Federal Environmental, Industrial and Nuclear Supervision Service

Scientific and Engineering Centre
for Nuclear and Radiation Safety

EUROSAFE 2019

ETSON EUROPEAN TECHNICAL SAFETY ORGANISATIONS NETWORK

Methodology of an explosion safety assessment of sorption processes for SNF and waste treatment

A. Rodin
PhD, Head of laboratory

FCF Explosion Accidents

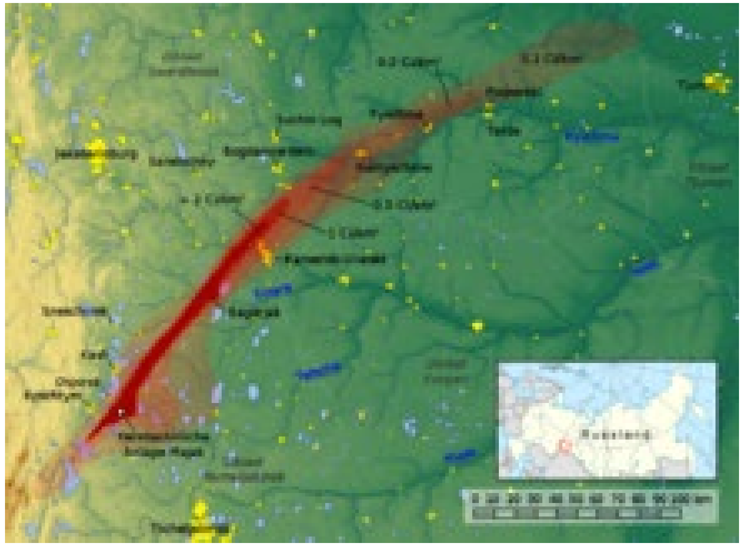
explosions of RW storage tank «Mayak», 1957.

«red oil» explosions:

- Savannah River plant,1953
- Hanford site,1953
- Oak Ridge laboratory, 1959
- Savanna River plant, 1975
- «SHK», Seversk, 1993

Sorption equipment explosions

- Fontenay-aux-Roses,1962
- Plant «Rocky Flats»,1963
- Hanford Site, 1963
- Savannah River, 1964
- Brookhaven National Laboratory,1965
- Kerr McGee, 1967
- Oak Ridge National Laboratory, 1967
- Hanford Site, 1976
- PA "Mayak" и "SHK"

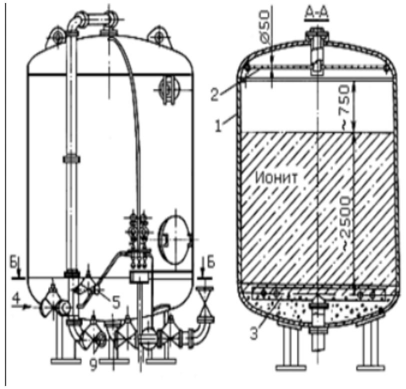


«SHK», Seversk, 1993

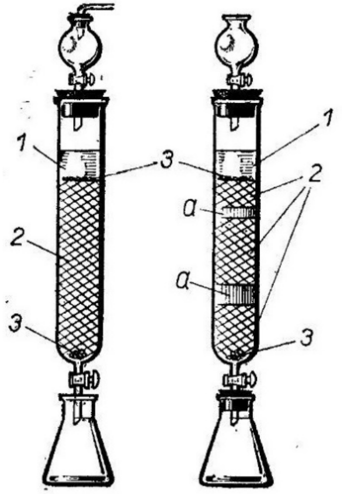
The usage of organic resins on Nuclear Fuel Cycle Facilities

- water conditioning
- selective separation of radionuclides (Pu/Am, Am/Cm)
- preparation chromatography
- LRW processing
- storage of spent resin

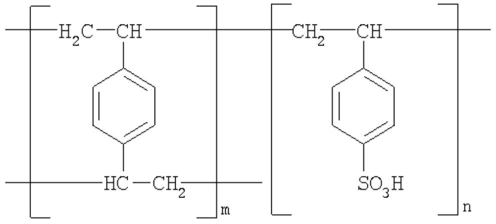
Sorption equipment:



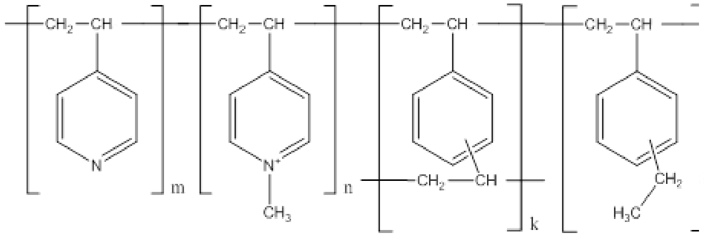
~ m^3
~ dm^3
~ cm^3



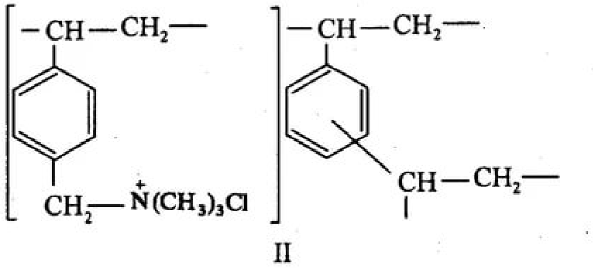
Resin Ku-2 (cationit)



