A decorative geometric pattern covers the left half of the slide. It features a repeating arrangement of hexagons and rhombuses in shades of orange, light orange, and blue, creating a complex, crystalline structure.

# Dynamic Simulation of a Recausticizing Plant

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# Contents

- Background & Introduction
- Dynamic Simulation Tools & Node Structure
- Kinetics & Equilibrium
- Simulation Interface & Building Flowsheet
- Kraft Recausticizing Process



- 1996-2023
  - KilnSimu - Steady-State simulation model of a rotary kiln.
- 2018-2020
  - Dynamic Model for the Lime Kiln in the Chemical Kraft Recovery developed in DeepCleanTech-project (funded by Business Finland).
- 2021-2023 (Ongoing)
  - Development of dynamic tools in CEIWA-project (funded by Business Finland),
  - and in AI-Proficient-project (funded by EU Horizon 2020).

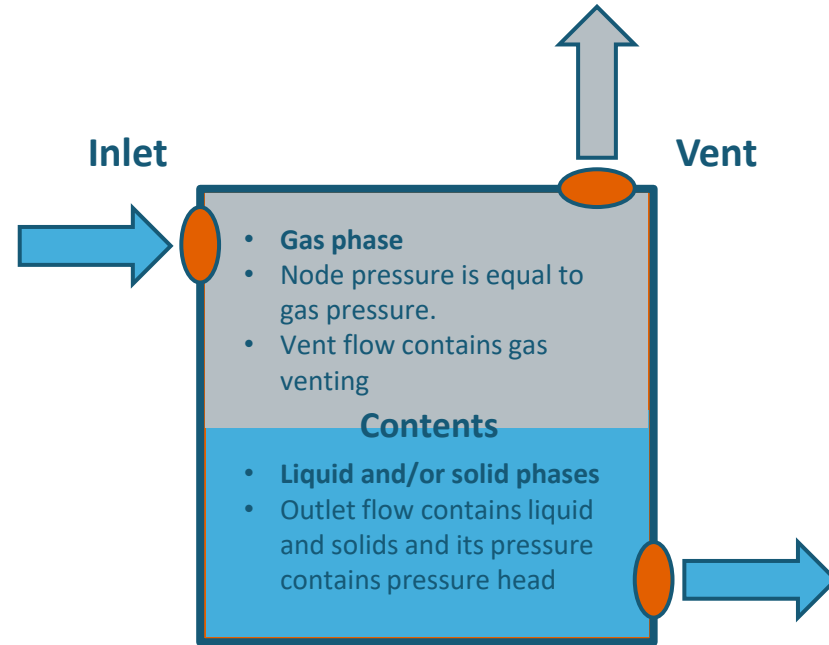
- Part of CEIWA (Circular Economy of water in industrial processes) Task 2.1
- **Task aim:** To develop tool with dynamic unit operation models for aqueous and HT processes that support equilibrium calculation, reaction kinetics and particle dynamics, a tool that could be used as a Digital Twin.
- **Target application:** Recausticizing process in the kraft pulp mill. The Kraft recausticizing process produces cooking liquor for the digester from recycled inorganic chemicals generated in the recovery boiler and the lime kiln.
- **Interest:** The behaviour of non-process elements in process.

- Dynamic simulation of chemical processes in aqueous and high temperature systems.
- Originally developed for **Submerged Arc Furnace** process in the ferro-**ChROM**ium production (working title **CROM**).
- Collection of dynamic process (Unit Operation) models.
- Sequential modular solver (handling of large number of species).
- Flowsheet tearing & partitioning & sequencing.
- Equilibrium & Kinetics & Particles.
- Uses ChemApp with compatible thermodynamic databases for calculation of equilibrium composition (reactions) and enthalpy.

