

From Optimization of industrial Crystallizers to Design of New Equipment using Advanced Modelling Tools

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R&D Process Engineering
Solvay

Who are we?

A major global player in Chemicals with compelling strengths



Created by Ernest Solvay in 1863, Solvay is a **Global** company, with historical anchorage in Europe, and headquartered in Brussels.

Our strengths

- 90% of sales in businesses among the top 3 global leaders
- A balanced portfolio of activities, directed at growth regions
- A culture of sustainability, innovation and operational excellence

€9.9 bn
NET SALES

€1,663
bn
Adjusted REBITDA

117
INDUSTRIAL SITES

15
MAJOR R&I

29,400
EMPLOYEES
55 COUNTRIES

Investments, energy and quality:

The key drivers of process improvements

- **Reduce the investments costs**

- Increase of the existing equipment capacity (“debottlenecking”)
- intensification of new equipment
- reuse of existing devices (“retrofitting”)



- **Reduce the energy consumption**

→ better control of heat transfers, continuous process



- **Best Product**



gCRYSTAL: an opportunity to develop advanced crystallization models

Why modelling crystallization?

- Major impact on most of the processes involving solid
- Complex operation

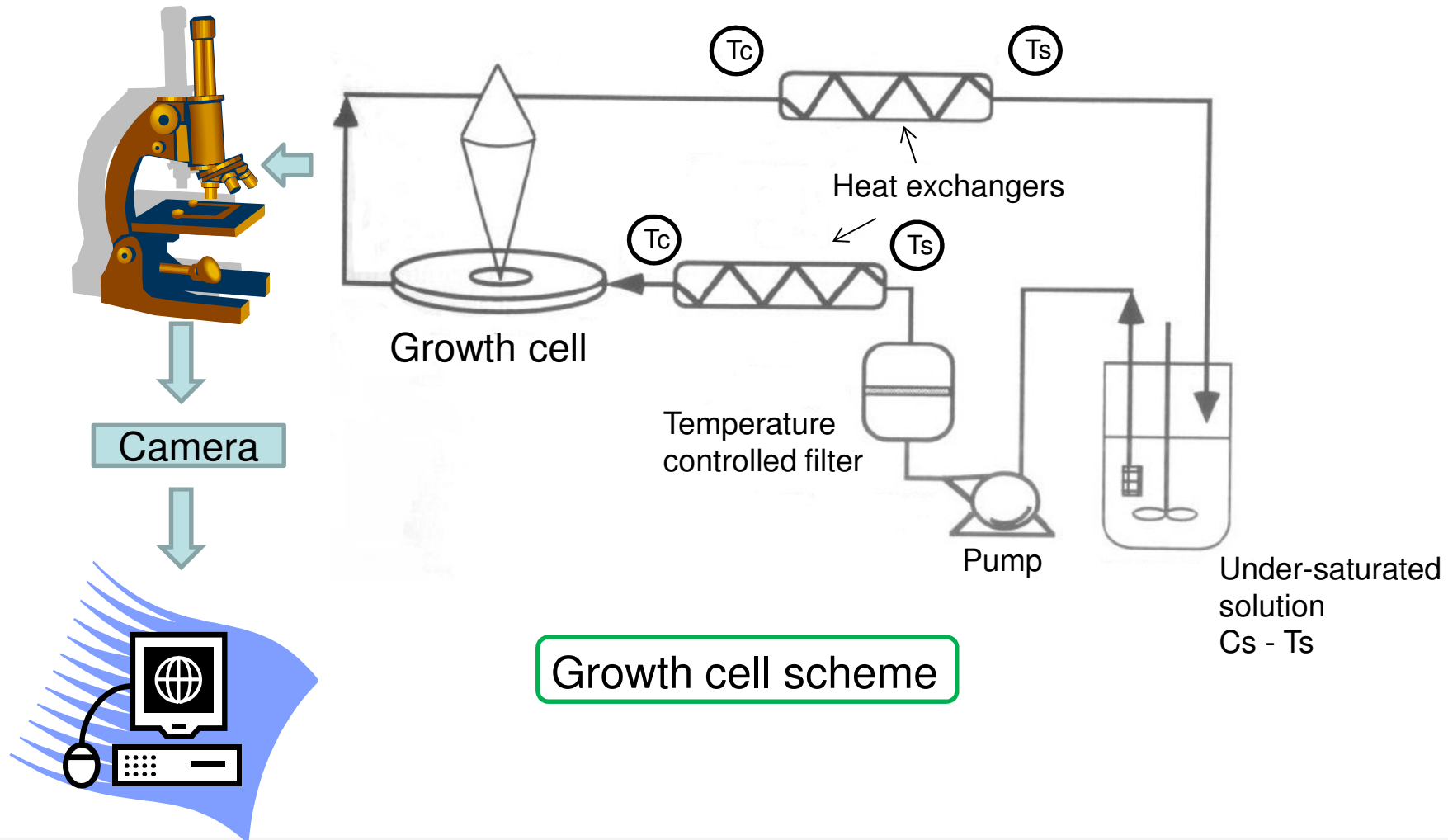
Why using gCRYSTAL?

- To avoid building a full “in-house” population balance code

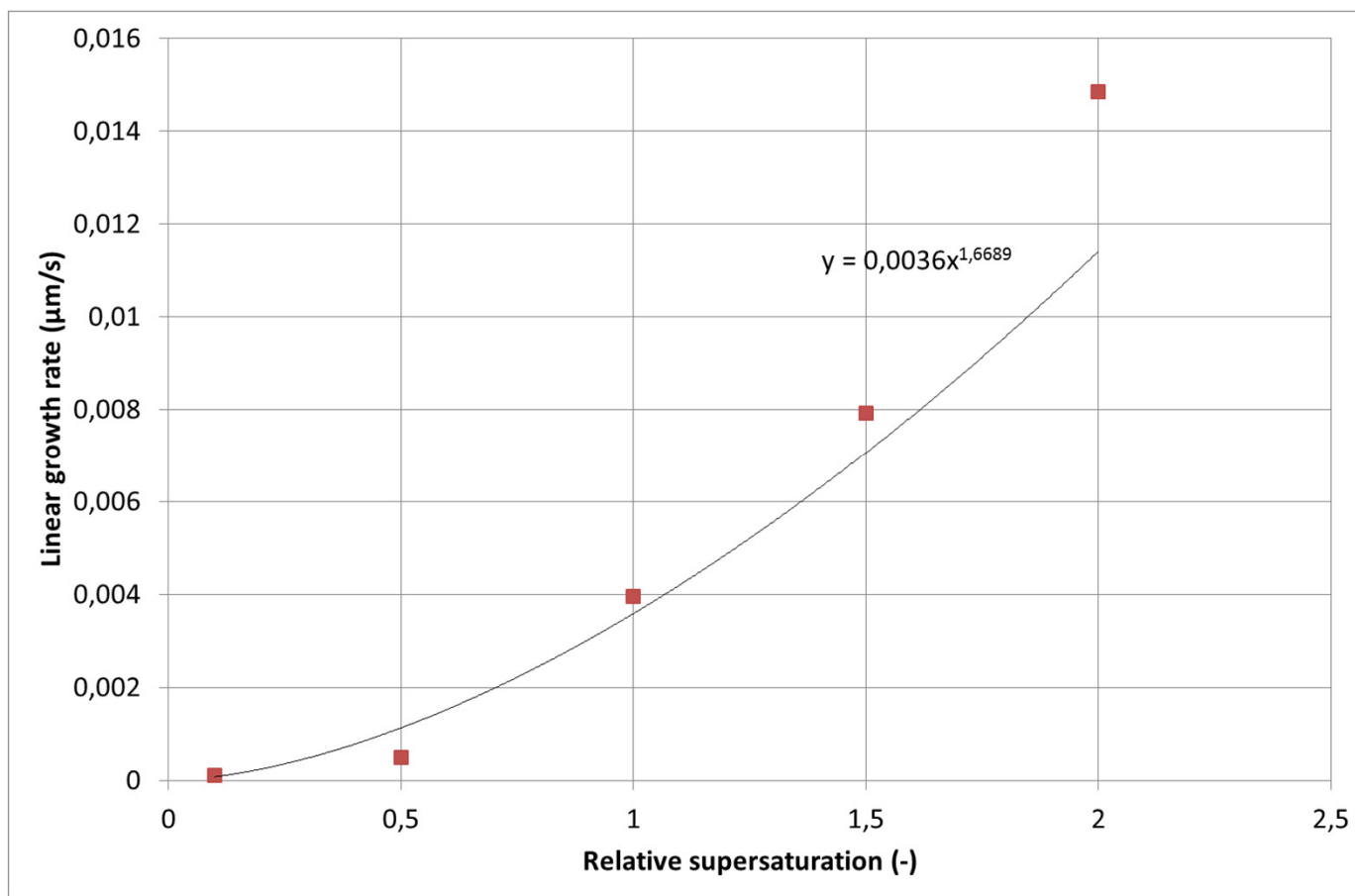
Outline

- Building a batch crystallization model using gCRYSTAL
 - Data acquisition
 - Model & Kinetic parameters estimation
 - Kinetic model development
- Optimizing an industrial crystallizer capacity and energy consumption
- Towards the Design of New Crystallizers

