CO_2PipeHaz

Modelling Dry Ice Formation Following Rapid Decompression of CO_2 Pipelines

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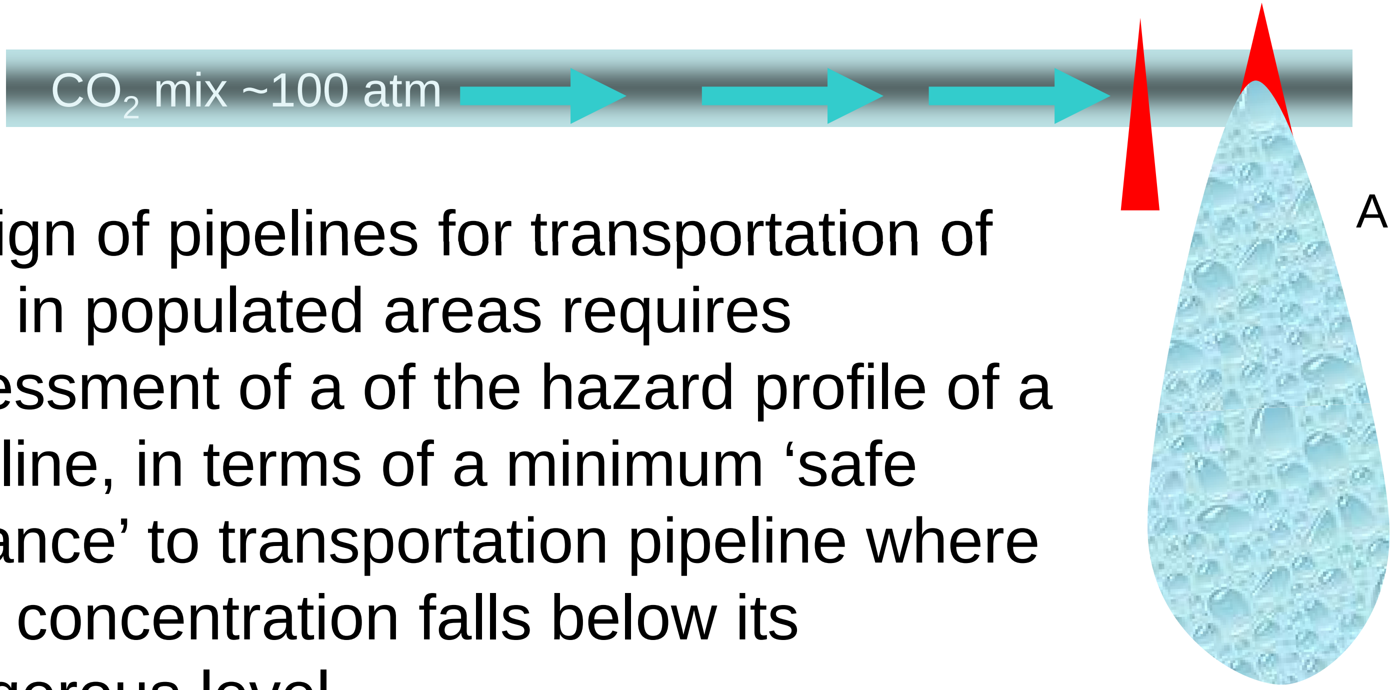
Presentation Structure

- Motivation and Objectives
- HEM model of an outflow from a pipeline
- A cubic EoS for solid-vapour CO_2
- Sensitivity study of the effect of dry ice formation on the outflow
- Conclusions

Motivation and Objectives

Modelling accidental releases



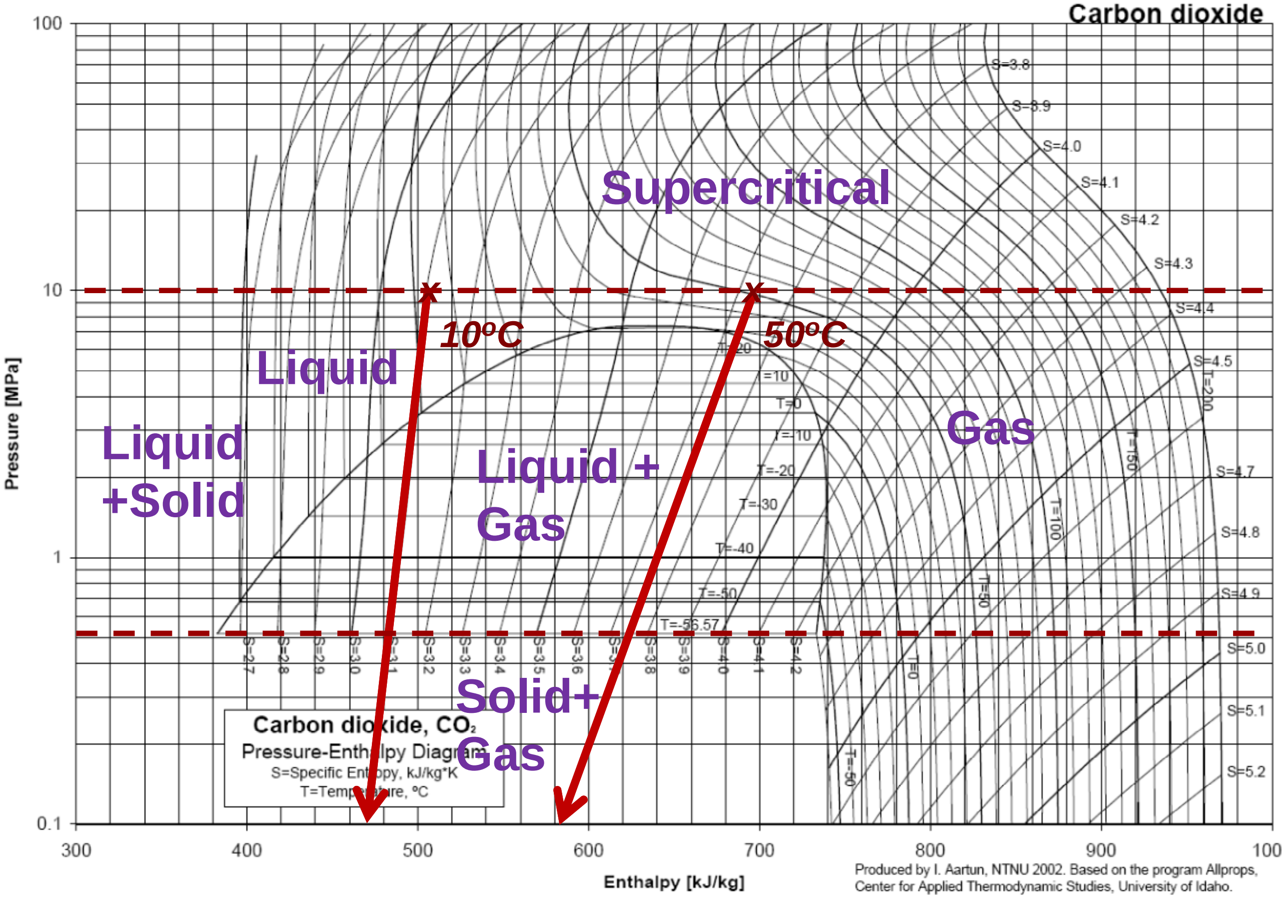
- Design of pipelines for transportation of CO_2 in populated areas requires assessment of a of the hazard profile of a pipeline, in terms of a minimum ‘safe distance’ to transportation pipeline where CO_2 concentration falls below its dangerous level
- This involves analysis of release ad atmospheric dispersion of the pipeline material caused by the pipeline puncture or rupture