# Node Structure

- Node represents a volume (for mass and energy balance), either the unit operation in whole (**Tank**, ...) or part of it (**Rotary Kiln**).
- Node has set of constant parameters such as area, diameter, height, volume, ...
- Node has set of variables such as temperature, pressure and composition as mass of gaseous, liquid and solid species.
- Node has number of inlet and outlet ports for its feed and products flows. Separation of phases in node is given by calculating the composition of flows flowing through the ports.
- Flowsheet is build by making connections between the nodes, i.e. connecting (external) outlet ports of nodes to (external) inlet ports.

Example of a generic Tank-node



Special **Contents**-port refers to the contents of the node!

# Kinetic Models

Differential form:

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

In the model  $\Delta\alpha/\Delta t$  is integrated over reaction time in small enough time steps using constant temperature.

Reaction conversion  $\alpha$ :

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

$c_0$  = Initial conc./mass

$c_t$  = Conc./mass 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	$3(1-\alpha)^{2/3}/[2(1-(1-\alpha)^{2/3})]$	$k' = k/R^2$
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 phases/species that are allowed to react (reactive part). These are then taken into equilibrium calculation to determine their reaction products. Other part of phases/species are inert (inert part). After the equilibrium calculation reactive and inert parts are combined. This method is suitable for decomposition/dissolution reactions of (pure) solids.
- Other method uses constraints (CFE\*) introduced as additional components and phases – requires modifications to the stoichiometry of the system. This method is suitable for cases where formation of a phase must be controlled (like precipitation of  $\text{CaCO}_3$  in causticizing).

\*Constrained and extended free energy minimisation for modelling of processes and materials, Risto Pajarre, Pertti Koukkari, and Petteri Kangas, Chemical Engineering Science, vol. 146, 2016.



# Example of Kinetics Method One

- $\text{CaCO}_3 \rightarrow$  Products ? (Same method used for all incoming phases!)

- $C_0 = 1.0$  kg (Additional stream parameter!)

- $C = 0.8$  kg

- $\alpha = 0.2$

- Kinetic model **D3** (3D-diffusion)

- $T = 800$  °C

- $A_0 = 1.0\text{E}6$  1/s

- $E_a = 2.0\text{E}5$  J/s

- $\Delta t = 600$  s

- $\Delta\alpha = 0.1$

➤ Reactive fraction = 0.1 kg of 0.8 kg

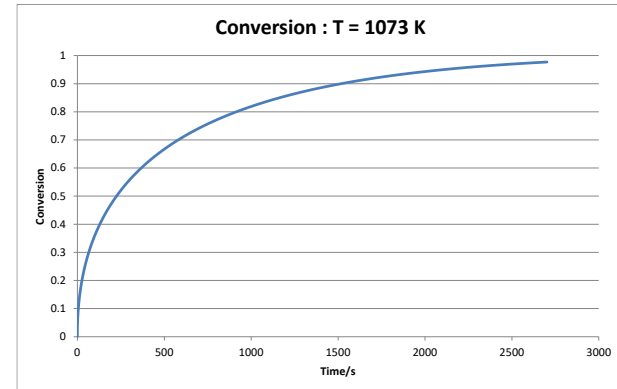
➤ **0.1 kg of  $\text{CaCO}_3$  to eq. calculation**

$$f(\alpha) = 3(1 - \alpha)^{2/3} / [2(1 - (1 - \alpha)^{2/3})]$$

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

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

$$\Delta c = -\Delta\alpha * c_0$$



# Example of Kinetics Method Two

Phase	Constituent	Molar mass g/mol	Ca 40.078	Na 22.990	O 15.999	C 12.011	H 1.008	EQ(AQU) 0.001	*S 0.000
AQU	H2O	18.015			1		2		
	H(+aq)	1.007					1	-1	
	OH(-aq)	17.008			1		1	+1	
	Ca(+2aq)	40.077	1					-2	
	Na(+aq)	22.989		1				-1	
	CO3(-2aq)	60.010			3	1		+2	
CaCO3(s)	CaCO3(s)	100.087	1		3	1			1
Ca(OH)2(s)	Ca(OH)2(s)	74.093	1		2		2		
CaO(s)	CaO(s)	56.077	1		1				
Na2CO3(s)	NaCO3(s)	105.988		2	3	1			
NaOH(s)	NaOH(s)	39.997		1	1		1		
Na2O(s)	Na2O(s)	61.979		2	1				
R_S+	R_S+	0.000							+1
R_S-	R_S-	0.000							-1