A direct measurement of the growth rate kinetic

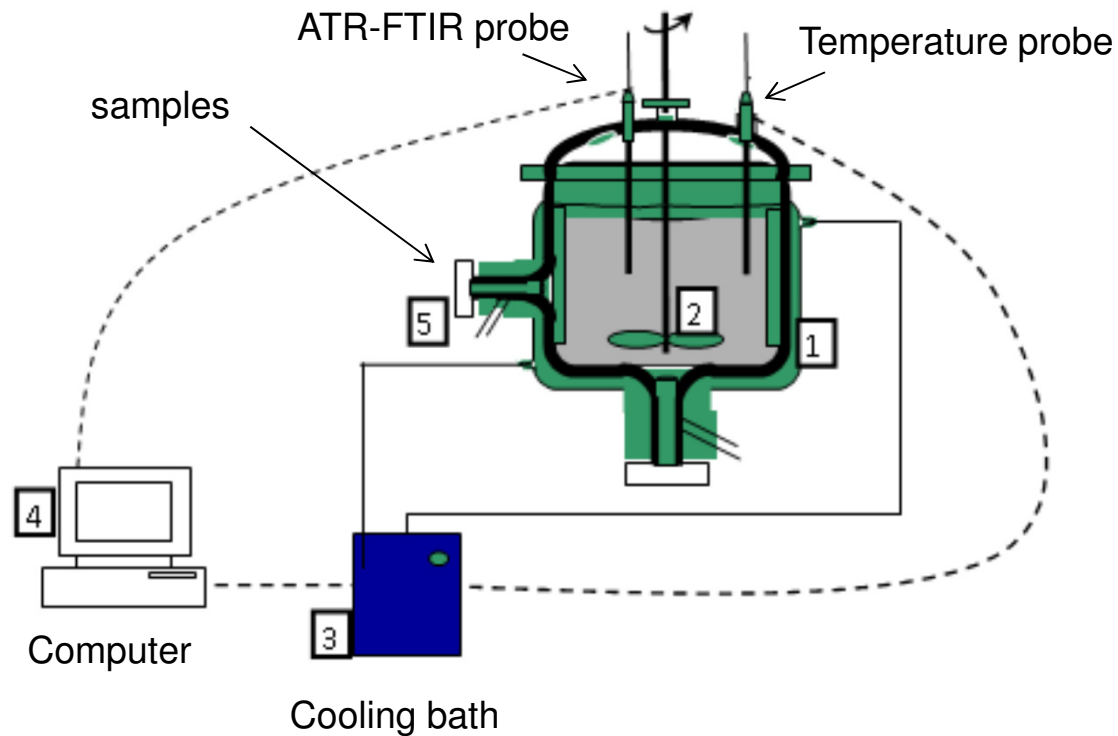


Growth rate function of the supersaturation



Power law kinetic

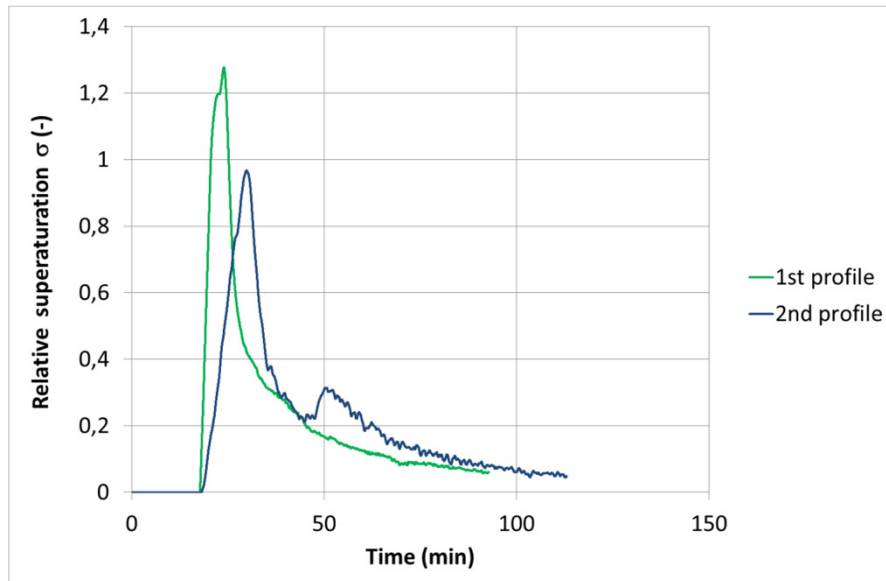
Monitoring temperature, concentration and crystal size during a batch cryst.



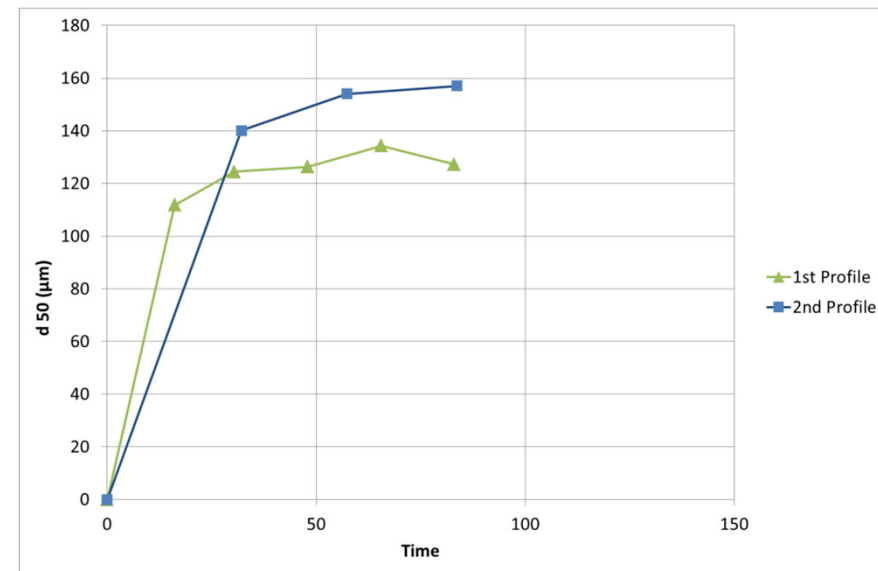
- 1- MSMPR
- 2- Mixell TT impeller
- 3- Cooling bath
- 4- Computer
- 5- Sampling

Effects of changing the temperature profile

Supersaturation profiles



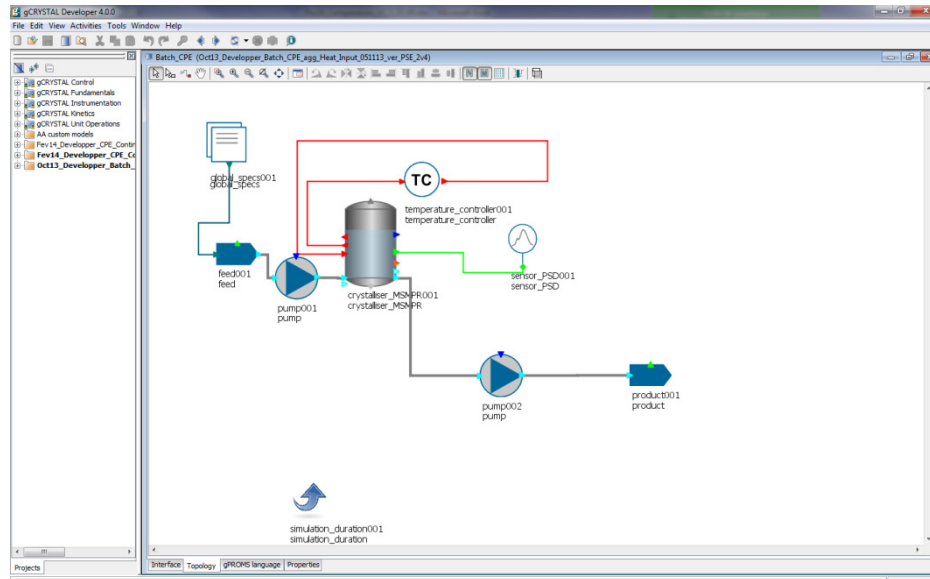
Crystal size



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gCRYSTAL model: a fast way to simulate a batch crystallization