Modelling accidental releases

- In the past methodologies for assessment of the pipeline hazard profile were developed assuming the fluid in a liquid or vapour state
- However, due to large values of the Joule-Thomson coefficient of CO_2, its rapid expansion from compressed state can be accompanied by significant cooling effect, resulting with formation of solids (“dry ice”)

Modelling accidental releases

An isentropic expansion in *p-h* diagram



Produced by I. Aartun, NTNU 2002. Based on the program Allprops, Center for Applied Thermodynamic Studies, University of Idaho.

Modelling accidental releases

- Experiments confirm that solid CO_2 can form upon release from high-pressure vessels

- The processes of sublimation and rainout of solids in the flow may affect

 - the atmospheric dispersion of CO_2 and
 - the hazard profile of the pipeline

Modelling accidental releases

- Many conventional packages for modelling of the fluid release and atmospheric dispersion calculate the physical properties of the fluid using cubic Equation of State (EoS)
- A cubic EoS typically covers the liquid and vapour states of a substance, and hence is not valid in the solid phase region

Objectives

- To develop a model for calculation of thermodynamic properties of CO_2 in the solid phase region, using the framework of cubic EoS
- To study the effect of solid formation on the outflow from a high-pressure CO_2 transportation pipeline

Homogeneous Equilibrium Mixture (HEM) model of an outflow from a pipeline (PipeTech code)

Model of Release from a Pipeline

Main assumptions about the flow :

- one-dimensional (a straight long pipeline),
- transient,
- compressible,
- viscous,
- HEM: local thermodynamic and dynamic equilibrium between the phases (liquid/solid and vapour)

HEM: Governing Equations

The set of equations describing 1D flow in a straight pipe is:

- Mass conservation: $$\frac{d\rho}{dt} + \rho\frac{\partial u}{\partial x} = 0$$
- Momentum equation: $$\rho\frac{\partial u}{\partial t} + \rho u\frac{\partial u}{\partial x} + \frac{\partial P}{\partial x} = \alpha$$
- Energy conservation: $$\rho\frac{dh}{dt} - \frac{dP}{dt} - \left(q_h - u\beta_y\right) = 0$$

Where:

ρ, u, P and h are the density, velocity, pressure and specific enthalpy of the homogeneous fluid as function of time t and space x;

q_h is the heat transferred through the pipe wall to the fluid, β_y is the friction force term.

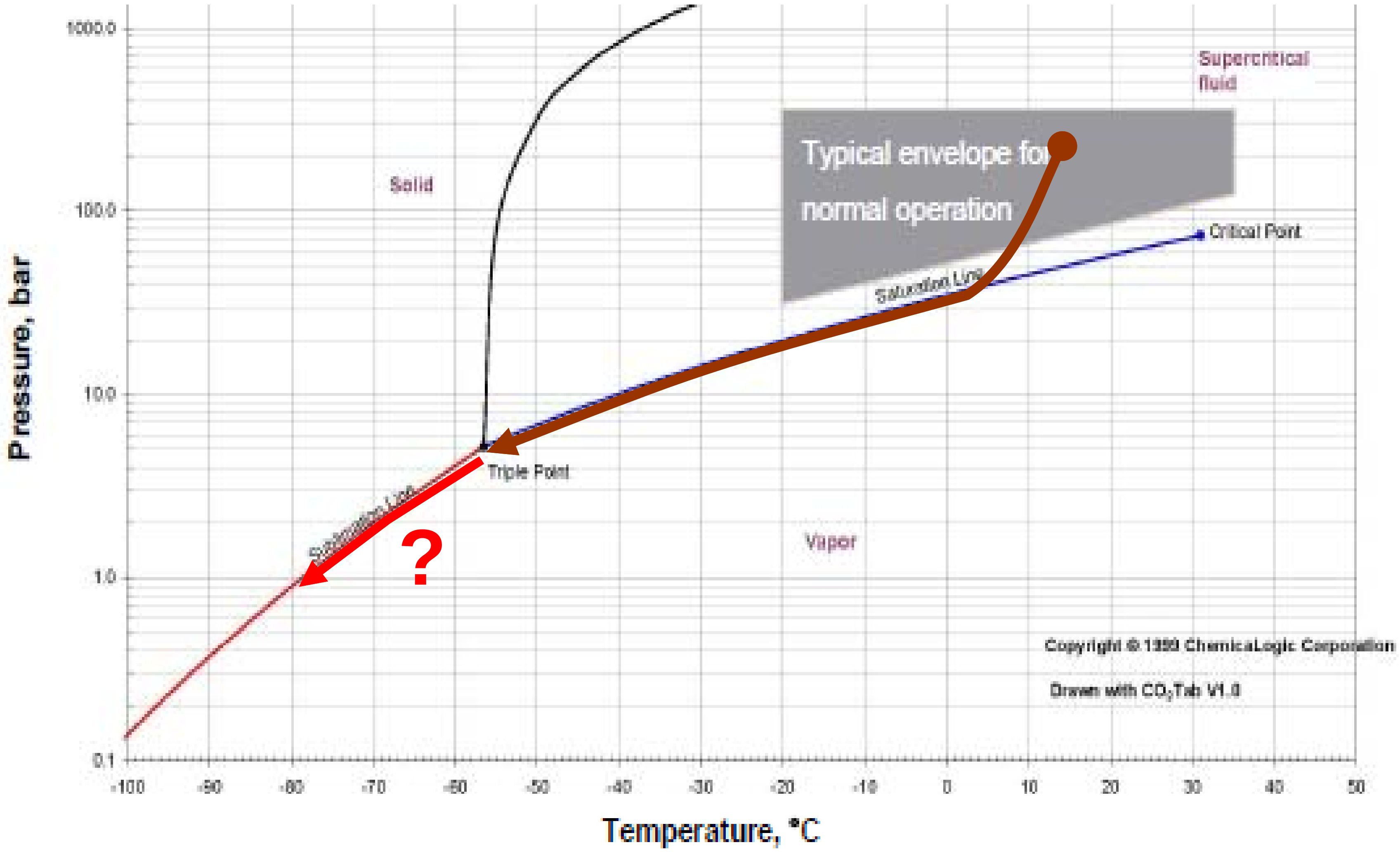
Numerical solution

The set of equation is completed by:

- correlations for calculation of the thermodynamic and transport properties of the homogeneous mixture
- the boundary and the initial conditions for the flow

The governing equations are solved numerically using the Method of Characteristics (MOC)