Sample with initial composition:

- H2O(aq) 12. kg
  - Na2CO3(aq) 2.0 kg
  - CaO(s) 1.0 kg
  - R\_S+ 1.0 mol (from kinetic model)
- 
- R\_S+ “ENTERED“
  - R\_S- “ELIMINATED“
- ✓ Only 1 mol of CaCO3(s) formed (0.1 kg)
  - ✓ Rest as Ca(OH)2(s) (1.22 kg)

- Mixing burned lime (CaO(s)) with green liquor (H2O + Na2CO3(aq))



Fast reaction, exothermic.

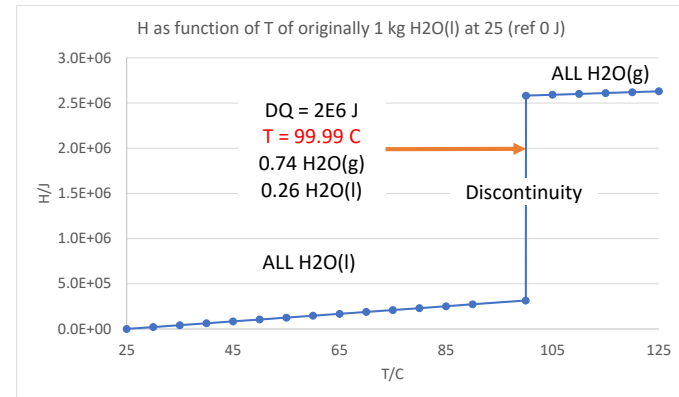


Initially fast reaction but slow towards the equilibrium in the end.

Some of Ca(OH)2(s) may be present at equilibrium, depends on T and X.

# Solving Node Heat&Mass Balance

- Masses of phases in node are divided into reactive and inert fractions. Reactive fractions are used as input for the equilibrium calculation, but both the result of the equilibrium calculation and the inert fractions must take part in the total enthalpy balance:  $(\Delta Q = H_{in}(T_{in}) - (H_{equil}(T_x) + H_{inert}(T_x)))$ .
- ChemApp contains target calculation ( $\Delta H \leftrightarrow \Delta T$ ), but it can only be used for the reactive fraction alone → Needed to implement own target calculation (temperature solver) using binary search / false position root-finding methods.
- Discontinuities in enthalpy as function of temperature due to phase changes. For example,  $H_2O(l) \rightarrow H_2O(g)$  requires interpolation between two equilibria around the boiling point at ~100 deg C.



# Simulation Interface

- Dynamic-Link Library:
  - Windows (10) crompoly.dll
  - Linux (Ubuntu) crompoly.so
- Current platform MS Visual Studio:
  - Intel oneAPI (IFORT-compiler).
  - Compatible with GNU Fortran.
  - Parallel computing with coarray Fortran (CAF) (compatible with ChemApp).
- ✓ (Python based web-server code for interfacing under development in another project (AI-Proficient).
- To use CROM for implementing dynamic version of KilnSimu.

Routine	Description
<b>crom_init</b>	Initializes crom-library. Called first.
<b>crom_done</b>	Deinitializes crom-library. Called last.
<b>crom_calcstep</b>	Calculates next time step.
<b>crom_loadcase</b>	Loads simulation case (flowsheet) from given file.
<b>crom_savecase</b>	Saves simulation case (flowsheet) to given file.
<b>crom_loadstate</b>	Loads state of current simulation case (values of all internal variables and parameters) from given file.
<b>crom_savestate</b>	Saves state of current simulation case (values of all internal variables and parameters) to given file.
<b>crom_loadparams</b>	Loads definitions of variables and parameters from given file.
<b>crom_saveparams</b>	Saves definitions of variables and parameters to given file.
<b>crom_getvalues</b>	Gets current values of given variables and parameters.
<b>crom_setvalues</b>	Sets current values of given variables and parameters.
<b>crom_getflow</b>	Gets current values of all variables in given flow.
<b>crom_getnode</b>	Gets current values of all variables in given node.