“Bulid-in” kinetics from gCRYSTAL were used

1st nucleation

$$r_{N1} = A_n \cdot e^{-\frac{B_n}{\ln(c/c^*)}}$$

Linear growth rate

$$G = k_c \cdot \frac{2 \cdot M_\omega}{\rho} \left(\frac{c - c^*}{c^*} \right)^{j_c}$$

Entering the experimental data

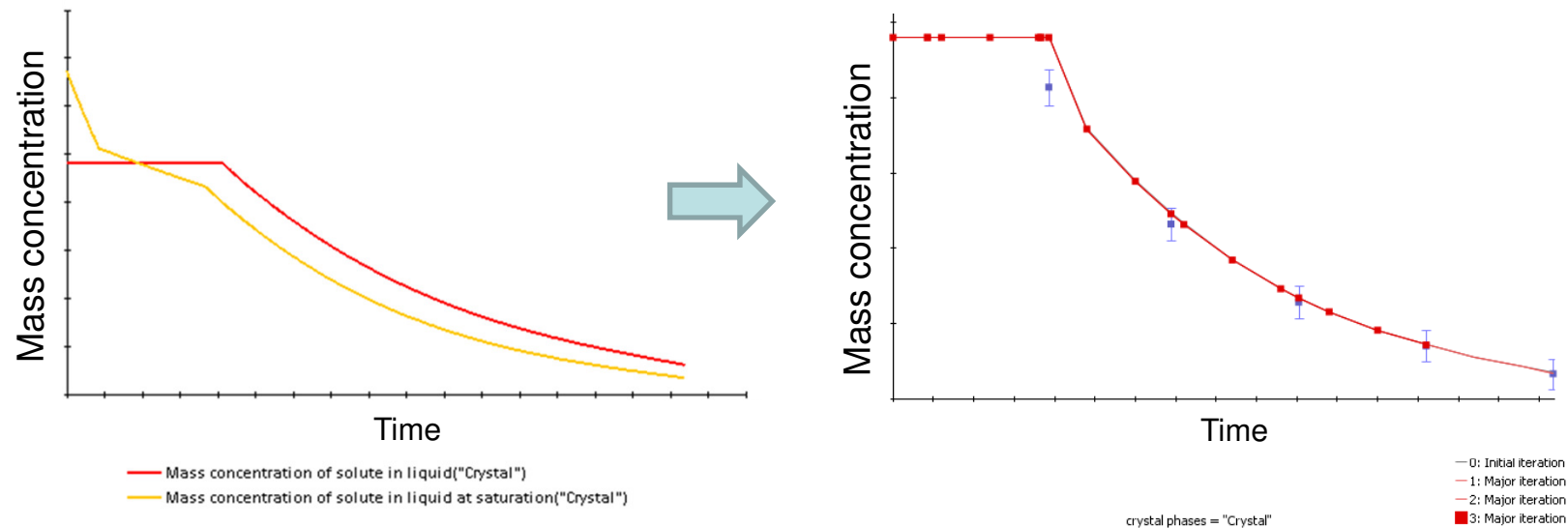
The screenshot shows the gCRYSTAL Developer 4.0.0 interface. On the left is a project tree with folders like 'gCRYSTAL Control', 'gCRYSTAL Fundamentals', 'gCRYSTAL Instrumentation', 'gCRYSTAL Kinetics', 'gCRYSTAL Unit Operations', 'AA custom models', 'Fev14_Model_GCrystal', 'Models', 'Processes', 'Experiments', and 'Parameter Estimations'. The 'Experiments' folder is expanded, showing 'Exp_Lab02'. A large blue arrow points from 'Exp_Lab02' to the 'Experimental data' section.

The 'Exp_Lab02 (Fev14_Model_GCrystal)' window displays a table with experimental data. The table has columns for 'Time', 'Variable Name', 'Sensor', 'Variance model', and five data columns. The data is as follows:

Time	Variable Name	Sensor	Variance model	col1	col2	col3	col4	col5
1929.0	crystallise... liquid ("AA_Crystal")	<unspecified>	<unspecified>	0.207	221.318	420.294	735.163	
3441.0		<unspecified>	<unspecified>	0.116	265.398	462.133	772.703	
5022.0		<unspecified>	<unspecified>	0.064	271.167	471.049	786.058	
6600.0		<unspecified>	<unspecified>	0.035	272.331	481.345	822.77	
8172.0		<unspecified>	<unspecified>	0.0165	268.216	468.369	784.224	

Below the table, a diagram shows the data structure with labels: 'time', 'Conc.', 'd₁₀', 'd₅₀', and 'd₉₀'. Below these labels is the text 'Experimental data'. At the bottom of the window are buttons: 'Select measured variables...', 'Delete row', 'Delete column', and 'Transpose'.

Good estimation of the kinetic parameters using the optimization feature

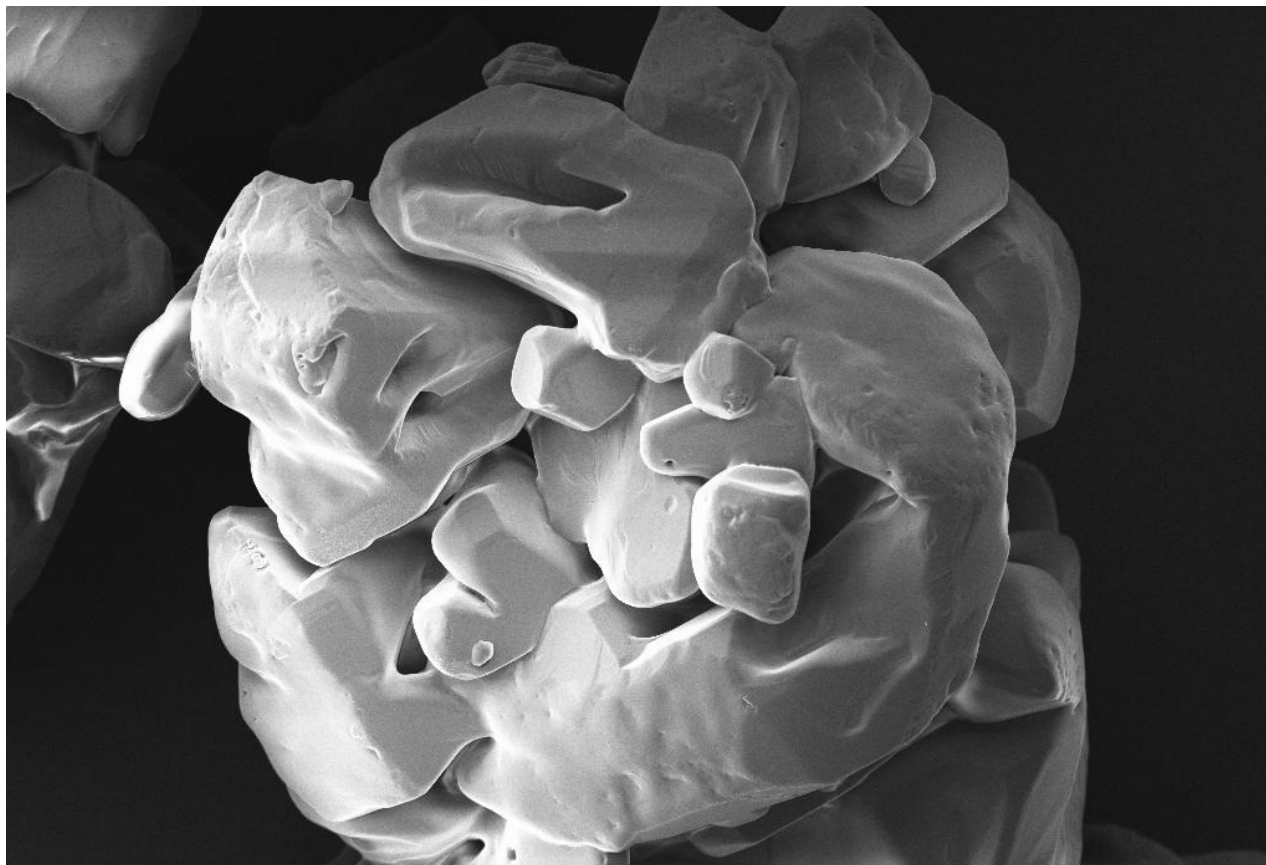


Good match between simulated and experimental concentration profiles for different cooling rate

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Crystal Habit



Crystals look like aggregates

Agglomeration model

Addition of an Aggregation kinetics (Mumtaz)

Agglomeration kernel $\beta_{agg} = \left(\sqrt{\frac{8\pi\varepsilon}{15\nu}} \cdot \bar{d}_{3,0}^3 \right) \cdot \frac{(\overset{\text{Fitting parameter}}{A_{50}} G) / (\varepsilon \rho \bar{d}_{3,0}^2)}{1 + (\overset{\text{Fitting parameter}}{A_{50}} G) / (\varepsilon \rho \bar{d}_{3,0}^2)}$