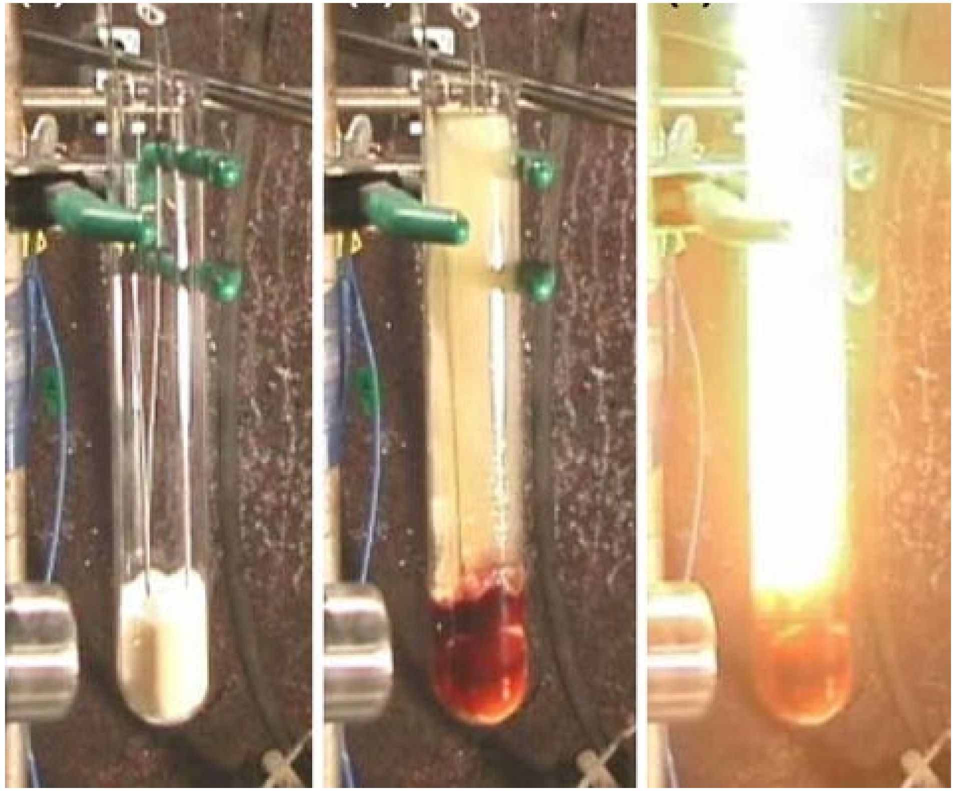
Resin VP-1AP



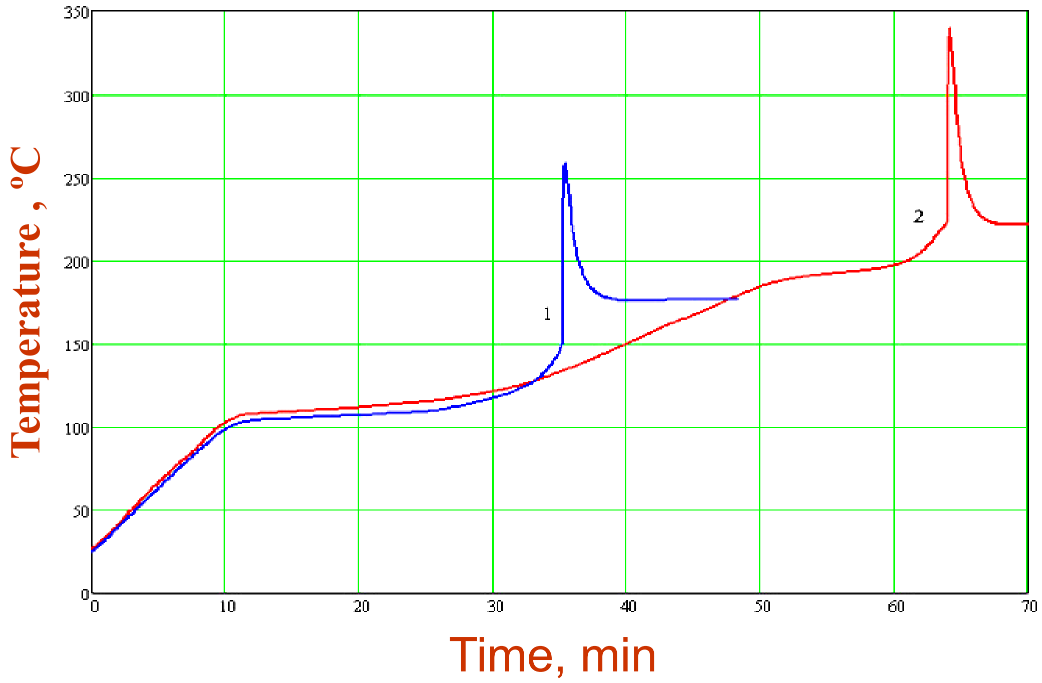
Resin AV-17x8 (Cl^- form)