- **FMI** “The Functional Mock-up Interface” is a free standard that defines a container and an interface to exchange dynamic simulation models.
- **OPC** “Open process control is a standard that defines data communication between devices from different manufacturers

# Building a Flowsheet

- Excel Interface for building and testing simulation of cases.
  - Model definitions given using excel tables and saved to files:
  - Unit operations.
  - Connections.
  - Initial parameters (time zero).
  - Input&Output parameters (time > zero).
- Examples of parameters:
- "Feed | Contents | T | C"
  - "Feed | Contents | P | bar"
  - "Feed | Out | F | kg/s"
- Parameter is used for mapping a process variable to its representative node/port/flow in the model.
  - String construct as Unit|Port|Variable[|Phase[|Constituent]]|Dimension.
  - Aliases can be defined for variables for mapping parameters having different tags in the actual plant process.

- New unit operations for dynamic control of the flow rates, the temperatures, the pressures, tank levels, etc.
- Pushed flows vs. pulled flows.
- New faster algorithm to solve the pressures (ongoing).
- New Excel Interface for testing purposes.

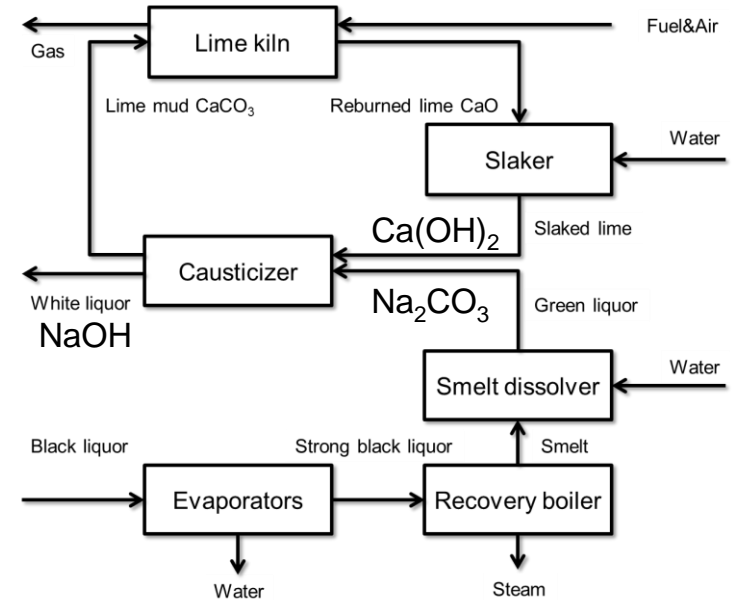
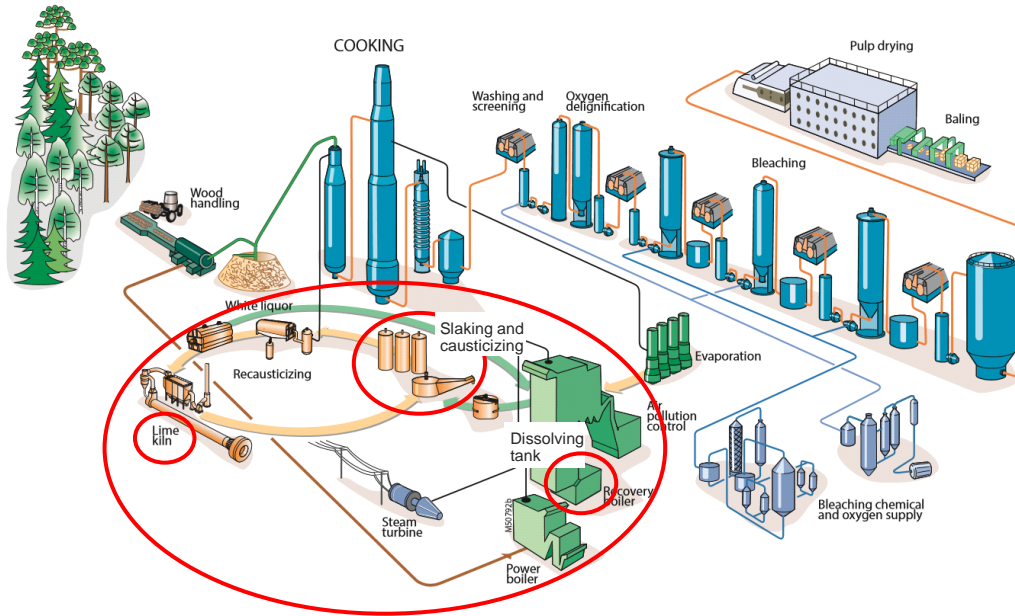
## New units for