Collision rate Agglomeration efficiency

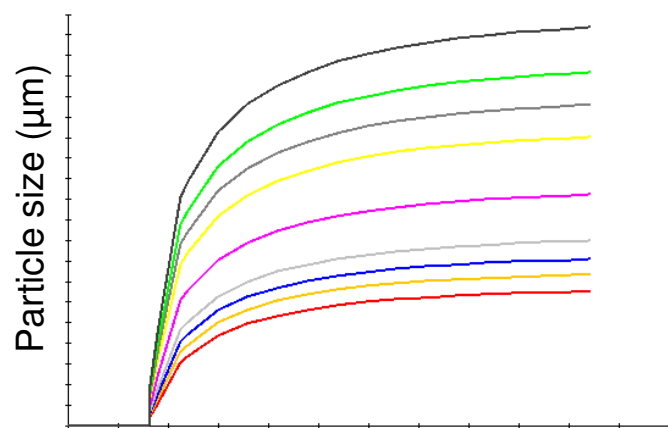
L	length of the line of contact between two collided crystals
σ^*	apparent yield strength
G	linear growth rate of crystals
ε	energy dissipation rate
ρ	liquid density
$\bar{d}_{3,0}$	3,0 mean particle size

Particle size prediction with the new model

Good match !!

Without agglomeration

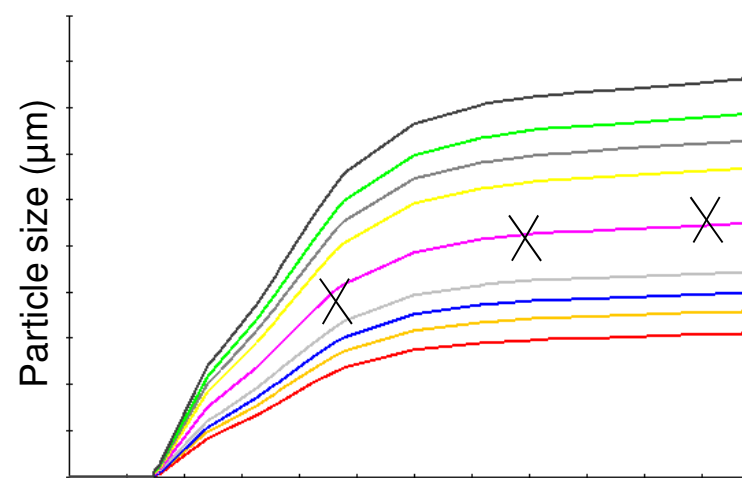
50 μm



Time

— Quantile("AA_crystal", "05%")
— Quantile("AA_crystal", "10%")
— Quantile("AA_crystal", "16%")
— Quantile("AA_crystal", "25%")
— Quantile("AA_crystal", "50%")
— Quantile("AA_crystal", "75%")
— Quantile("AA_crystal", "84%")
— Quantile("AA_crystal", "90%")
— Quantile("AA_crystal", "95%")

300 μm With agglomeration



Time

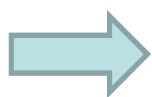
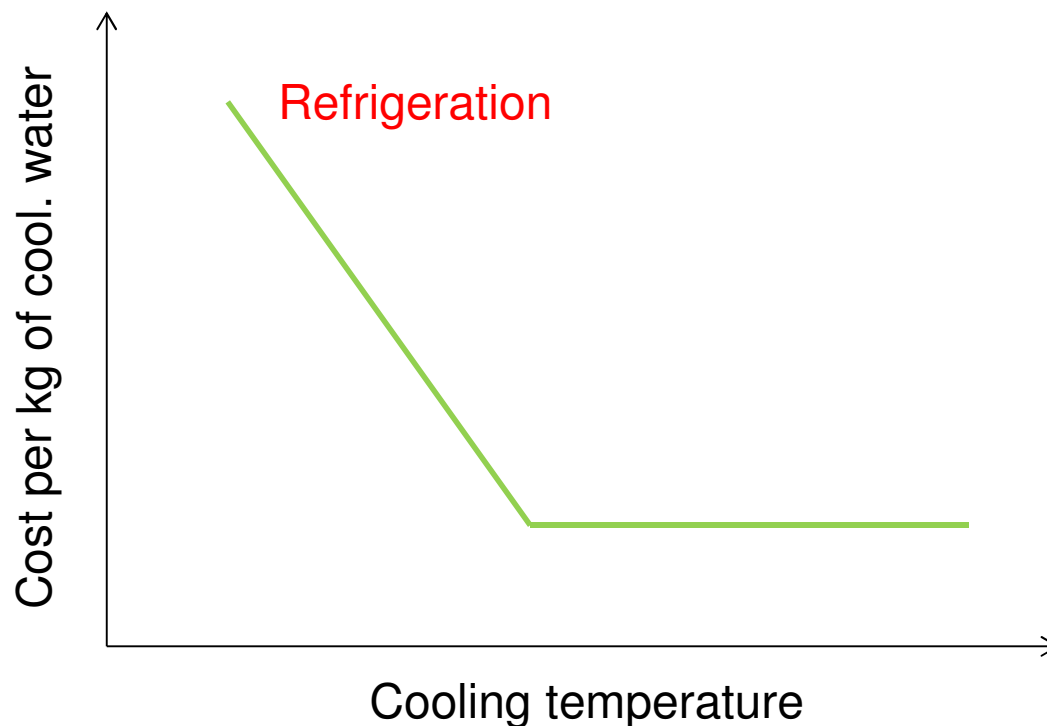
— Quantile("AA_crystal", "05%")
— Quantile("AA_crystal", "10%")
— Quantile("AA_crystal", "16%")
— Quantile("AA_crystal", "25%")
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— Quantile("AA_crystal", "90%")
— Quantile("AA_crystal", "95%")

X Experimental data

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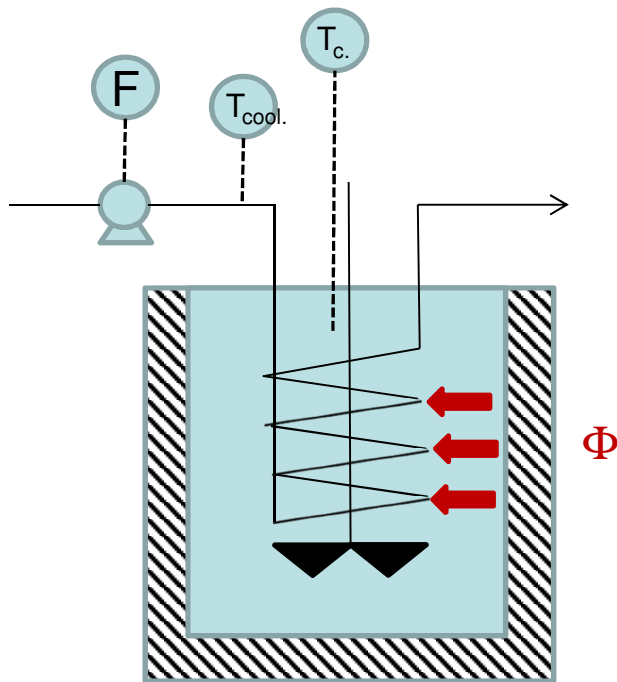
Energy cost for cooling crystallization



The temperature of the cooling water has to be controlled for better economical results

How to control the heat exchange?

$$\Phi = U \cdot A \cdot (T_{cryst.} - T_{cool.})$$

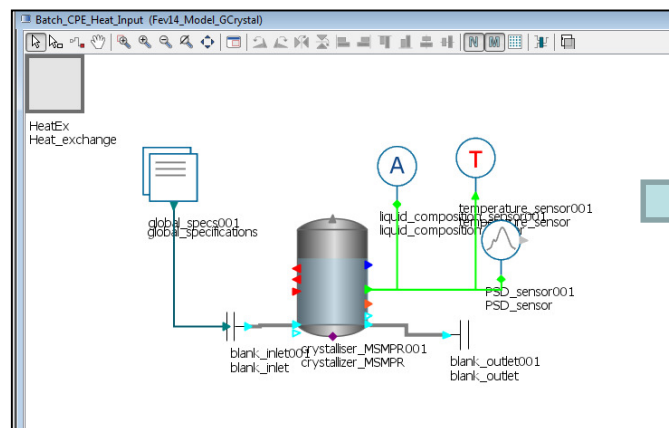


Modeling of a heat controlled crystallizer

T_{cryst}	$T_{cryst} - T_{cool}$
T1	$\Delta T1$
T2	$\Delta T2$
T3	$\Delta T3$
...	...