Runaway processes with resins

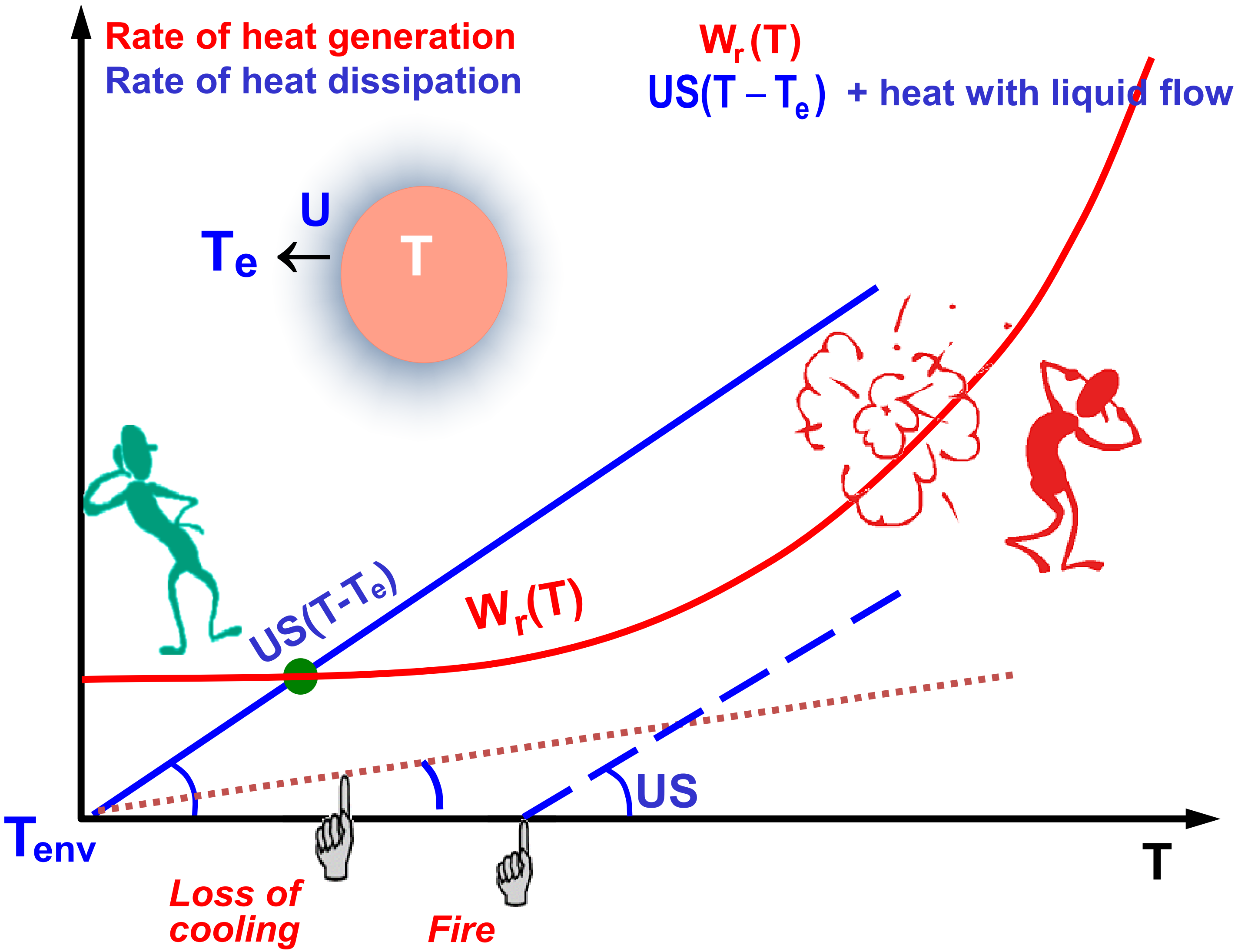


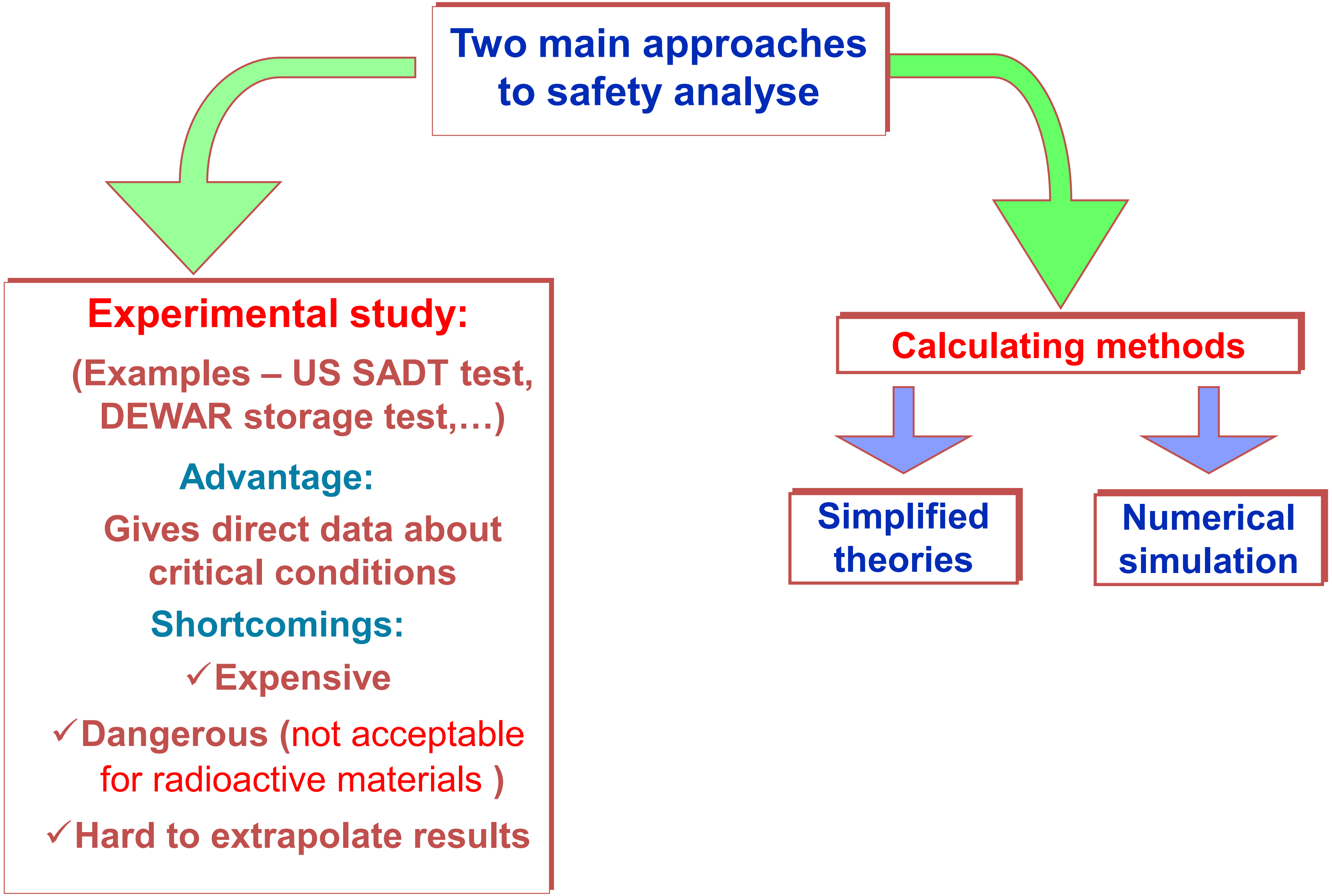
J Therm Anal Calorim (2009) 97:769–774



A-500U with complex thorium gexanitrat in 8 M HNO_3.
1 - with exposure to 2 MGy, 2 - without irradiation.

Theory of runaway reactions




Two main approaches to safety analyse
Experimental study:
(Examples – US SADT test, DEWAR storage test,…)
Advantage:
Gives direct data about critical conditions
Shortcomings:
✓Expensive
✓Dangerous (not acceptable for radioactive materials)
✓Hard to extrapolate results
Calculating methods
Simplified theories
Numerical simulation

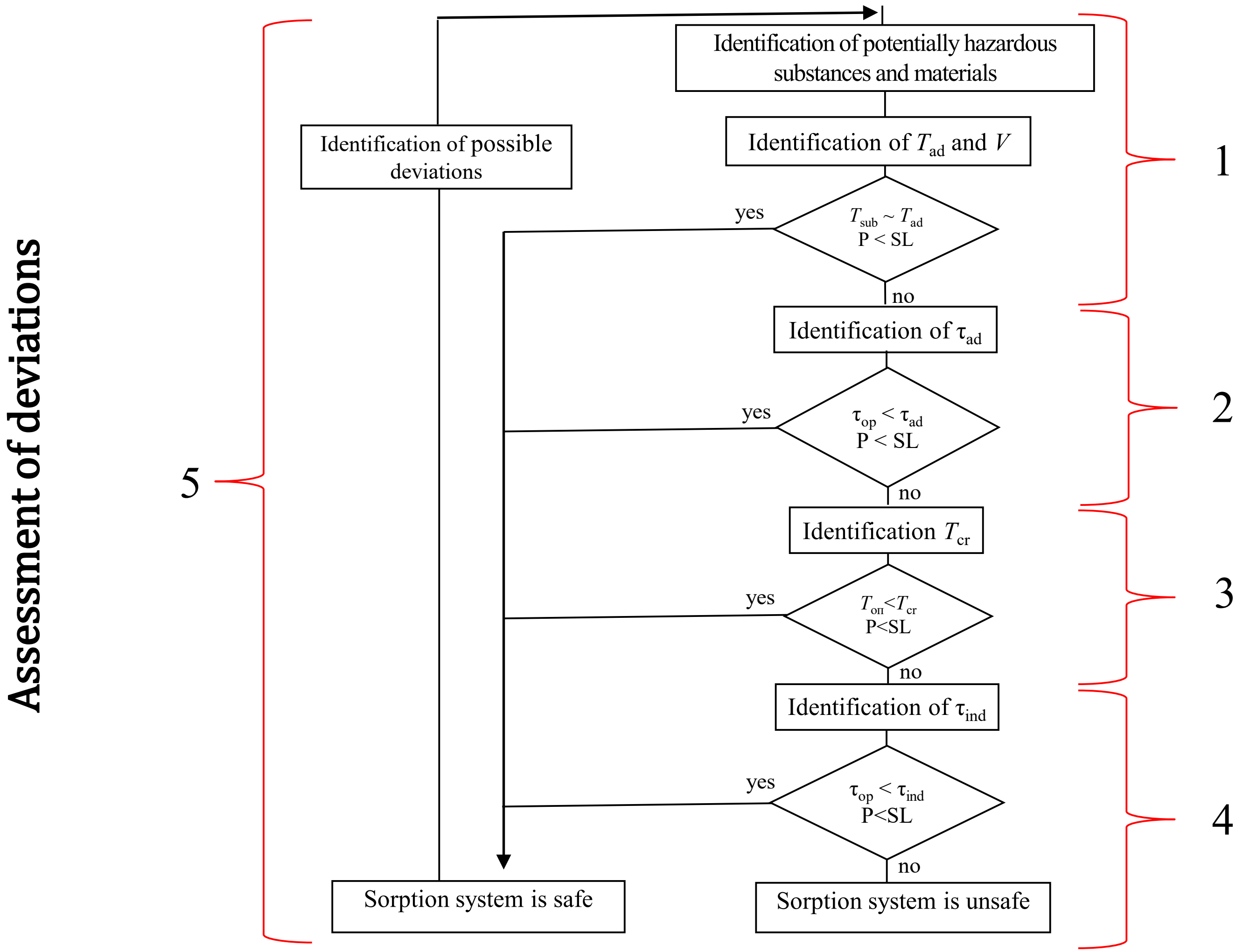
Limitations of «classical» methods:

- only one stage reaction (**zero-order reaction, auto-catalytic reaction**);
- only simple geometry;
- simple boundary condition;
- not allow to take into account additional external (Fire) and internal heat source (Rad.nuclides).

$$\left.\begin{aligned} \mathbf{Pu}^{238}\,(\alpha) &= 0.57\ W/g \\ \mathbf{Cm}^{244}\,(\alpha) &= 2.8\ W/g \\ \mathbf{Cm}^{242}\,(\alpha) &= 122\ W/g \end{aligned}\right\} \simeq 36\ W/K\_cu$$

$$\mathbf{Cs}^{137}\,(\beta, \gamma) = 0{,}15\ W/g \qquad \simeq 4{,}8\ W/K\_cu$$