CO_2 pipeline decompression in *p-T* diagram



Properties of CO_2 in the vapour, liquid and solid phase regions

Equation of State (EoS) for solid CO_2

Peng-Robinson EoS:

$$Z^3 - (1-B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0$$

$$Z = \frac{pv}{RT}; \quad A = \frac{a(T)p}{R^2T^2}; \quad B = \frac{b(T)p}{RT}$$

$$a(T) = a_c \cdot \alpha(T)$$

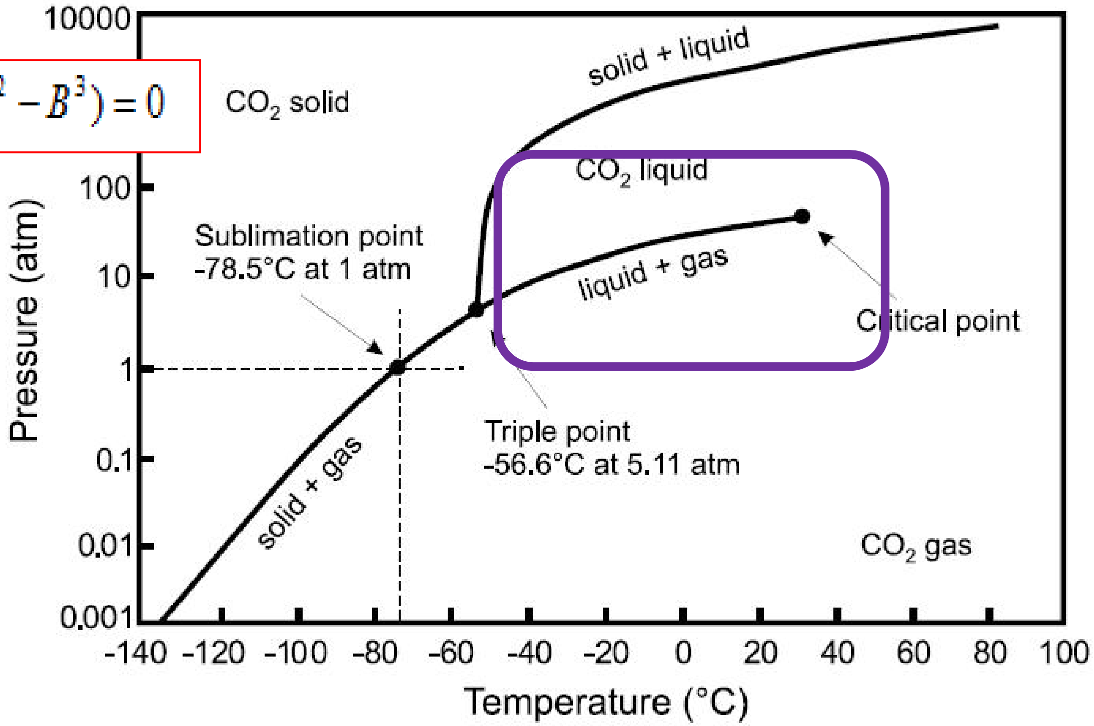
$$b(T) = b_c$$

$$a_c = 0.457 \cdot T_c^2 / p_c$$

$$b_c = 0.0778 \cdot T_c / p_c$$

$$\alpha(T) = \left[1 + \kappa(\omega)\left(1 - \sqrt{T/T_c}\right)\right]^2$$

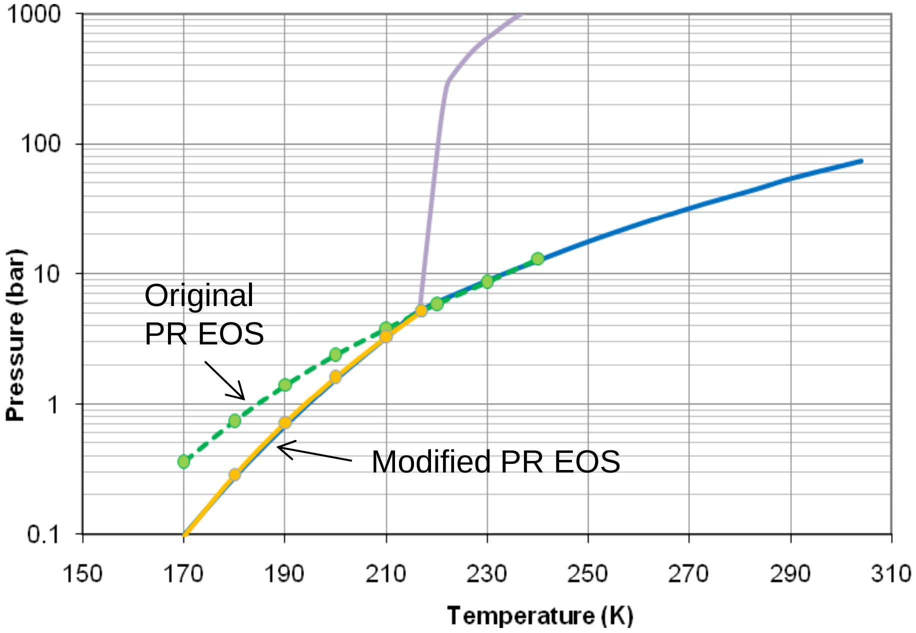
$$\kappa(\omega) = 0.37464 + 1.54226\omega - 0.26992\omega^2$$



In order to describe the solid-vapour equilibrium for CO_2, the parameters *a* and *b* are modified for temperatures below *Ttr* = 216.55 K.

Equation of State (EoS) for solid CO_2

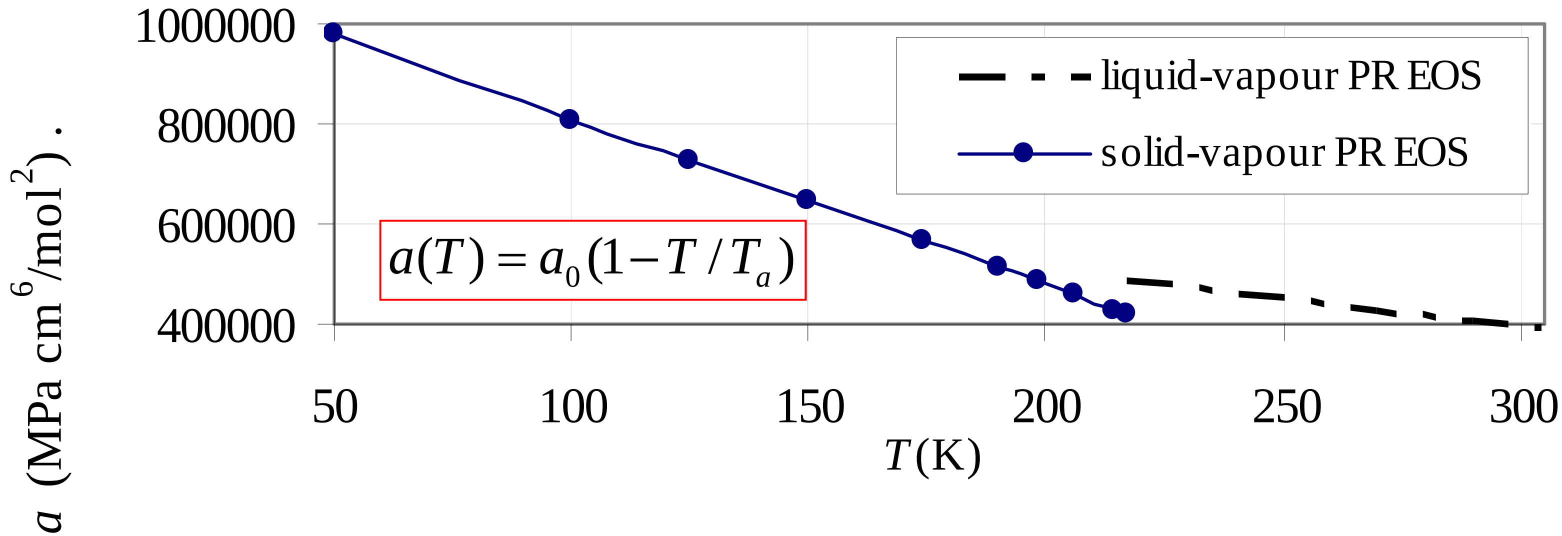
The functions *a(T)* and *b(T)* are fitted to match fugacities of solid and vapour states at sublimation line, assuming that sublimation pressure and density of the subliming solid are known from experiments