- Valves
- Pipes
- Junctions
- Pumps
- Compressors
- **Controller**
  - Off
  - Manual
  - Auto
  - Cascade

## Controller parameters

- Mode
- Action
- Process variable
- Set point
- Minimum
- Maximum
- $K_c$
- $T_i$
- $T_d$

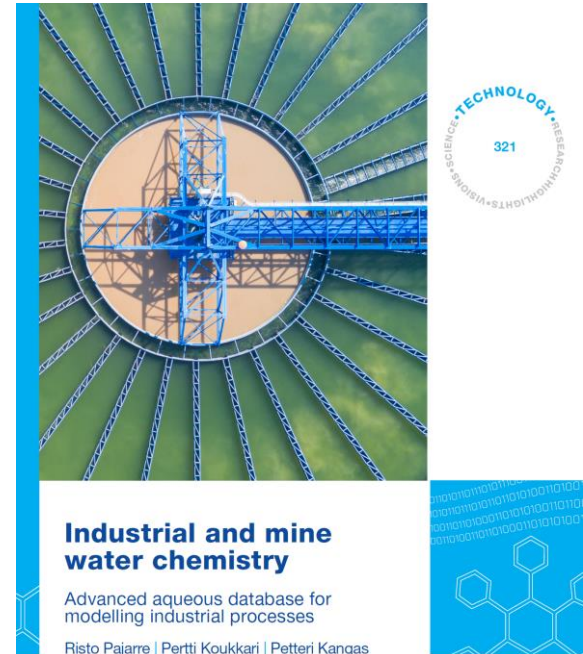
# Kraft Recausticizing Process



- In chemical pulping cooking the 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 *calcium 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.