The safety assessment scheme

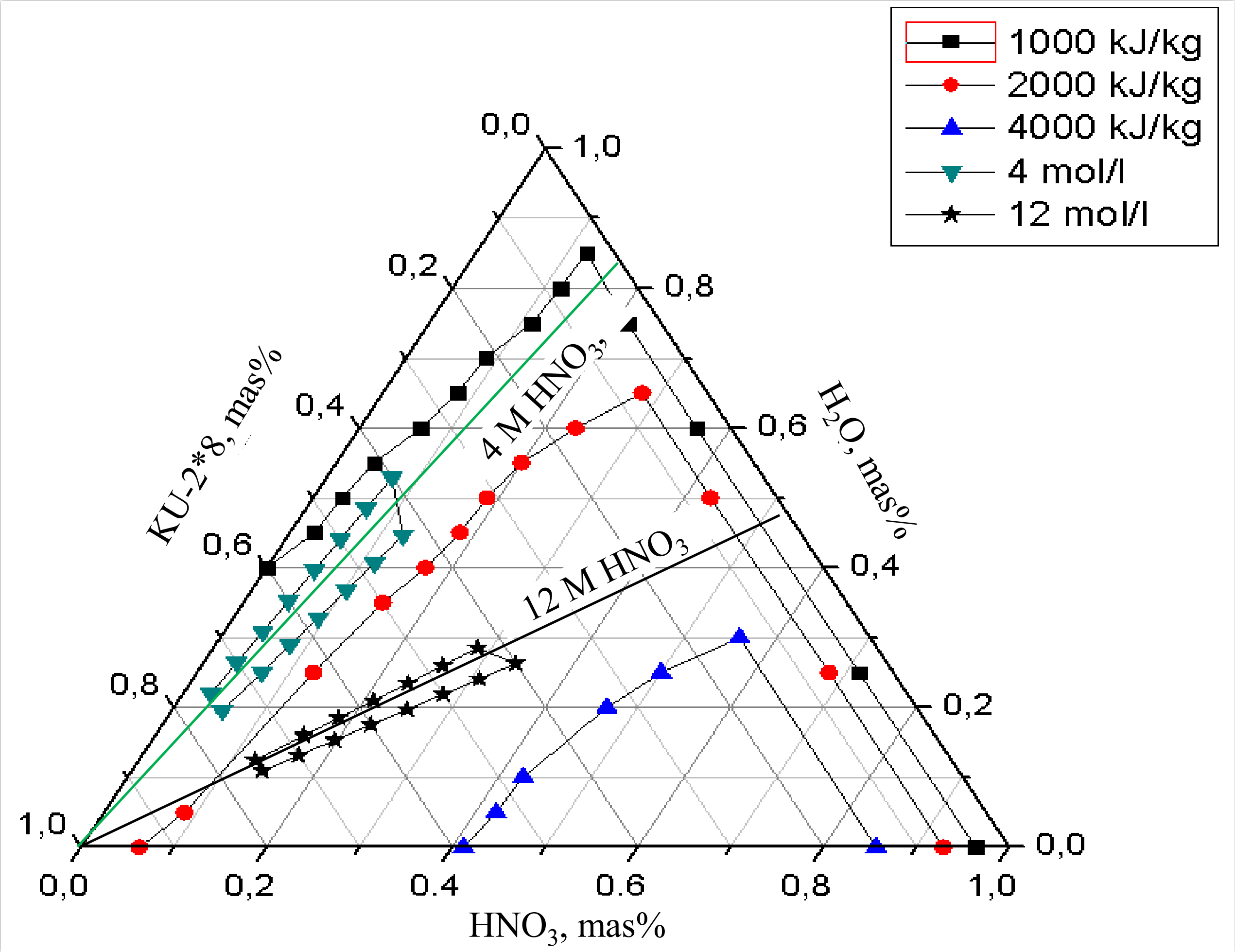


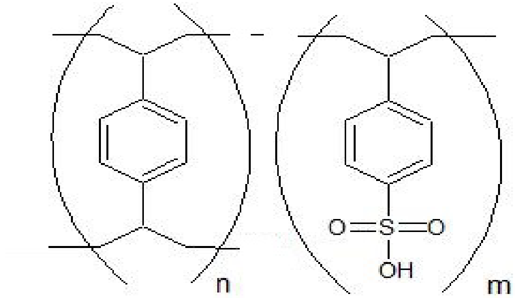
Thermodynamic assessment

Adiabatic calculation
(+ experimental study of reactions chemistry)

Non-adiabatic calculation

Thermodynamic assessment





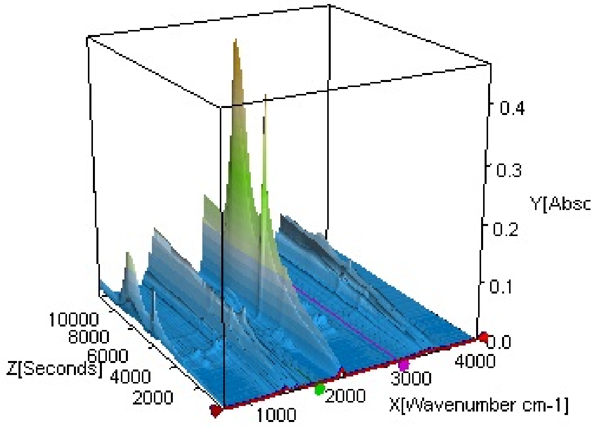
$C_{18}H_{16}SO_3H_s + nHNO_{3_l}$

- n=1.5 → $16.875C_s + 0.75N_{2_g} + S_s + 4.5H_2O_l + 1.125CH_{4_g}$
- n=7 → $12.25C_s + 3.5N_{2_g} + S_s + 12.5H_2O_l + 5.75CO_{2_g}$
- n=20 → $9N_{2_g} + 17H_2O_l + 18CO_{2_g} + 2HNO_{3_l} + H_2SO_{4_l}$

$$\Delta T_{ad} \approx Q / C_p > 500\ °C$$

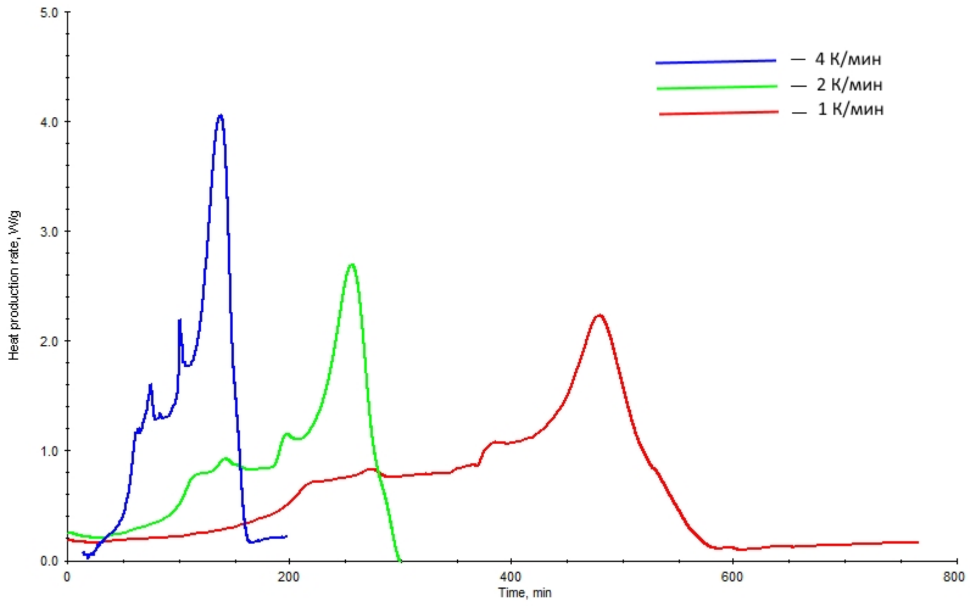
Adiabatic calculation

Main issues:
- create kinetic model of chemical reactions;
- take into account all heat source during modeling.