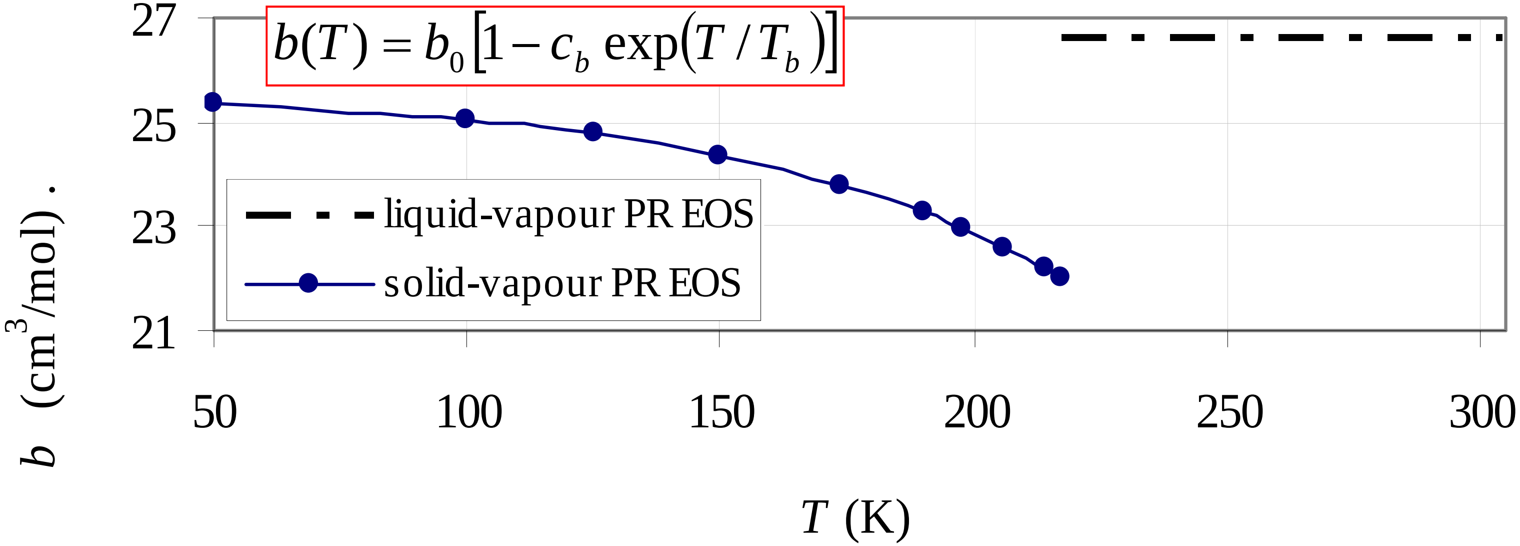


$$f_s(T_*, p_{subl}(T_*)) = f_g(T_*, p_{subl}(T_*))$$

$$\ln\frac{f}{p} = Z - 1 - \ln(Z - B) - \frac{A}{2\sqrt{2}B}\ln\left(\frac{Z + 2.414B}{Z - 0.414B}\right)$$

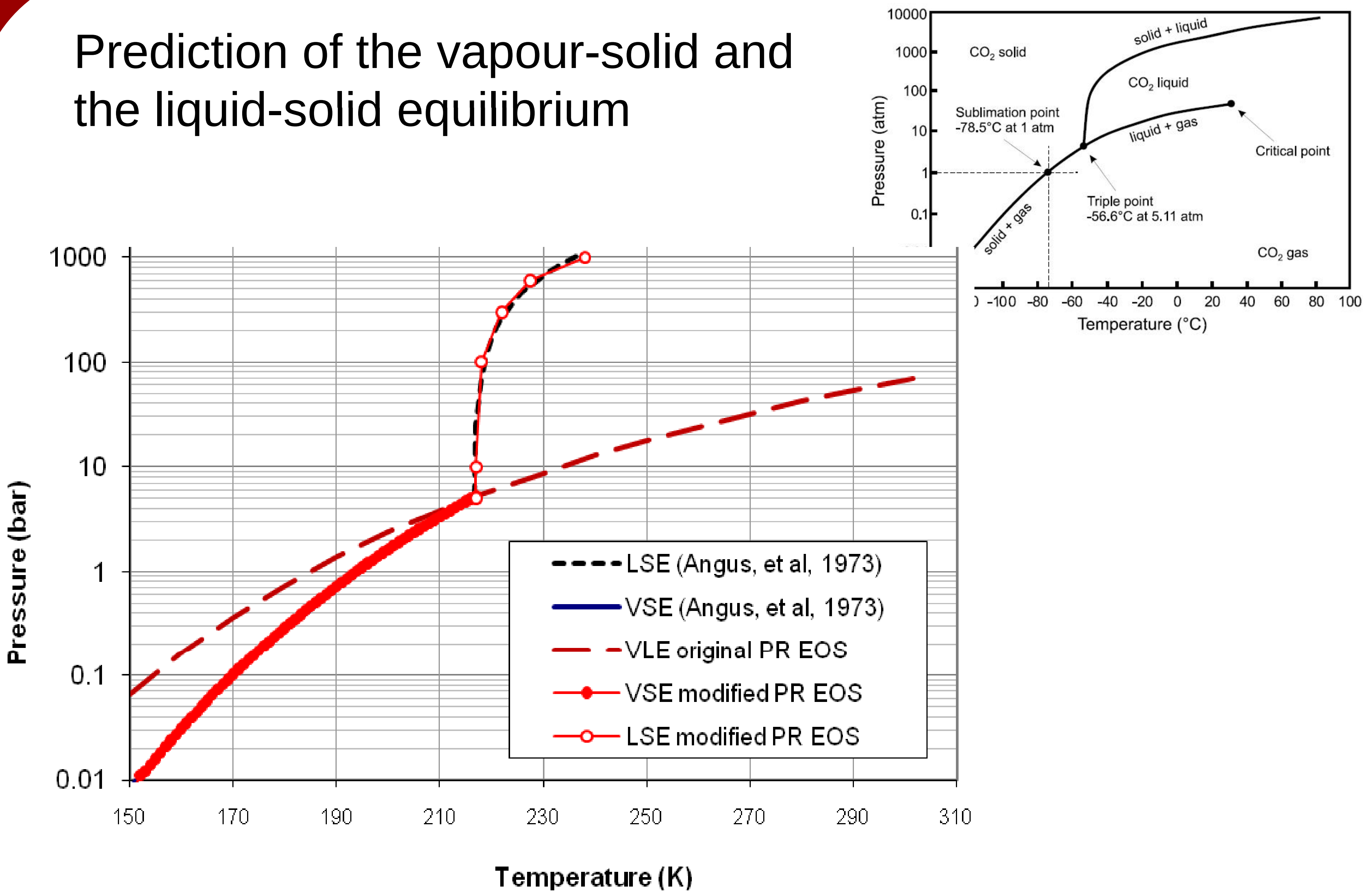
Parameters of the P-R EOS for solid CO_2