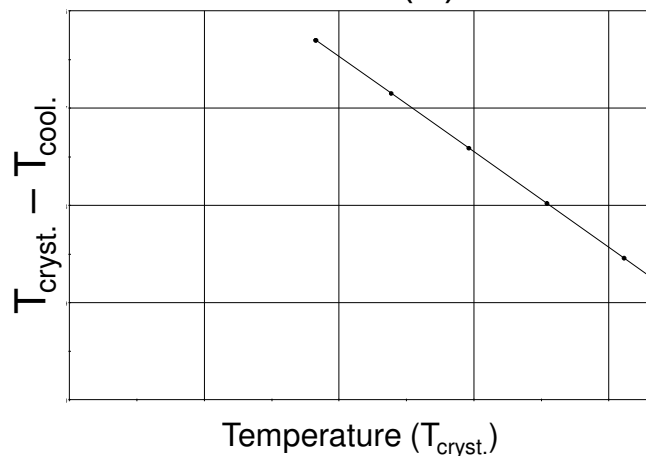
Coupling heat balance and population balance

gCRYSTAL developer version

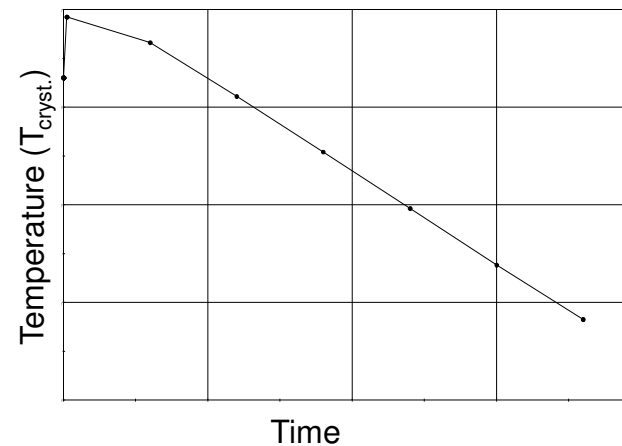


Instead of being directly controlled by a T° profile, the crystallization is controlled by the **heat output profile**

$$\Delta T = f(T)$$



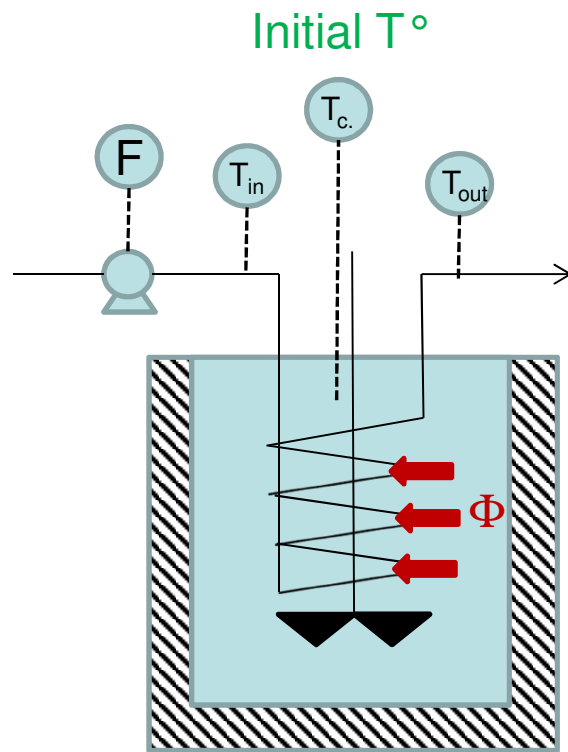
$$T = f(\text{Time})$$



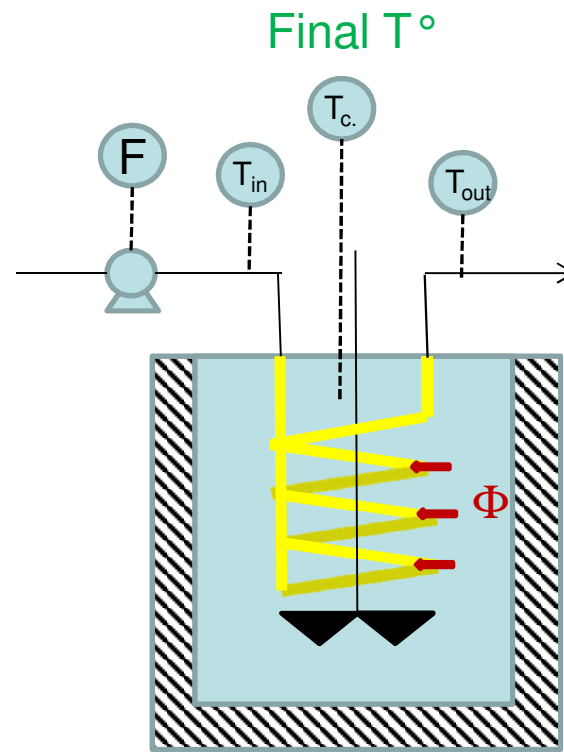
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What is scaling?



Beginning of crystallization



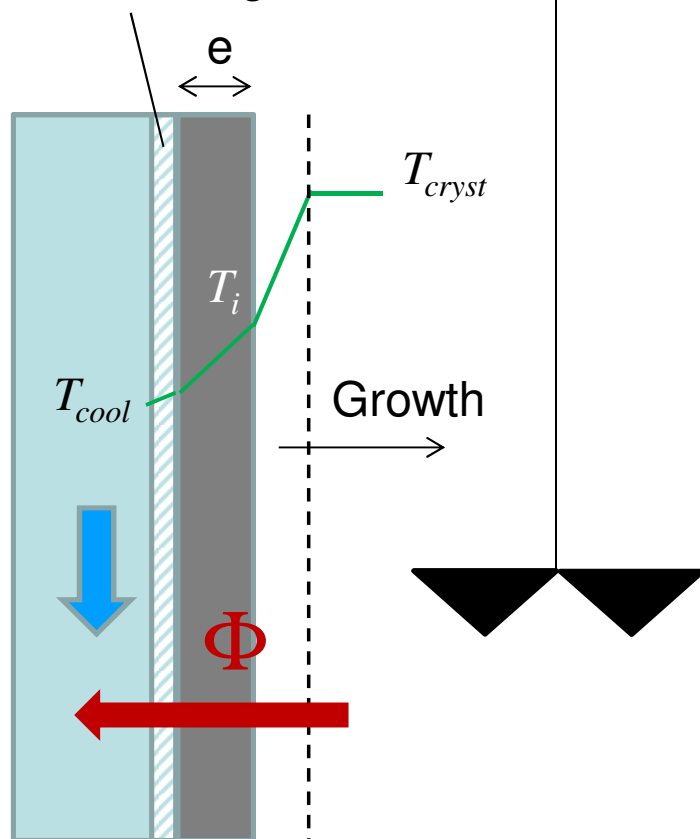
End of crystallization

$$\Phi = \underset{\uparrow}{U} \cdot A \cdot \Delta T$$

Scaling affects the heat exchange coefficient

How to model scaling?

Heat exchange surface



$$U(t) = \frac{U_0}{1 + f \cdot e(t)}$$

U : heat exchange coefficient
 U_0 : Initial heat exchange coefficient
 e : Scaling thickness
 f : Thermal conductivity factor