NETZSCH STA 449 f3 Jupiter + FTIR Bruker

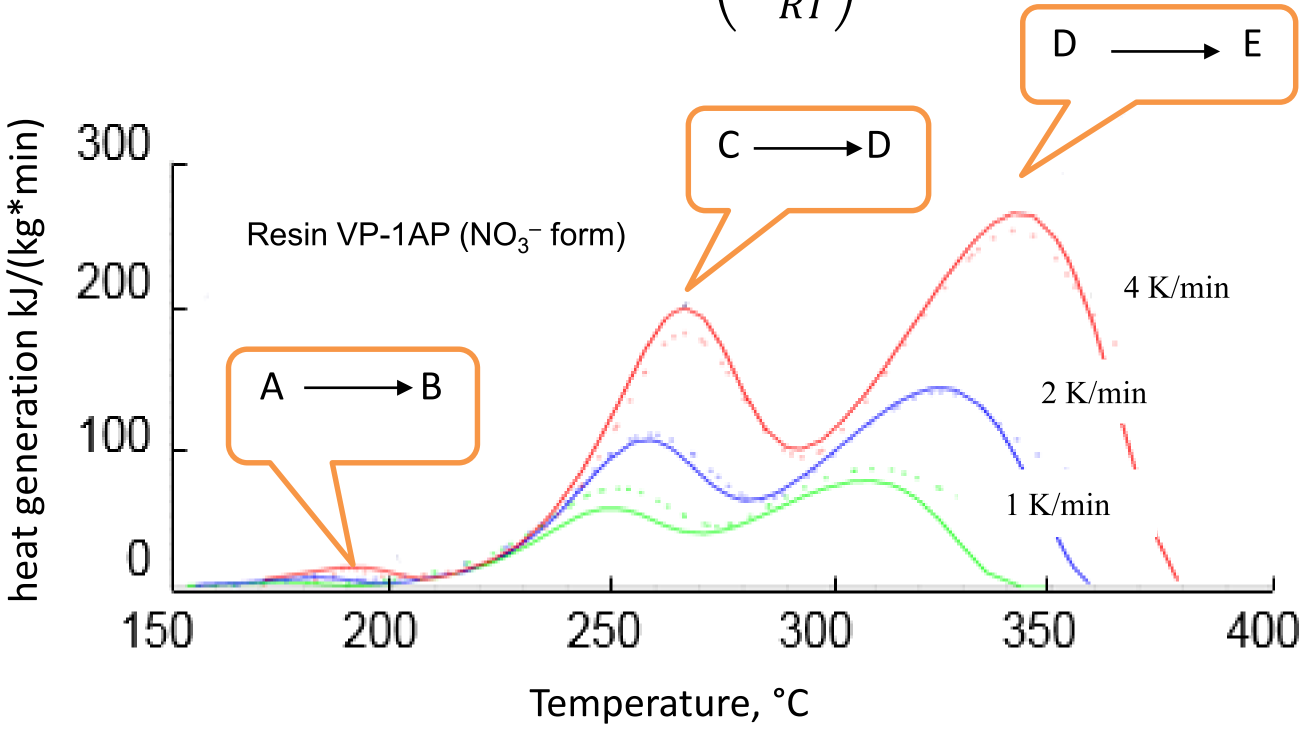
DSC experiment



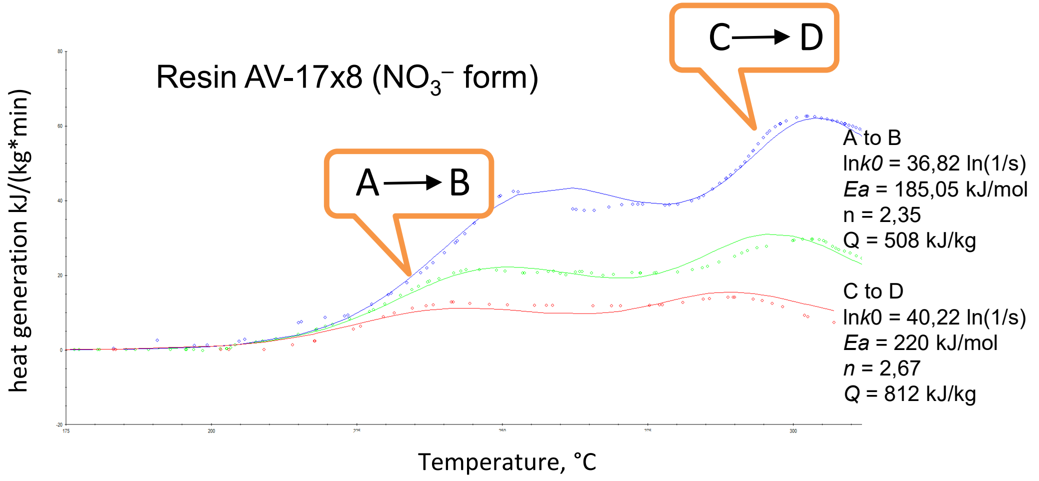
Data processing, estimation kinetic parameters and modeling by using TSS (CISP spb)

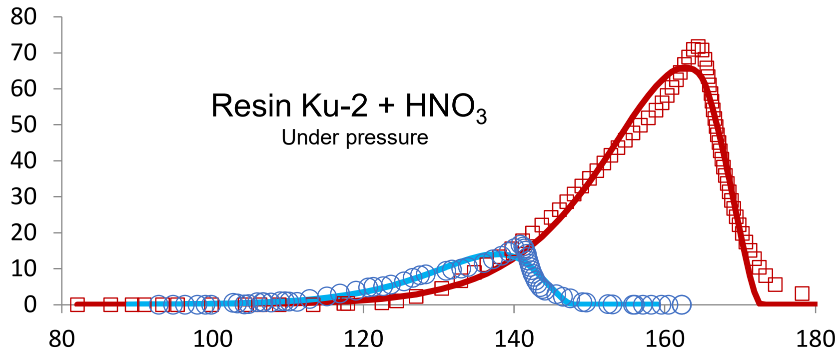
Developing the 'formal' model of chemical reactions

n - order reactions → $w_i = k_{0i} * \exp\left(-\frac{E_{a_i}}{RT}\right) * (1-\alpha)^{n_i}$



	A to B	C to D	D to E
$\ln(k_{0i})$, ln(1/s)	31,1±1,1	33,2±1,2	24,6±0,9
Ea_i, kJ/mol	140±4,2	172,1±4,4	151,2±3,9
N_i	0,8±0,06	1,35±0,12	3,05±0,35
Q_i, kJ/kg	130±18	2090±120	6450±270





proto reaction → $q_i = k_{0_i} \times exp\left(-\frac{E_{a_i}}{RT}\right) \times \alpha^{n_2} \times (1-\alpha)^{n_3} Q_i$

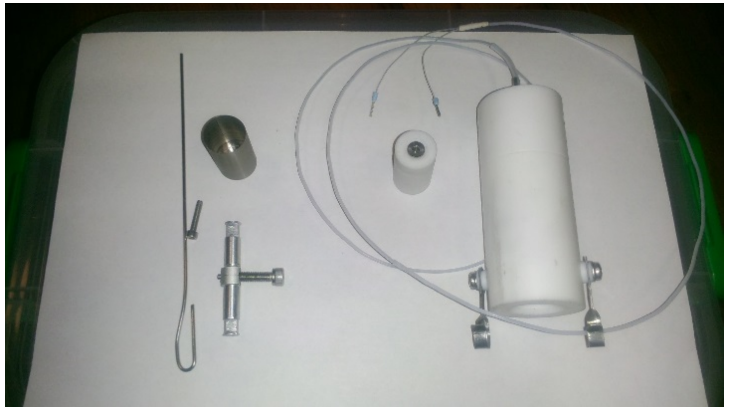
$\ln(k_0)$, ln(1/c)	E_a, kJ/mol	n_2	Q, kJ/kg	n_3
21,1	93,5	0,41	287	0,62

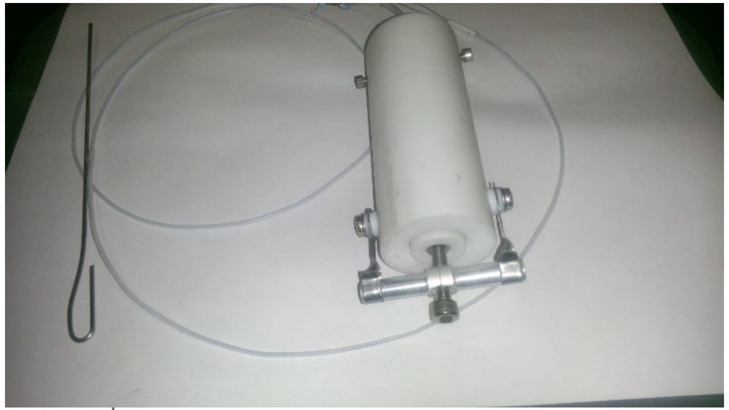
Validation of the models

Scale Up experiment:

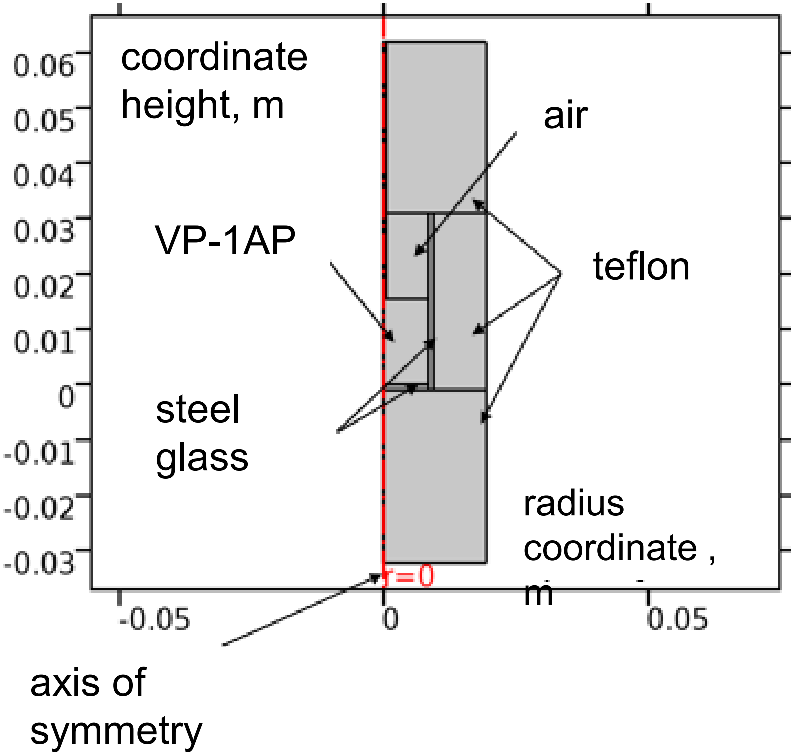
from 10 - 15 mg to 2 - 3 g (~200 times)

Experimental cell

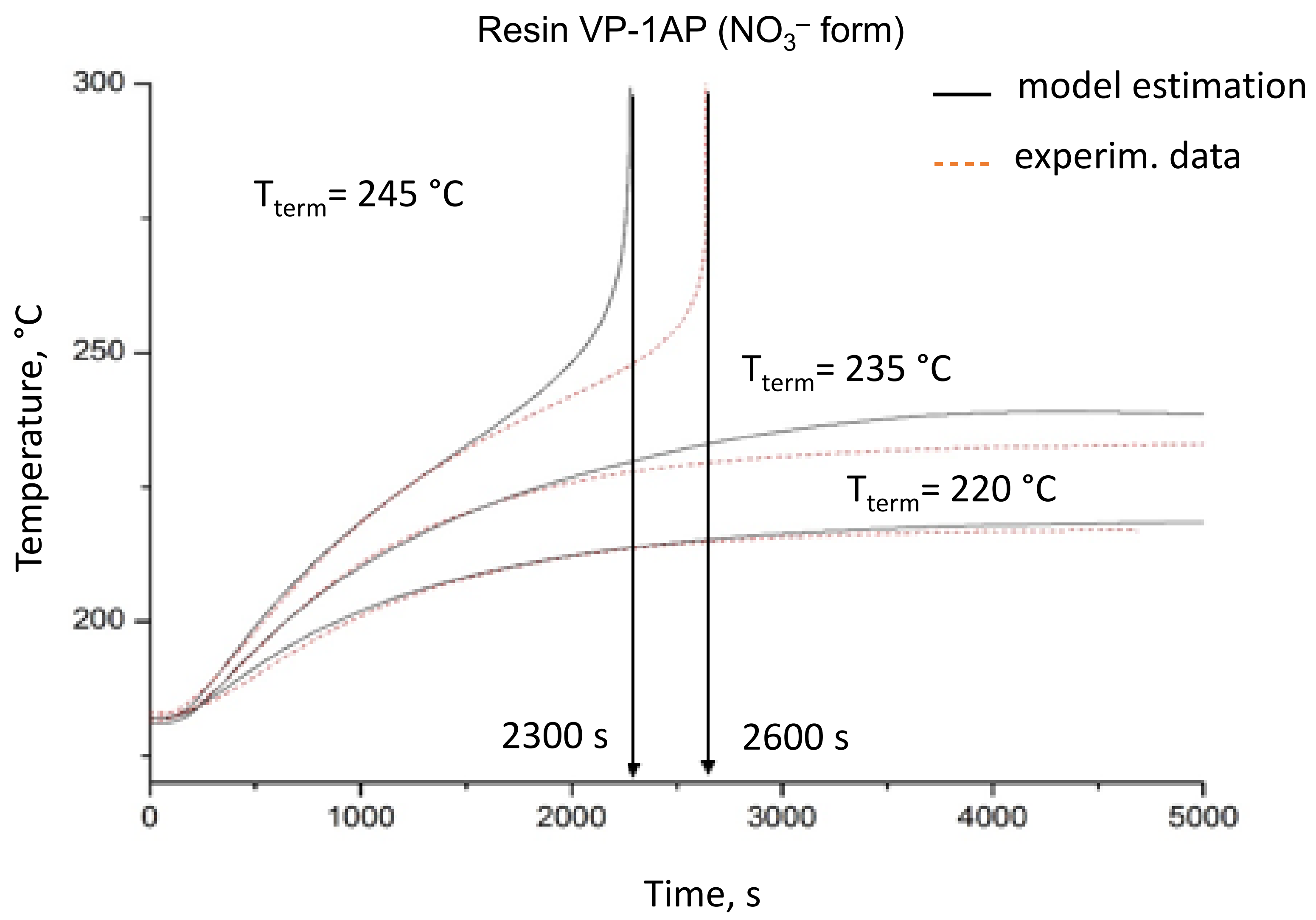


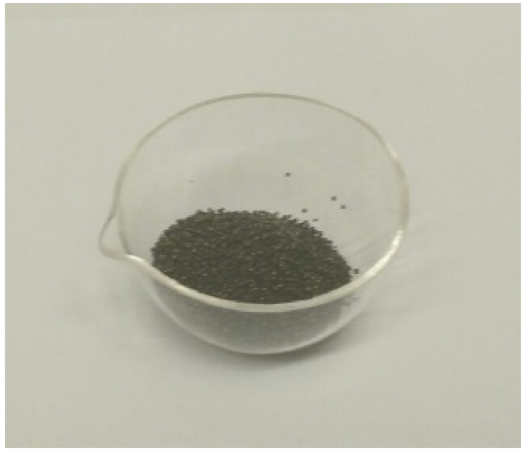


Mathematical model of cell



Results of Scale Up experiment:





Adiabatic calculation (conservative assumption)