$$a(T) = a_0(1 - T/T_a)$$


$$b(T) = b_0\left[1 - c_b \exp\left(T/T_b\right)\right]$$

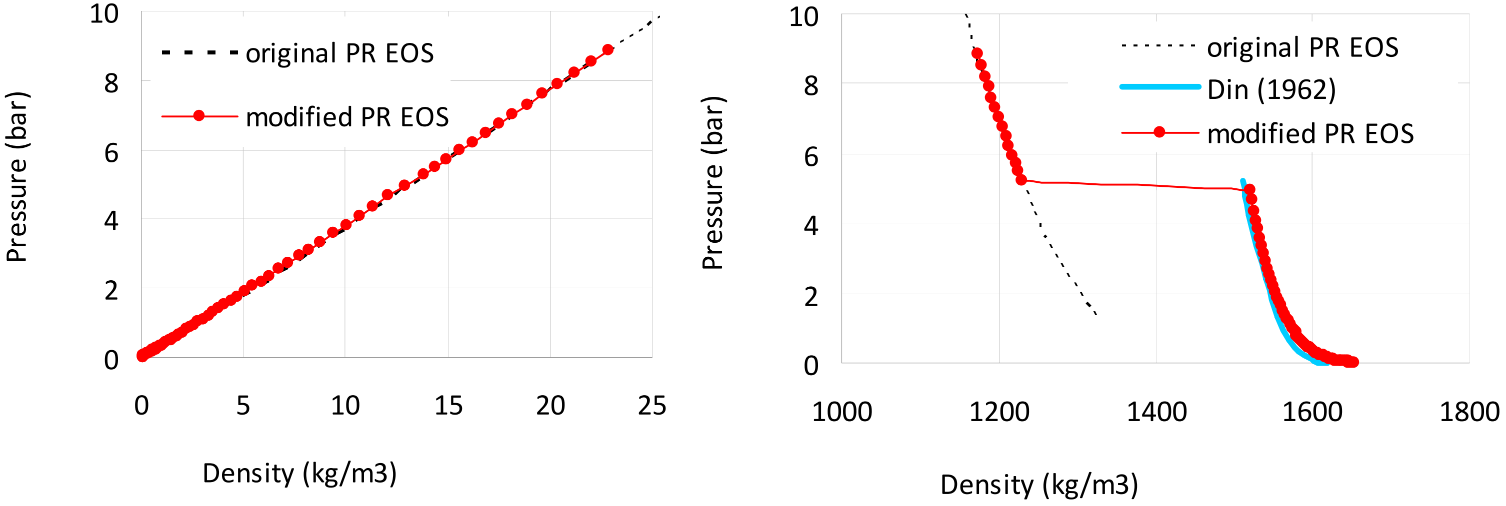
Thermodynamic properties of solid CO_2

Prediction of the vapour-solid and the liquid-solid equilibrium

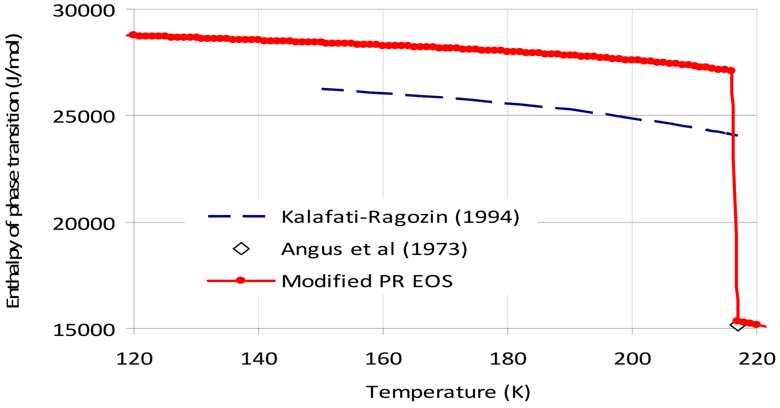


Thermodynamic properties of solid CO_2

Density of the subliming solid

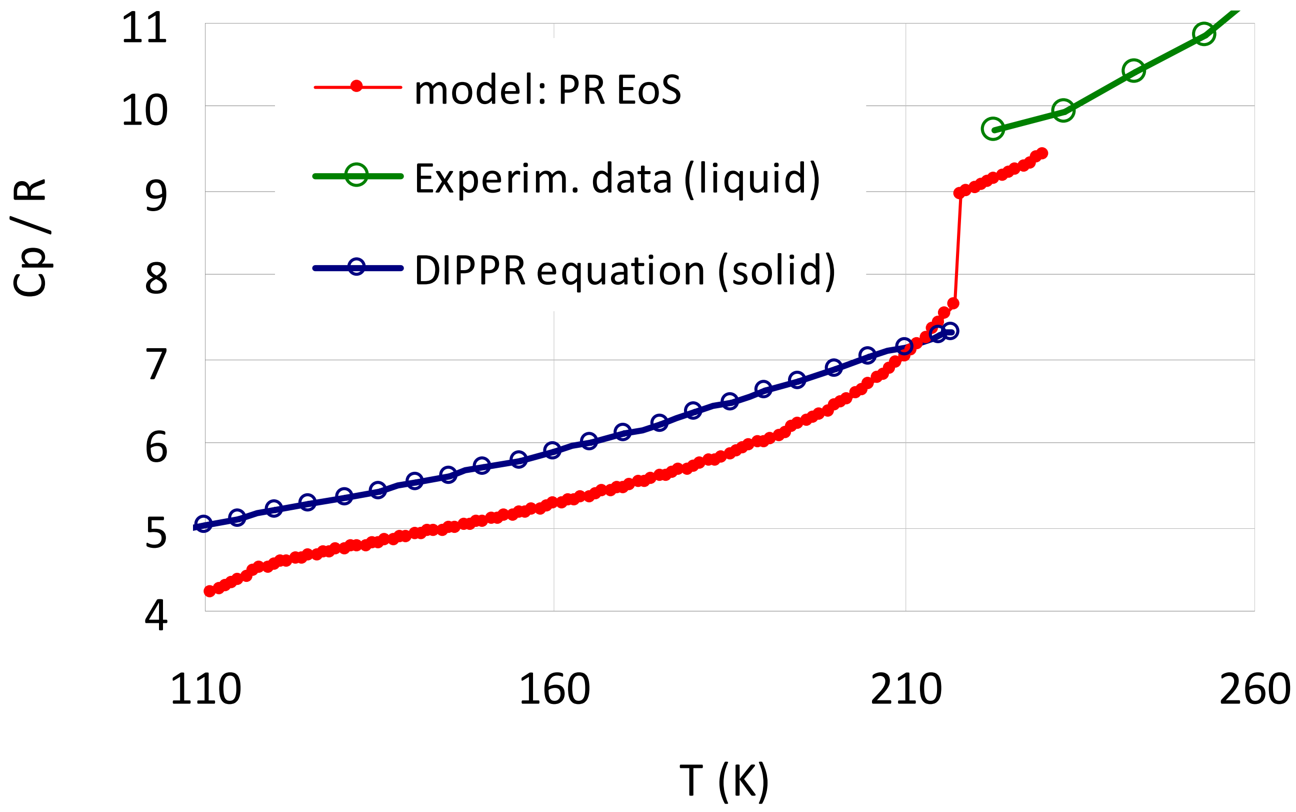


Heat of sublimation



Thermodynamic properties of solid CO_2

Heat capacity of the solid phase



Study of the effect of solid formation on the CO_2 pipeline releases