$$e(t) = f(\sigma_s, \sigma_c)$$

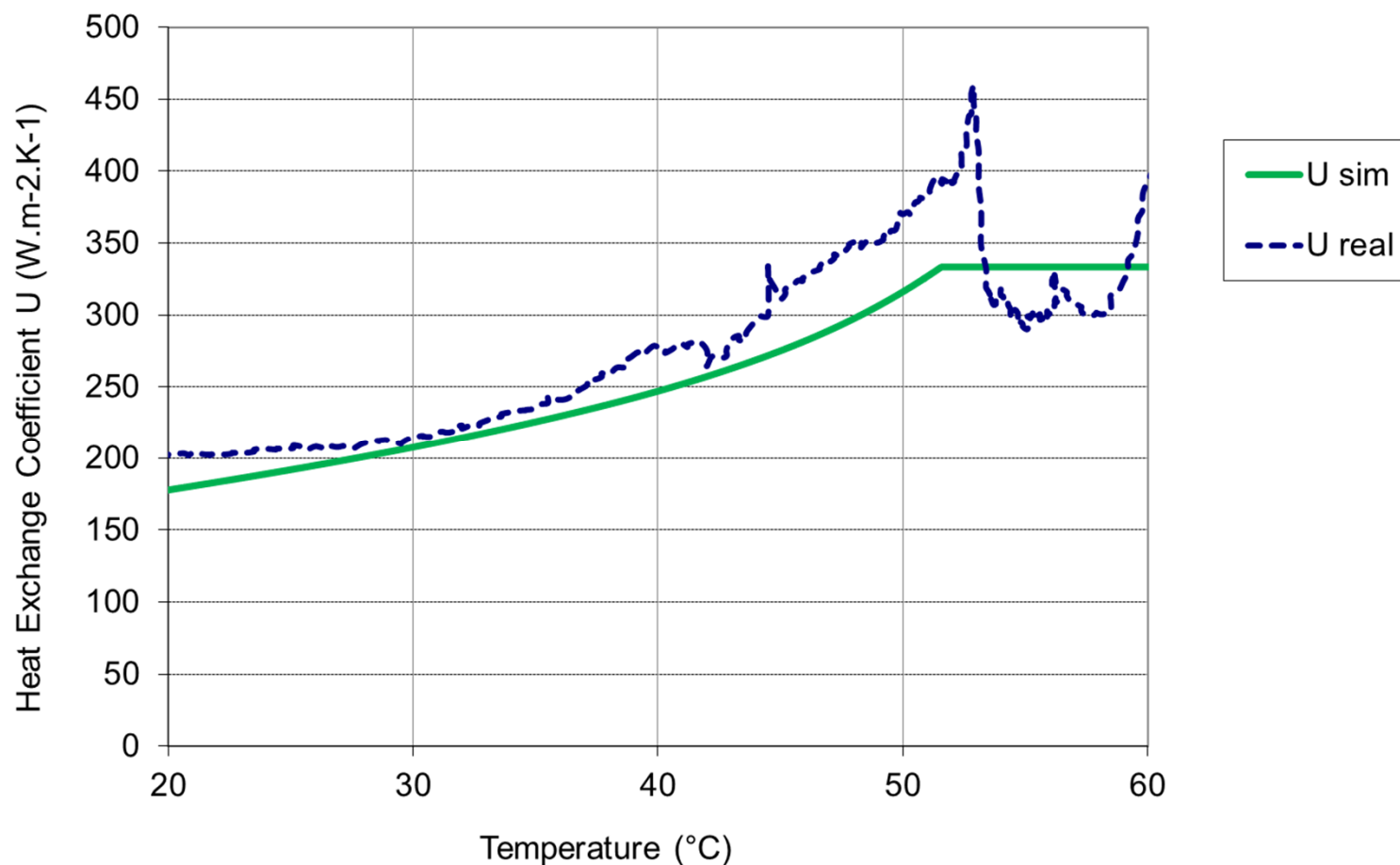
With local supersat. σ_c



Implementation in gCRYSTAL
Developer version

Evolution of the heat exchange coefficient

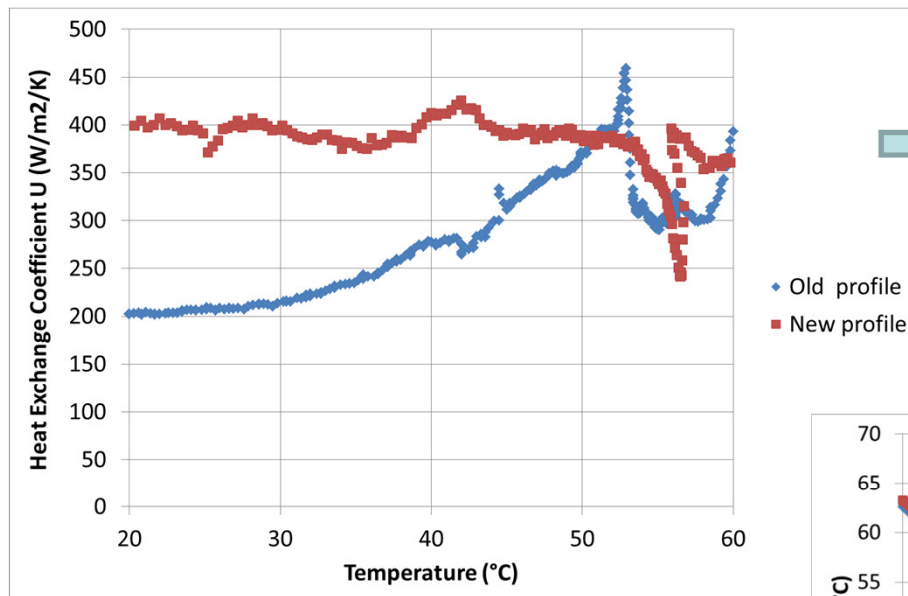
Scaling mechanism



Good match between simulated and real Heat Exchange Coefficient

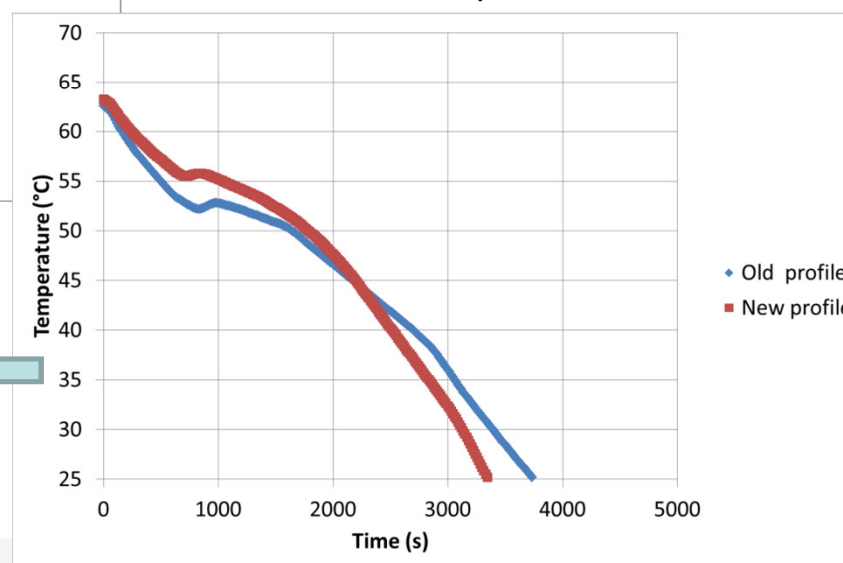
New cooling profile to avoid scaling

Stability of the heat exchange coefficient !



- No risk of residues in the crystallizer
- Decrease the energy cost by 15%

Decrease of the operation duration !!