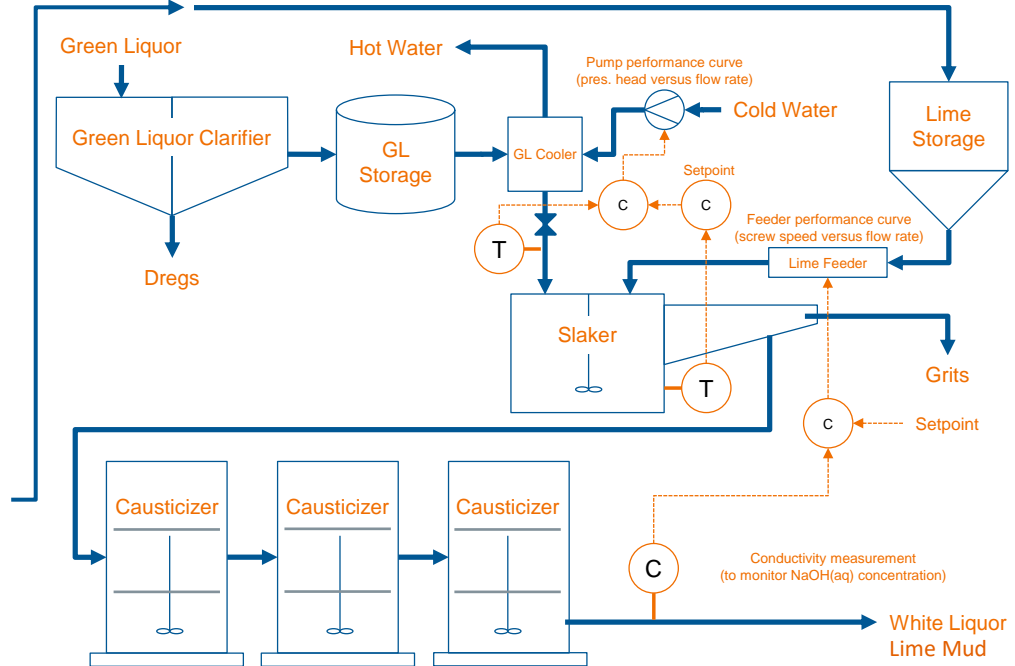
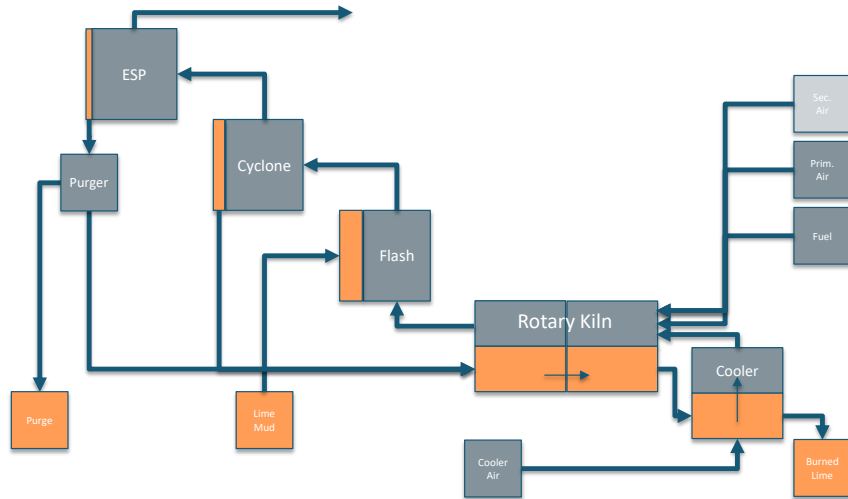
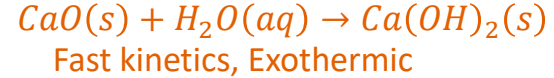
# Thermodynamic System

- Thermodynamic data-file for the recausticizing process is based on Risto Pajarre's aqueous Pitzer database. Optimized for aqueous systems but works with Lime kiln as well.
- Limited set of elements selected to reduce the total number of species:
- Ca-K-Cl-S-P-(Si-Al)-Mg-Na-O-N-C-H-EA
- GAS/IDMX (79), AQU/PIMZ (52), GLASERITE/SUBL (2), BURKEITE/RKMP (2) and pure condensed phases (102)



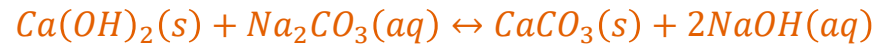


# Lime kiln, slaking and causticizing



## Unit Operation Models

- Rotary Kiln
- Clinker Cooler
- Flash
- Cyclone
- ESP
- Clarifier
- Storage Tank
- Slaker
- Causticizer
- Screw Feeder...