Study of CO_2 releases from a pipeline

Viscosity of the solids-gas mixture

$$\mu = \left[\frac{1-\alpha_s}{\mu_g} + \frac{\alpha_s}{\mu_s} \right]^{-1}, \qquad \mu_s \to \infty : \quad \mu \approx \frac{\mu_g}{1-\alpha_s}$$

where

α_s is the volume fraction of the solid phase,

μ_g is the coefficient of dynamic viscosity of the vapour phase,

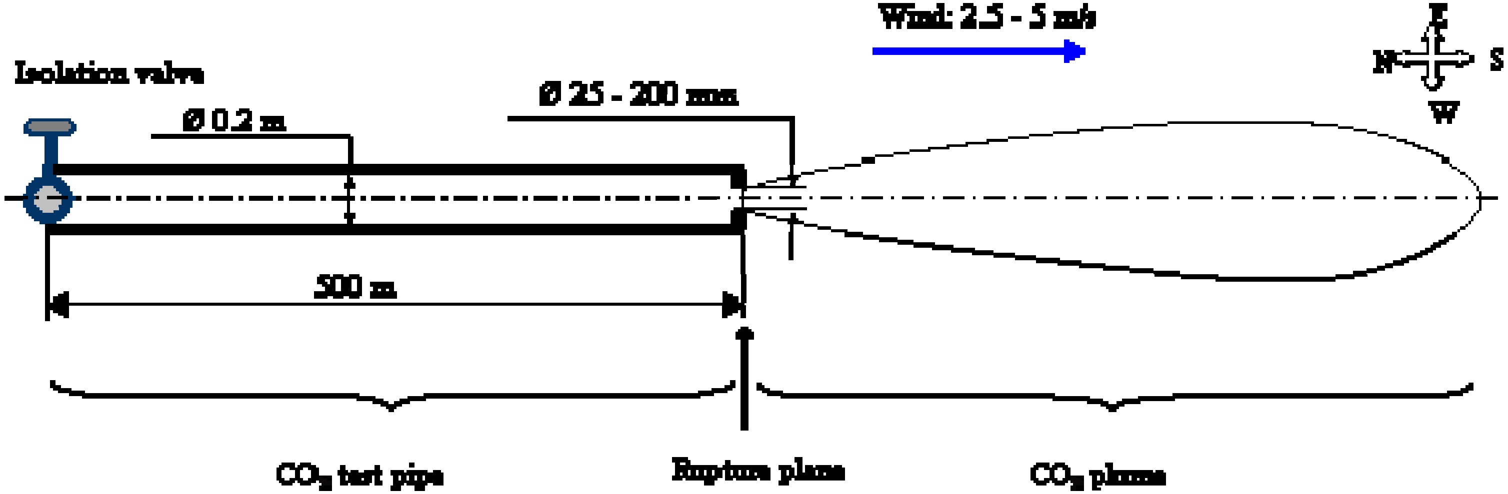
μ_s is the coefficient of dynamic viscosity of the solid phase.

Thermal conductivity of the solid phase

$\lambda_s \approx 0.2$ W/m/K [Cook and Davey, 1976]