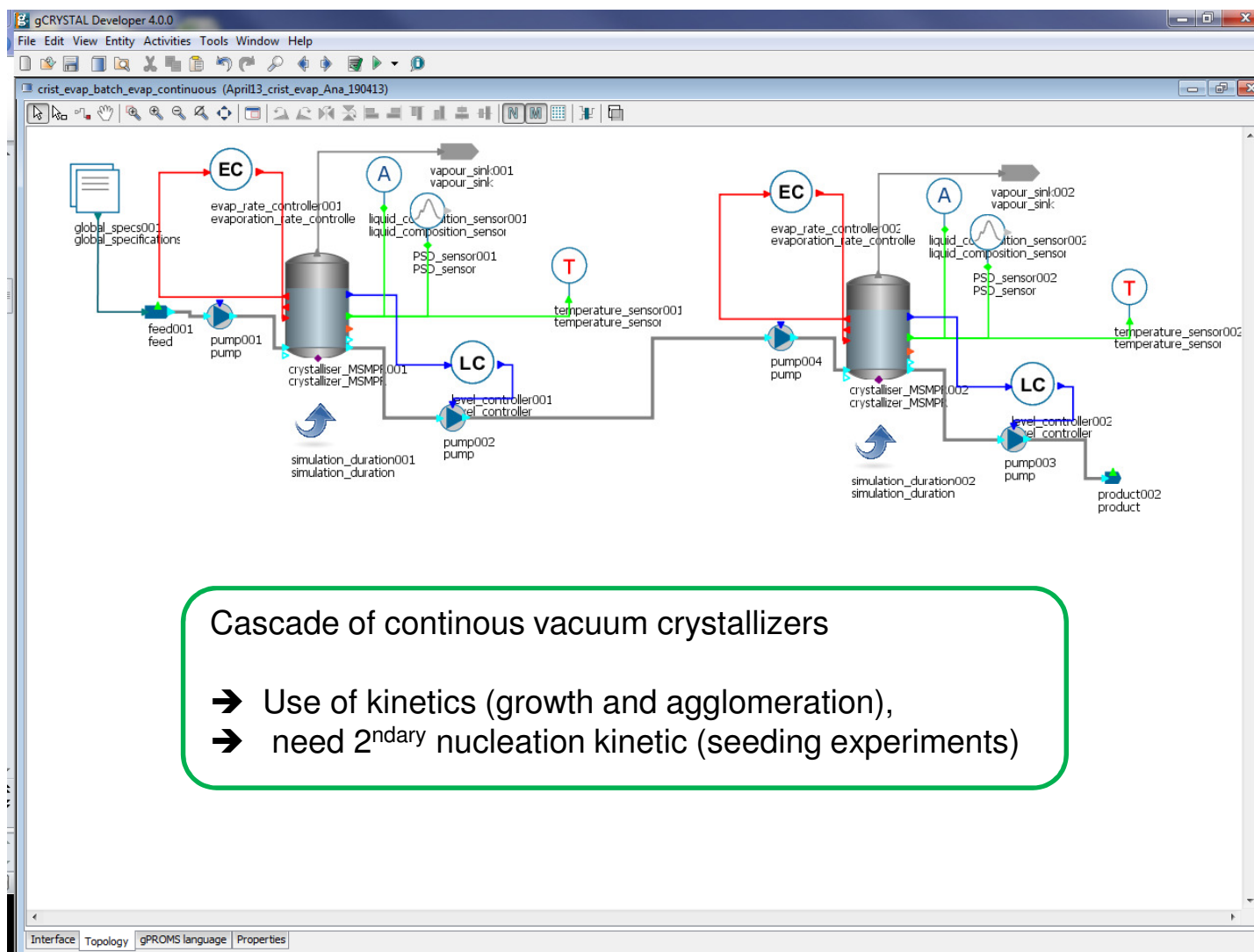


Higher productivity 10%

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Prospects: New crystallizer configurations



Conclusions

- Thanks to a simple “Step-by-Step” approach we managed to simulate the evolution with time of the supersaturation and of the DTC for a batch cooling crystallization
- The kinetic laws available in gCRYSTAL were sufficient to produce a satisfying model
- Using the developer version of gCRYSTAL , a specific heat exchange model was added to the initial one.
- This allowed us to simulate the effect of the scaling mechanism and later to optimize the cooling profile. The production capacity was increased by 10% and 15% of the electricity consumption was saved.

Acknowledgments


Hassan Mumtaz, PhD, Senior Consultant at PSE, Solids Business

P. Carvin, Solvay - Expert in solid processes

E. Chateigner, Solvay - Process Engineering Technician

Solar Impulse

Pioneering sustainable chemistry

A photograph of the Solar Impulse solar-powered aircraft in flight. The aircraft is a high-wing, four-engine plane with extremely long, thin wings, flying horizontally across the upper half of the frame. Below it is a scenic landscape featuring a winding river, green fields, and a range of mountains under a clear blue sky. A white text box is overlaid on the right side of the image.

**Solar Impulse needs
our Chemistry for
energy management
and weight reduction**

Crystallization mechanisms

Kinetic models considered in a 1st step

“Bulid-in” kinetics from gCRYSTAL were used

1^{ary} nucleation
$$r_{N1} = A_n \cdot e^{-\frac{B_n}{\ln(c/c^*)}}$$

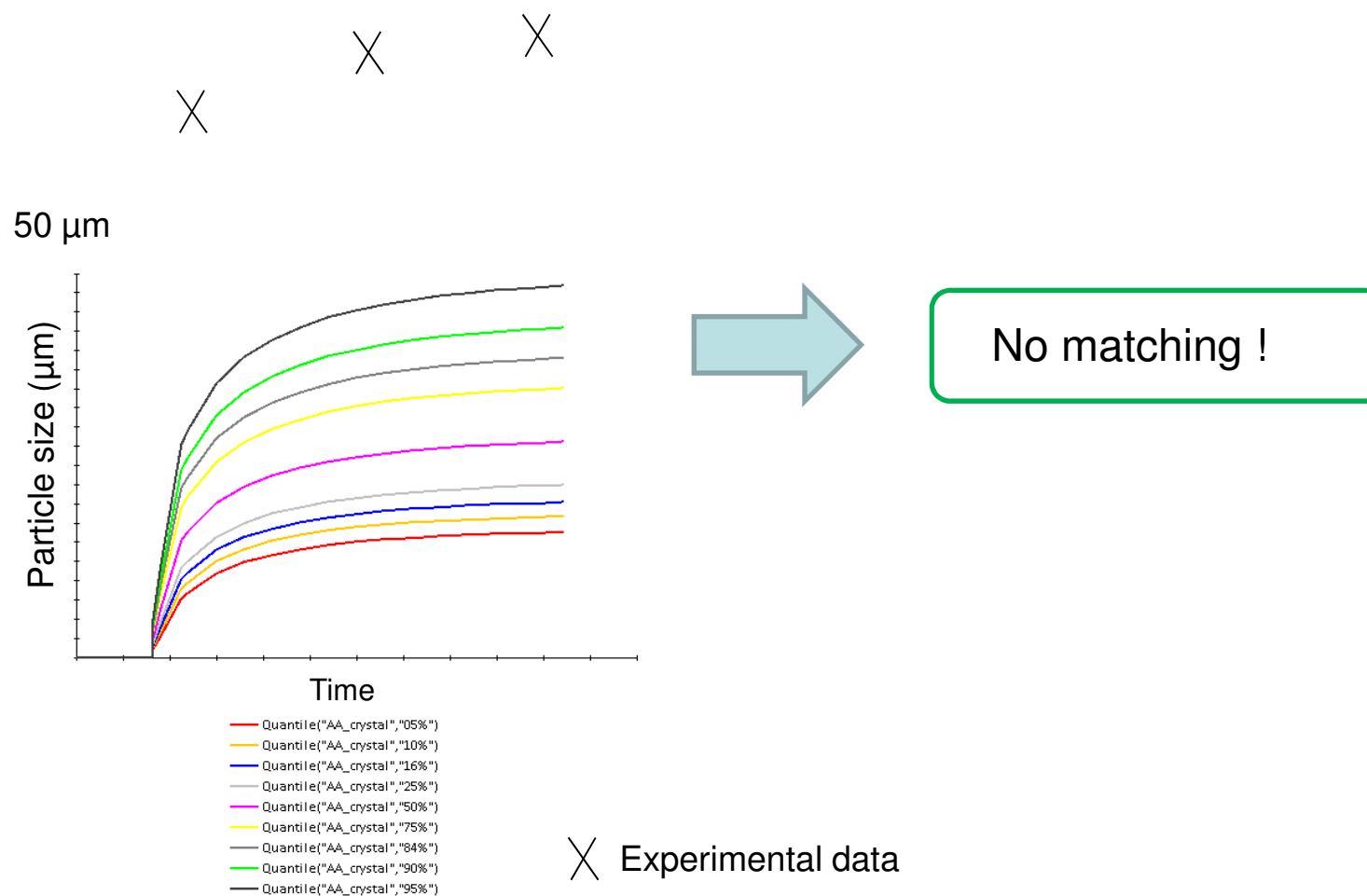
Linear growth rate
$$G = k_c \cdot \frac{2 \cdot M_\omega}{\rho} \left(\frac{c - c^*}{c^*} \right)^{j_c}$$

A_n :	Pre-exponential factor of the primary nucleation	[s ⁻¹]
B_n :	Exponential factor of the primary nucleation	[-]
c :	Solute concentration	[kg.kg ⁻¹]
c^* :	Solubility in the crystallization medium	[kg.kg ⁻¹]
k_c :	Crystal growth factor	
j_c :	Crystal growth supersaturation exponent	
n :	Distribution function	[m ⁻¹]
M_w :	Molar mass of the crystals	[kg.mol ⁻¹]
t :	Time	[s]
L :	Crystals characteristic size	[m]
G :	Crystal growth rate	[m.s ⁻¹]
R_{N1} :	Distribution of the primary nucleation rate	[m ⁻¹ .s ⁻¹]

Outline

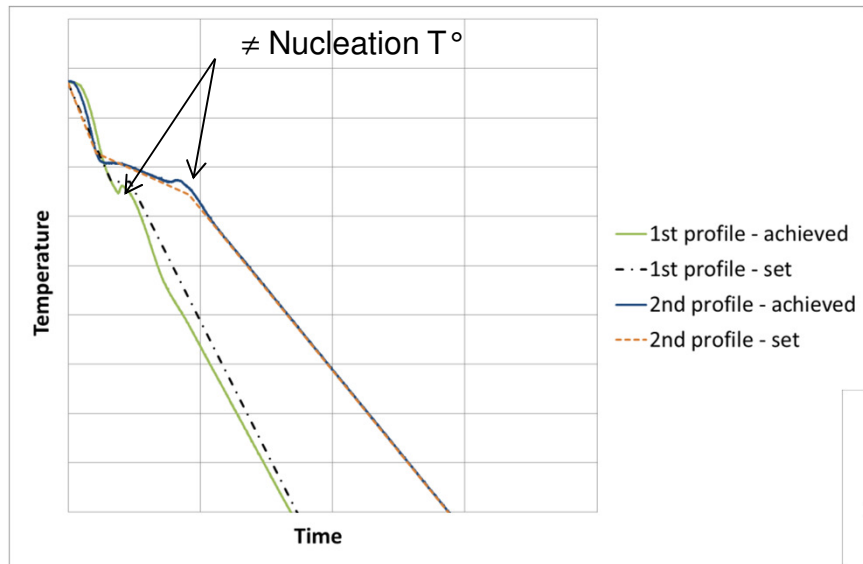
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Fitting the experimental results