Faster kinetics in Slaker up to 70% conversion

Slower kinetics in causticizers, final conversion up to 85%

# Results for Slaking and Causticizing

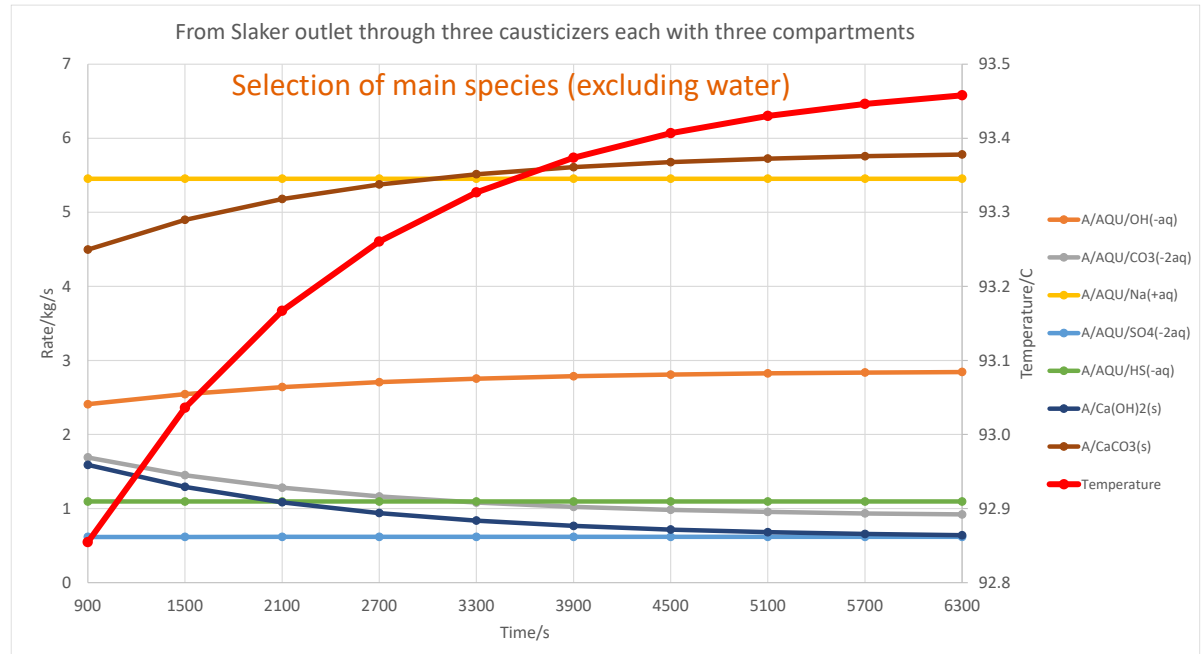
## Exemplary inputs

Green Liquor		
T	70 C	
P	1 bar	
Rate	220.000 t/h	
	61.111 kg/s	
H2O	48.889	80.000 %
NaOH	1.017	1.665 %
Na2S	2.310	3.781 %
Na2CO3	7.299	11.944 %
Na2S2O3	0.383	0.627 %
Na2SO4	0.547	0.895 %
NaCl	0.054	0.089 %
KOH	0.054	0.088 %
K2S	0.122	0.199 %
K2CO3	0.384	0.629 %
K2S2O3	0.020	0.033 %
K2SO4	0.029	0.047 %
KCl	0.003	0.005 %
Total	61.111	100 %
Lime		
T	150 C	
P	1 bar	
Rate	15.000 t/h	
	4.167 kg/s	
CaO	3.750	90.000 %
CaCO3	0.146	3.500 %
MgO	0.125	3.000 %
Na2O	0.042	1.000 %
P2O5	0.083	2.000 %
SiO2	0.021	0.500 %
Total	4.167	100.000 %

## Result

Causticity	
NaOH/(NaOH+Na2CO3)	
Slaker	0.655
CaustA1	0.700
CaustA2	0.733
CaustA3	0.756
CaustB1	0.772
CaustB2	0.784
CaustB3	0.792
CaustC1	0.798
CaustC2	0.802
CaustC3	0.804

~ Final steady-state



Slaker  $\tau = 900s$   
 CaustA  $\tau = 1800s (=3*600s)$   
 CaustB  $\tau = 1800s (=3*600s)$   
 CaustC  $\tau = 1800s (=3*600s)$

Formation of CaCO3(s) constrained with CFE method using simple kinetics. Outlet from 3rd causticizer already close to equilibrium.

**Thank You  
For Your Attention!**