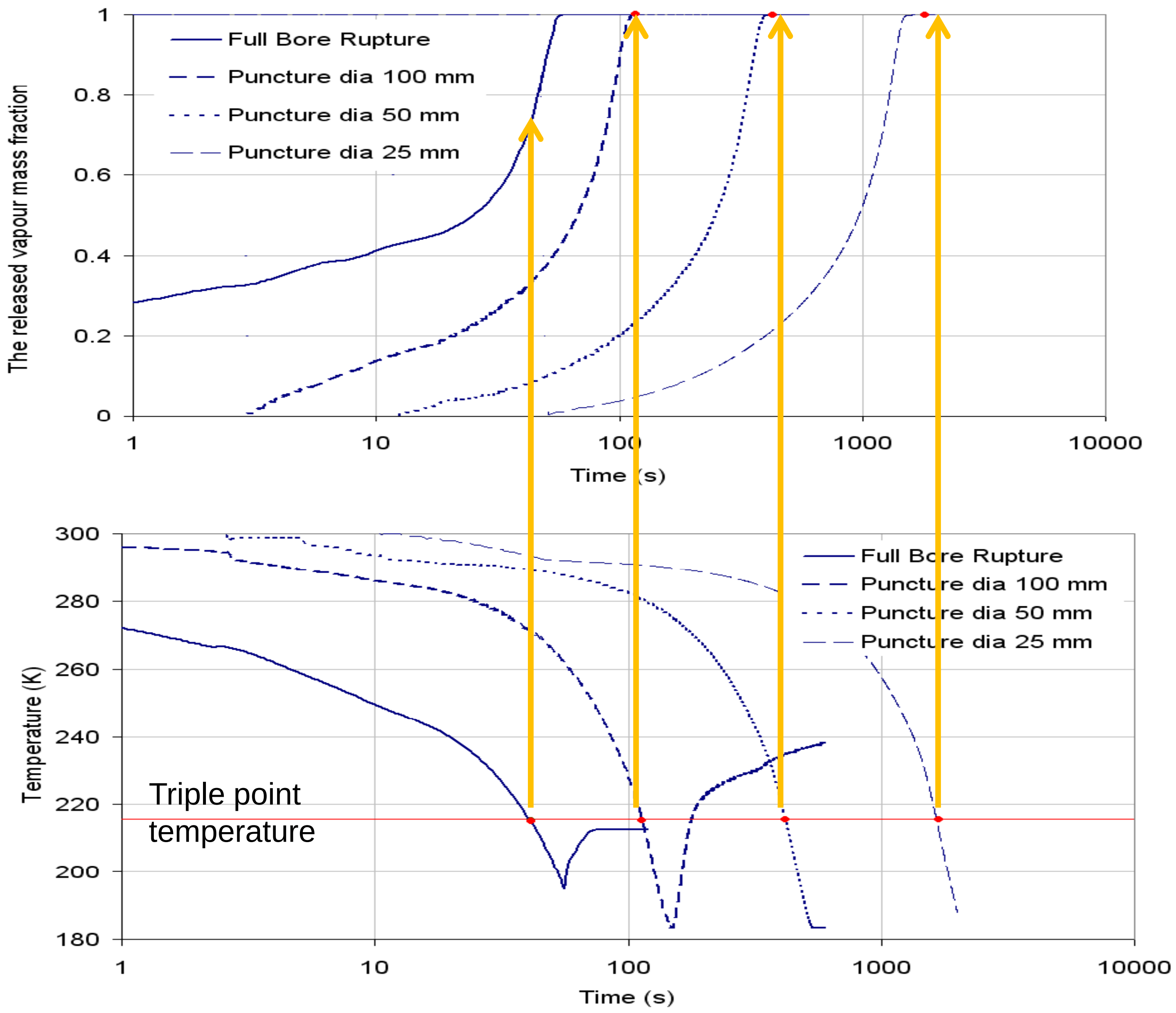
Study of CO_2 releases from a pipeline

CO_2: P = 120 .. 240 bar, T = -20 .. 20 deg C



Schematic representation of the test pipe section and the horizontally released CO_2 discharge plume

Preliminary Results: Original Peng-Robinson EOS



Preliminary Results: Original Peng-Robinson EOS

The results indicate that the solids are expected to form when the triple point conditions (p, T) are reached

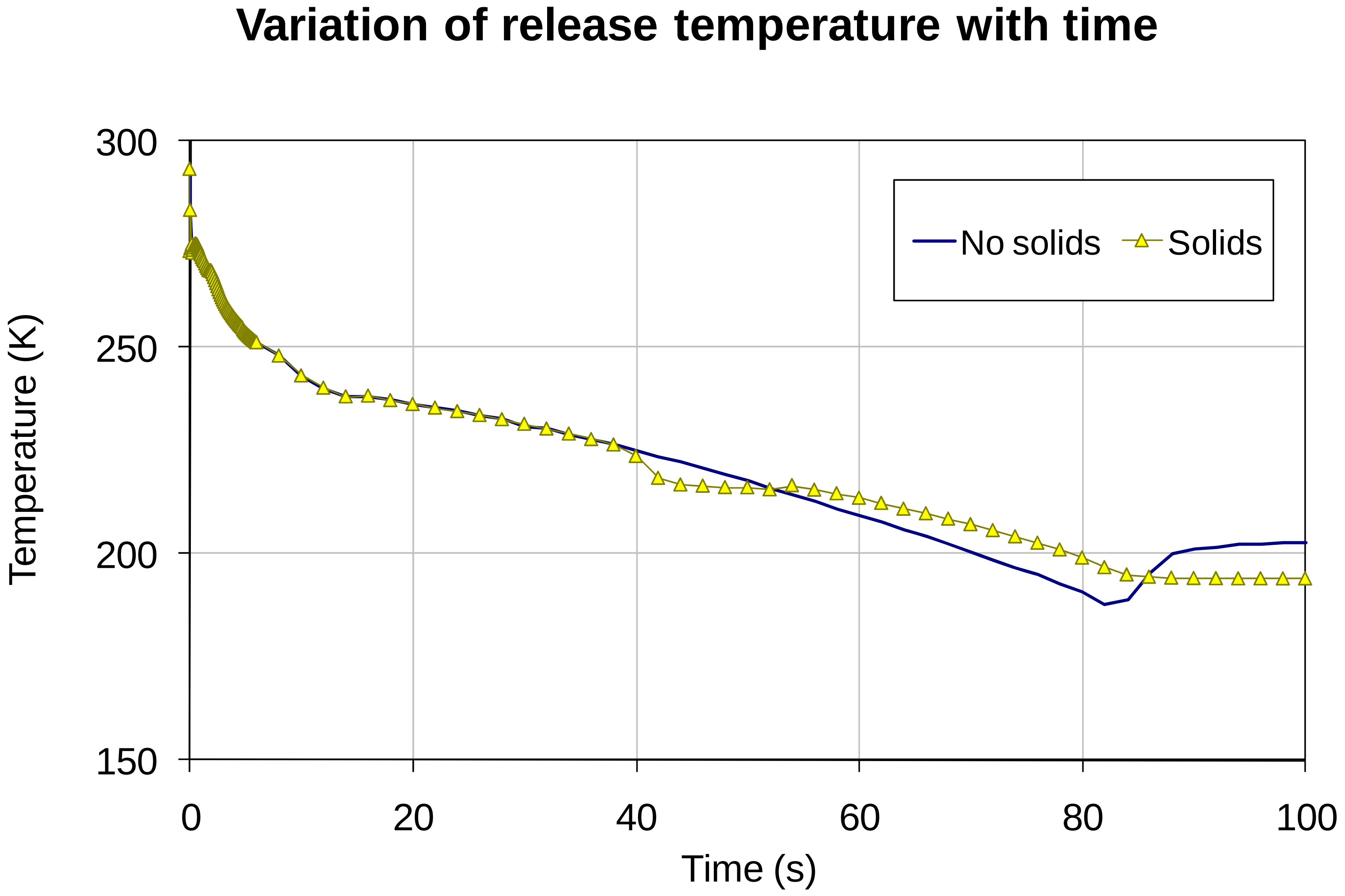
Sensitivity analysis is performed to clarify the effect of solids formation on the results of outflow simulations

