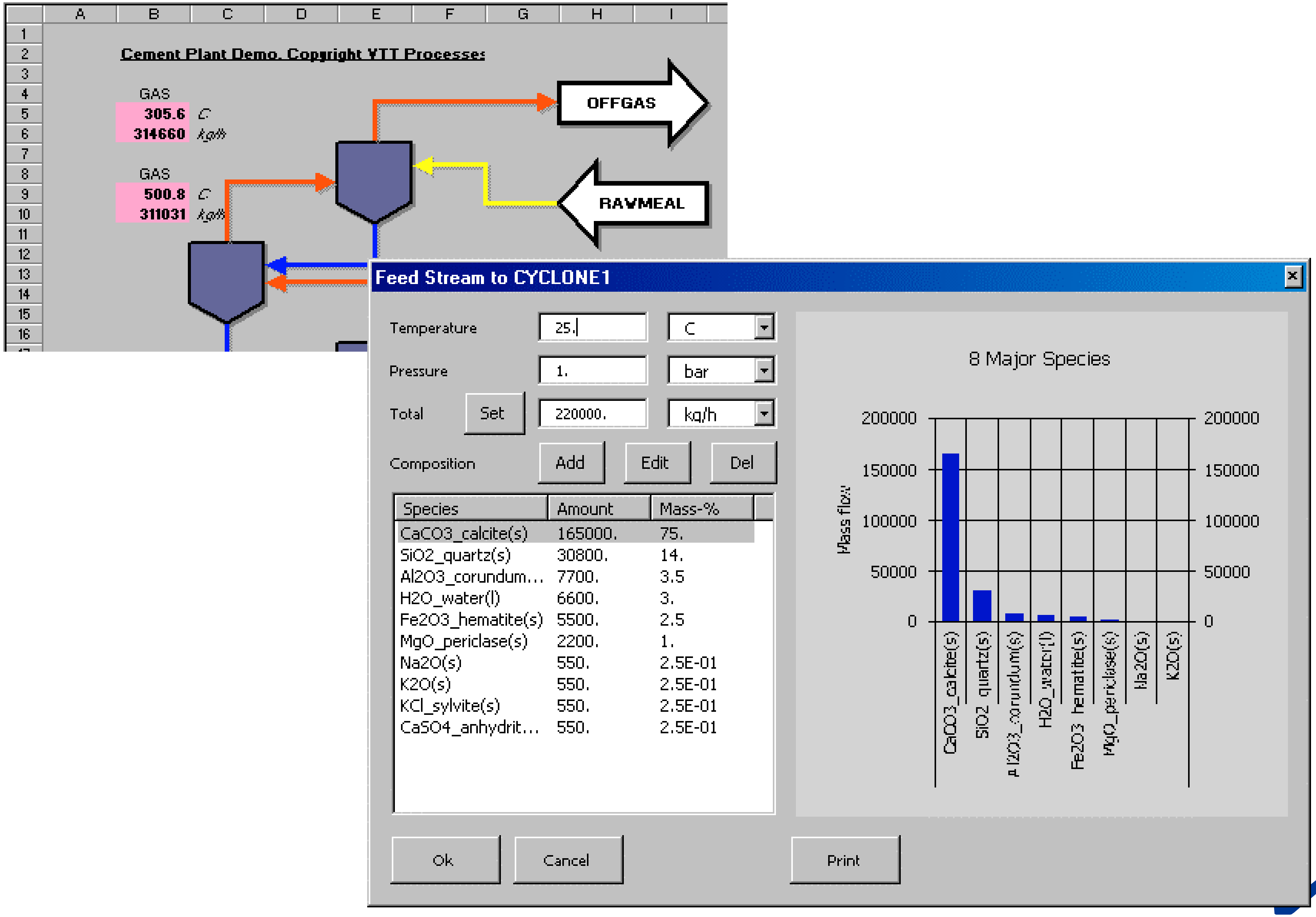
Tol. 0.5
MaxIter. 5

Calculate Cement Plant

Iter 5
Tolerance 1.302973

OUT			IN		
CLINKER	142057.6	kg/h	RAWMEAL	218350	kg/h
OFFGAS	303537.2	kg/h	COAL	5700	kg/h
EXHAUST	200000	kg/h	FUEL	5050	kg/h
			AIR1	100000	kg/h
			AIR2	75000	kg/h
			AIR3	200000	kg/h
TOTAL	**645594.9**	kg/h		**604100**	kg/h
ERROR	**6.87 %**				

Current Development



Cement Plant Demo. Copyright VTT Processes

GAS
305.6 C
314660 kg/h

GAS
500.8 C
311031 kg/h

Feed Stream to CYCLONE1

Temperature: 25. C
Pressure: 1. bar
Total: 220000. kg/h

Composition

Species	Amount	Mass-%
CaCO3_calcite(s)	165000.	75.
SiO2_quartz(s)	30800.	14.
Al2O3_corundum…	7700.	3.5
H2O_water(l)	6600.	3.
Fe2O3_hematite(s)	5500.	2.5
MgO_periclase(s)	2200.	1.
Na2O(s)	550.	2.5E-01
K2O(s)	550.	2.5E-01
KCl_sylvite(s)	550.	2.5E-01
CaSO4_anhydrit…	550.	2.5E-01