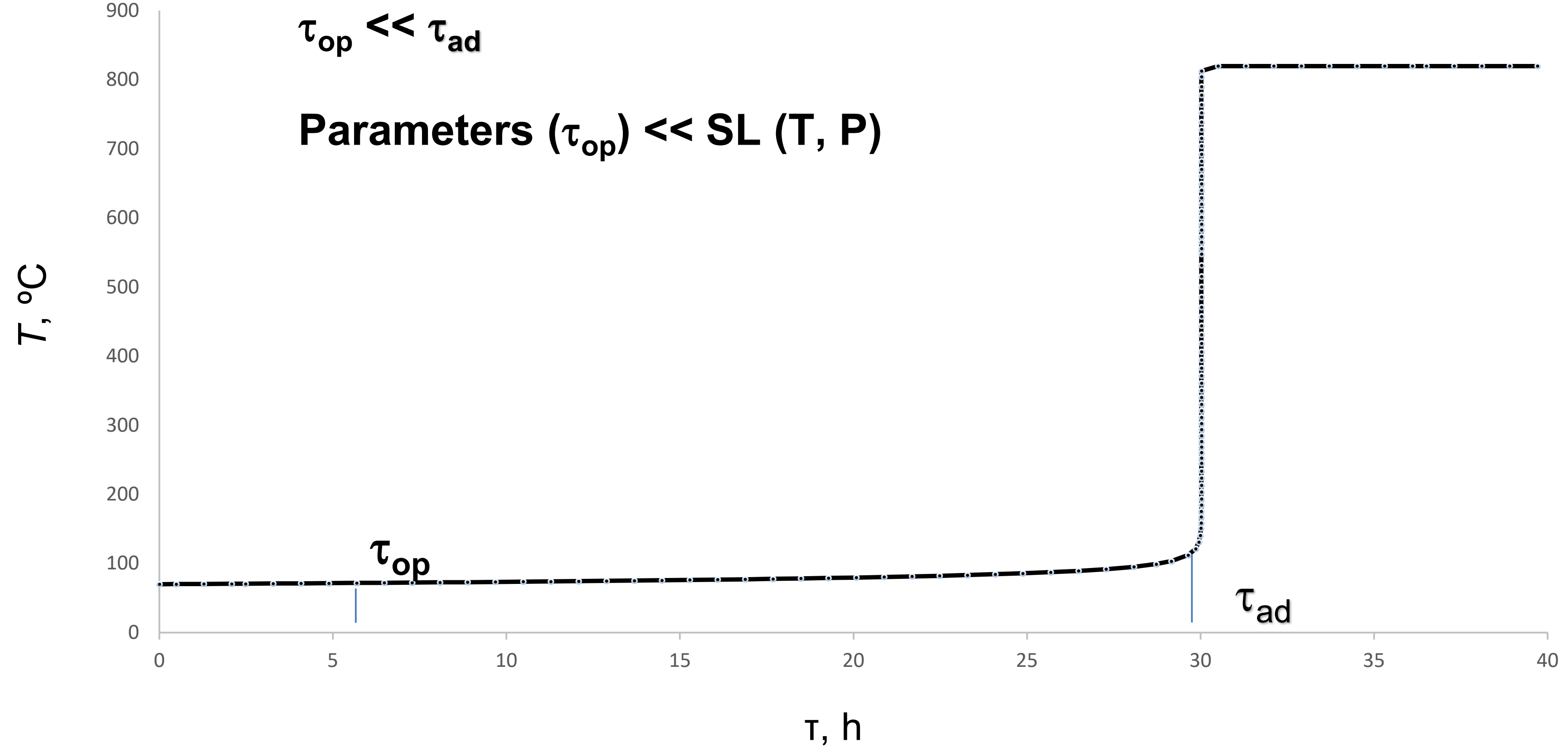
τ_{op} – time of normal operation

τ_{ad} – time to maximum rate under adiabatic condition

Safety criteria:

$\tau_{op} << \tau_{ad}$

Parameters (τ_{op}) << SL (T, P)

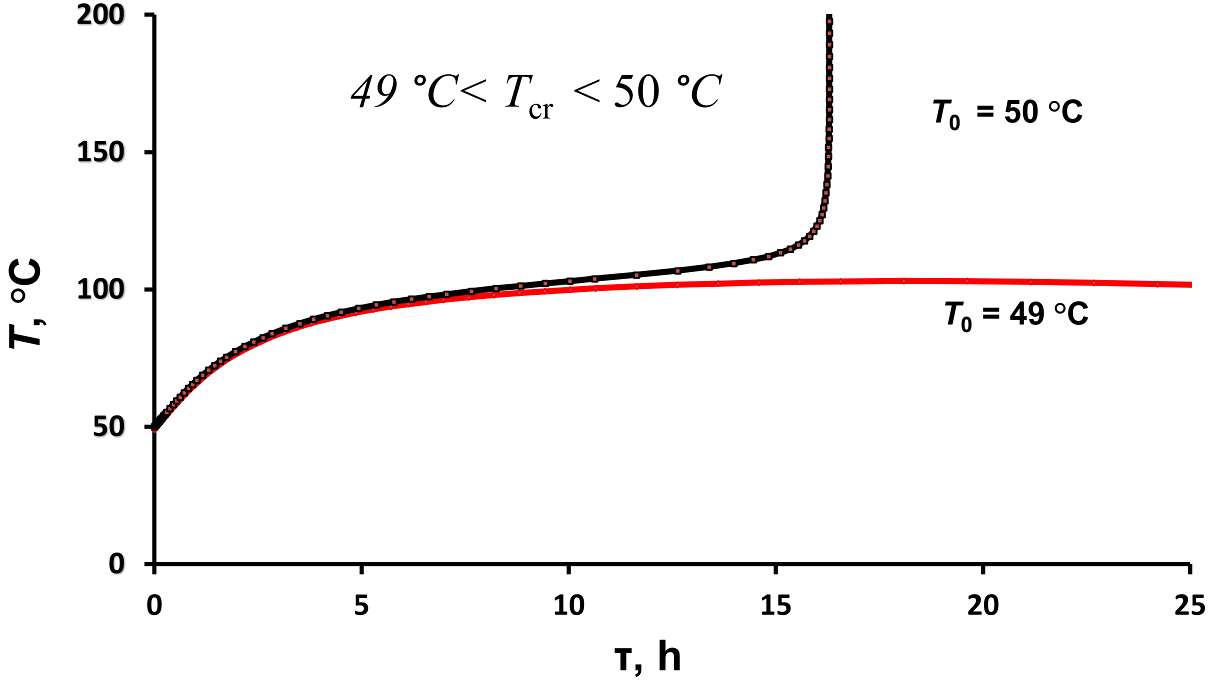


Non-adiabatic calculation

- critical temperature (step 3)
- time to maximum rate (step 4)

τ_{op} – time of normal operation

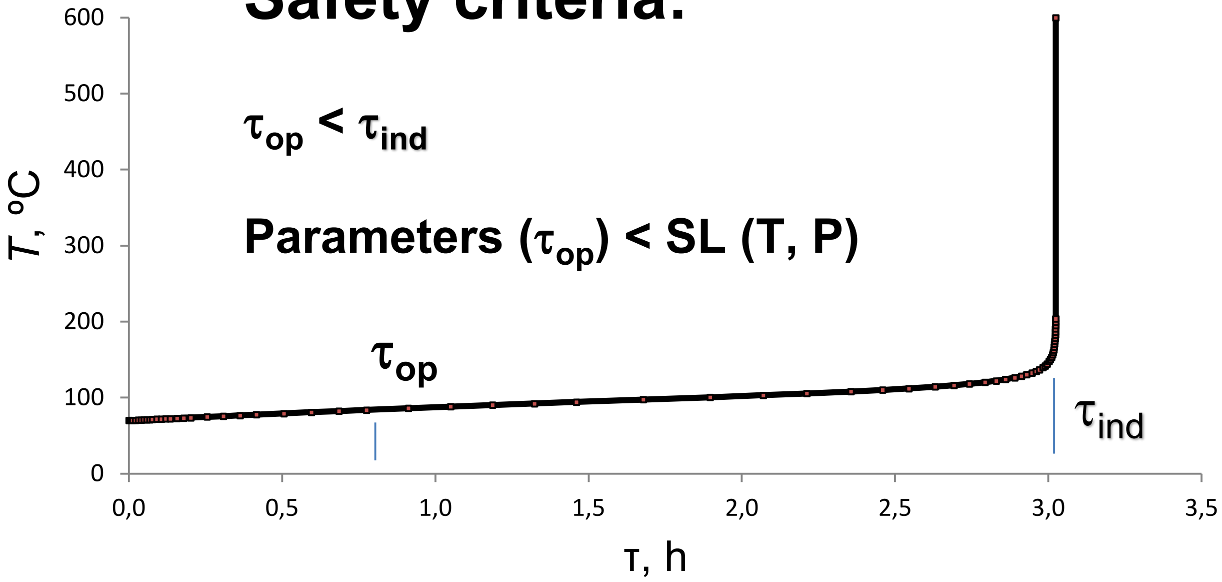
τ_{ind} – time to maximum rate



Safety criteria:

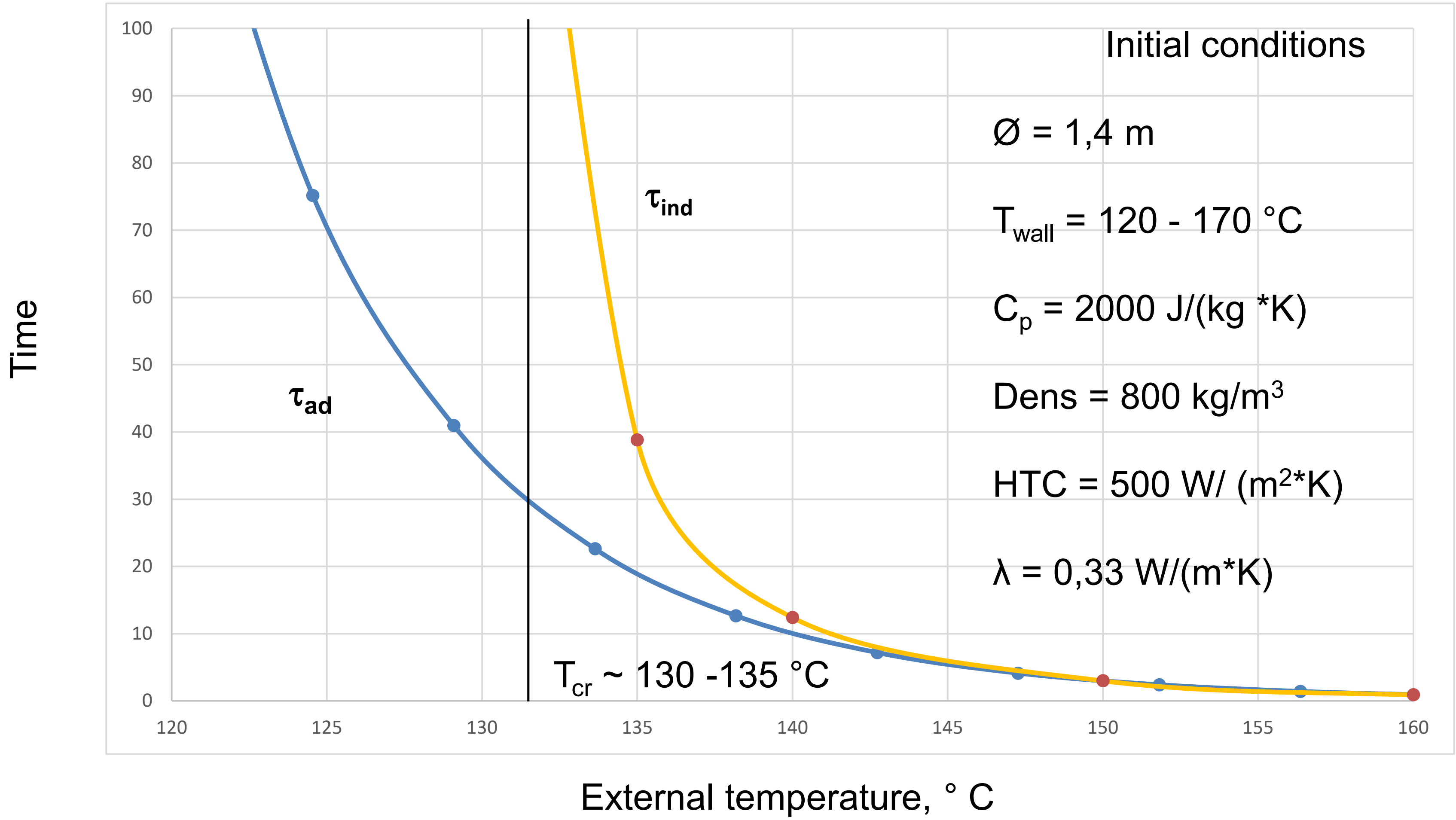
$\tau_{op} < \tau_{ind}$

Parameters (τ_{op}) < SL (T, P)



Difference between τ_{ind} and τ_{ad}

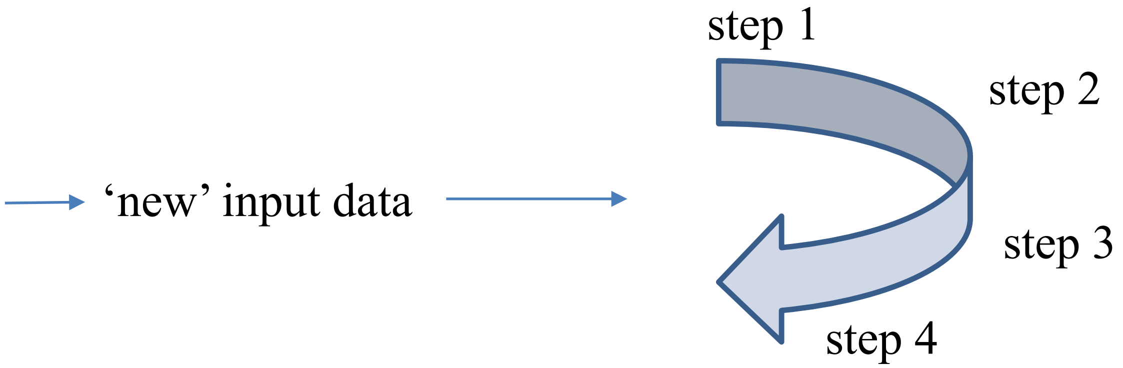
AV-17*8 in nitrate form

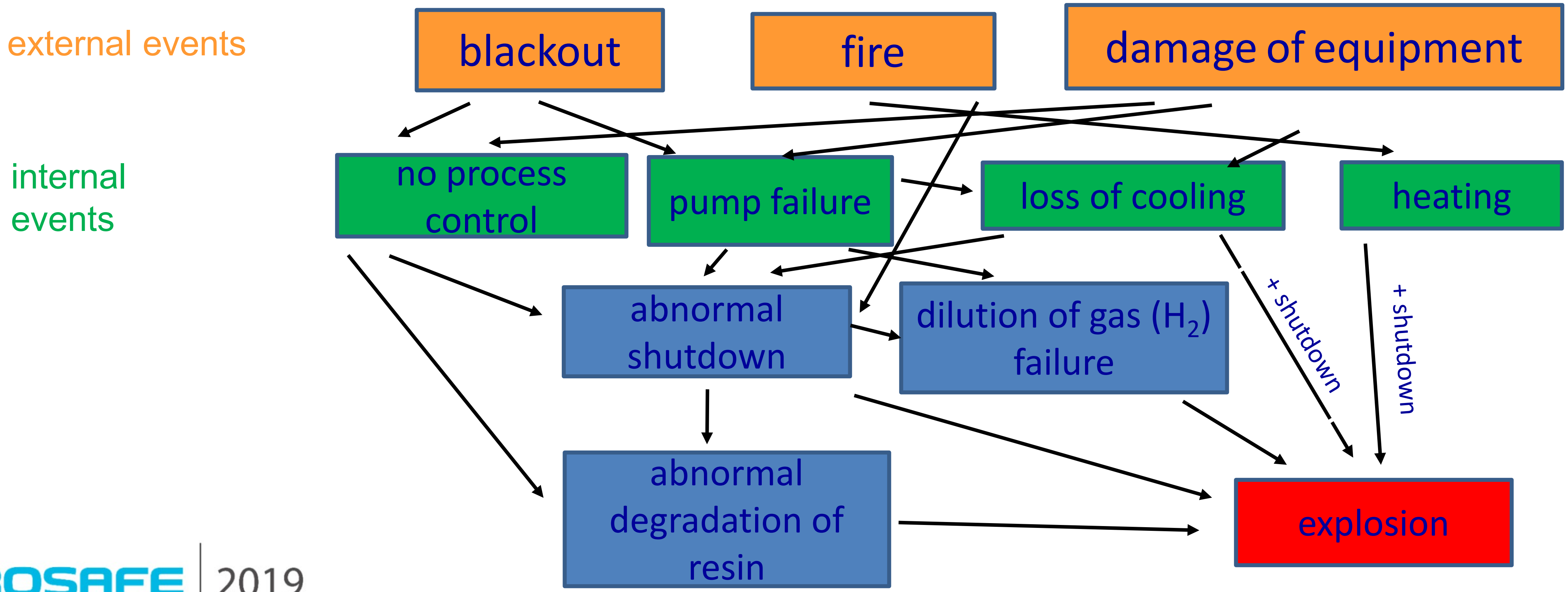


Analysis of process parameters deviations

Major events are recommended to be considered:

– errors or failures that lead to the loading of additional heat sources (increased concentration of radionuclides);
– process shutdown for a long period;
– contact of the resin with high concentration nitric acid;
– errors in reagent dosing sequence.





Approach allows

- to assess safety under normal operation condition;
- to estimate influence of process parameter deviation, including scenario of DBAs and DEC;
- to estimate time to take a decision;
- to develop emergency measures (estimation of effectiveness);
- to justificate safety for NFCF operator.

- for TSO it allows to save a resource, when process parameters far away from critical points, and provide detailed safety assessment with taking into account many aspects, if necessary

Thank you for attention!