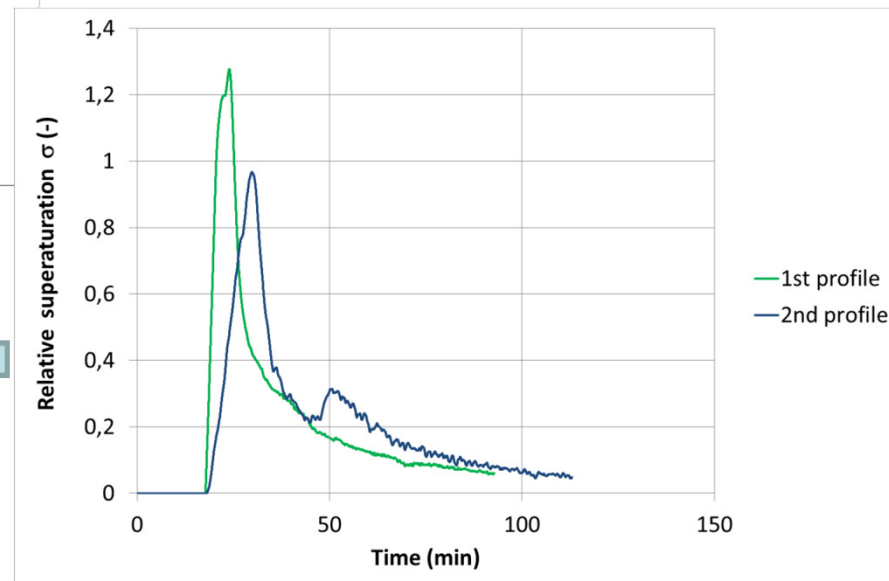


Effects of changing the temperature profile

Temperature profiles

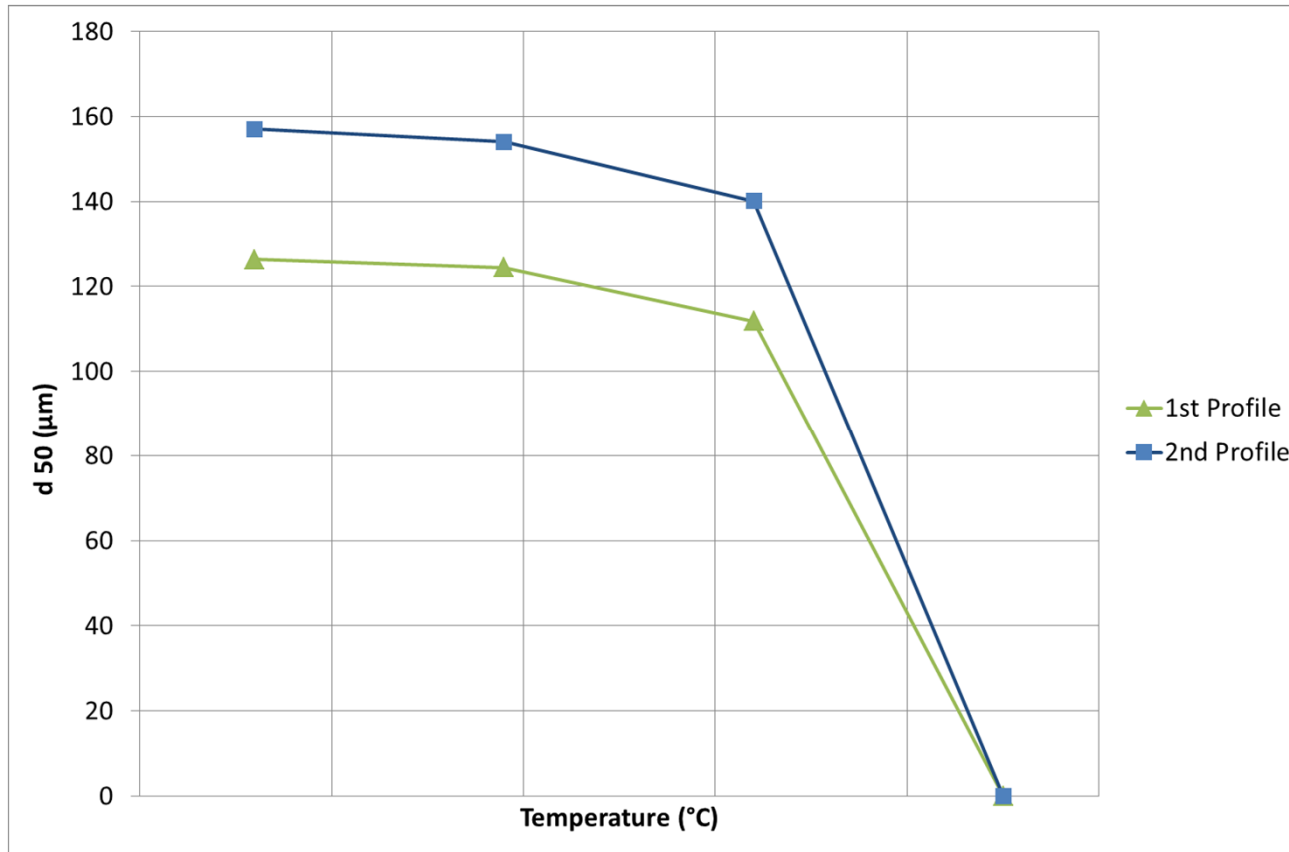


Supersaturation profiles



Different crystallization intensities

Experimental results: Evolution of the particle size



Decrease of the crystal size with the increase of the cooling rate

Setting-up the parameter estimation

gCRYSTAL Developer 4.0.0

File Edit View Entity Activities Tools Window Help

estimation_1 (Oct13_Developer_Batch_CPE_agg_Heat_Input_051113_ver_PSE_2v4)

Experiment	Include in estimation
Exp_Lab01	<input checked="" type="checkbox"/>
Exp_Lab02	<input checked="" type="checkbox"/>

Experiments accounted for

Sensor group ... Experiment : Sensor ... Variable	Variance model
Sensor group 1	Constant (0.01)
Sensor group 2	Constant (>0)
Sensor group 3	Constant (10.0)
Sensor group 4	Constant (20.0)
Sensor group 5	Constant (0.01)
Sensor group 6	Constant (5.0)
Sensor group 7	Constant (10.0)
Sensor group 8	Constant (20.0)

Variance for each variable

Group selected Ungroup selected Set variance model...

To estimate: 2 physical model parameters, and 0 variance model parameters

Experiments & measurements Parameters to be estimated gPROMS language Properties

Setting-up the parameter estimation

The screenshot shows the gCRYSTAL Developer 4.0.0 interface. On the left, a project tree lists various components including 'gCRYSTAL Control', 'gCRYSTAL Fundamentals', 'gCRYSTAL Instrumentation', 'gCRYSTAL Kinetics', 'gCRYSTAL Unit Operations', 'AA custom models', and 'Fev14_Model_GCrystal'. Under 'Fev14_Model_GCrystal', there are sub-items for 'Models', 'Processes', 'Experiments', and 'Parameter Estimations'. The 'Parameter Estimations' folder is expanded, showing 'estimation_1', 'Test_Indus', 'Test_Indus_1', 'Test_Ramp', and 'test'. The main window displays the 'estimation_1' configuration. It features a table with the following columns: 'Parameter to be estimated', 'Initial guess', 'Fixed?', 'Lower bound', and 'Upper bound'. The table contains two rows: 'crystalliser_MSMPR001 → Activation energy' with an initial guess of 300.0 and bounds of 150.0 to 400.0, and 'crystalliser_MSMPR001 → Rate constant' with an initial guess of 200.0 and bounds of 150.0 to 400.0. A large blue arrow points to the table with the text 'Kinetic parameters being estimated'. At the bottom, a status bar indicates 'To estimate: 2 physical model parameters, and 0 variance model parameters'.

Parameter to be estimated	Initial guess	Fixed?	Lower bound	Upper bound
crystalliser_MSMPR001 → Activation energy	300.0	<input type="checkbox"/>	150.0	400.0
crystalliser_MSMPR001 → Rate constant	200.0	<input type="checkbox"/>	150.0	400.0

Kinetic parameters being estimated

To estimate: 2 physical model parameters, and 0 variance model parameters