HEM results: the effect of solids

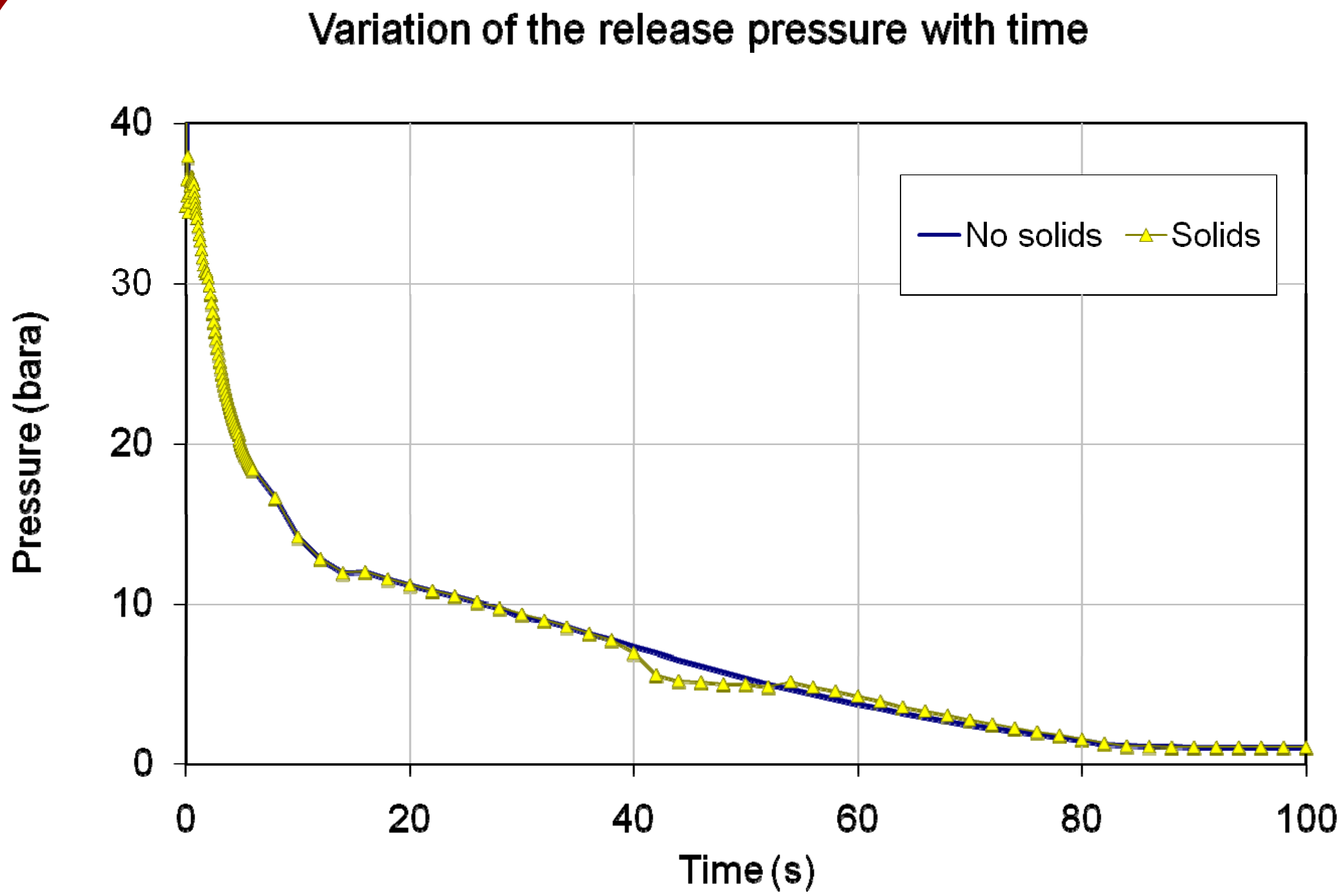
Base-line case:

Initial pressure = 140 bar
Initial temperature = 20 deg C
Ambient temperature = 20 deg C
Full Bore Rupture (200 mm dia)

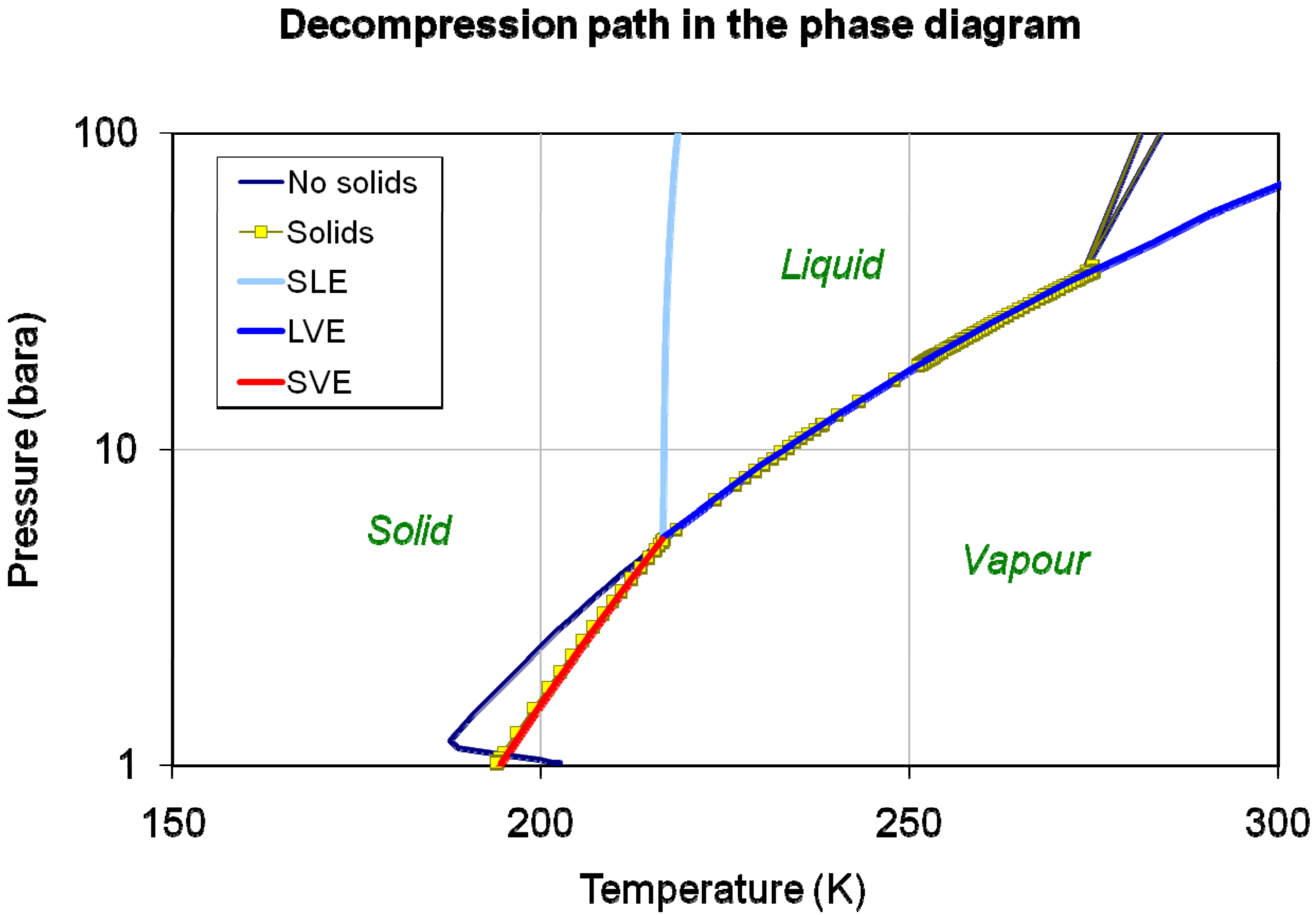
HEM results: Initial cond’s: 140 bar, 20ºC



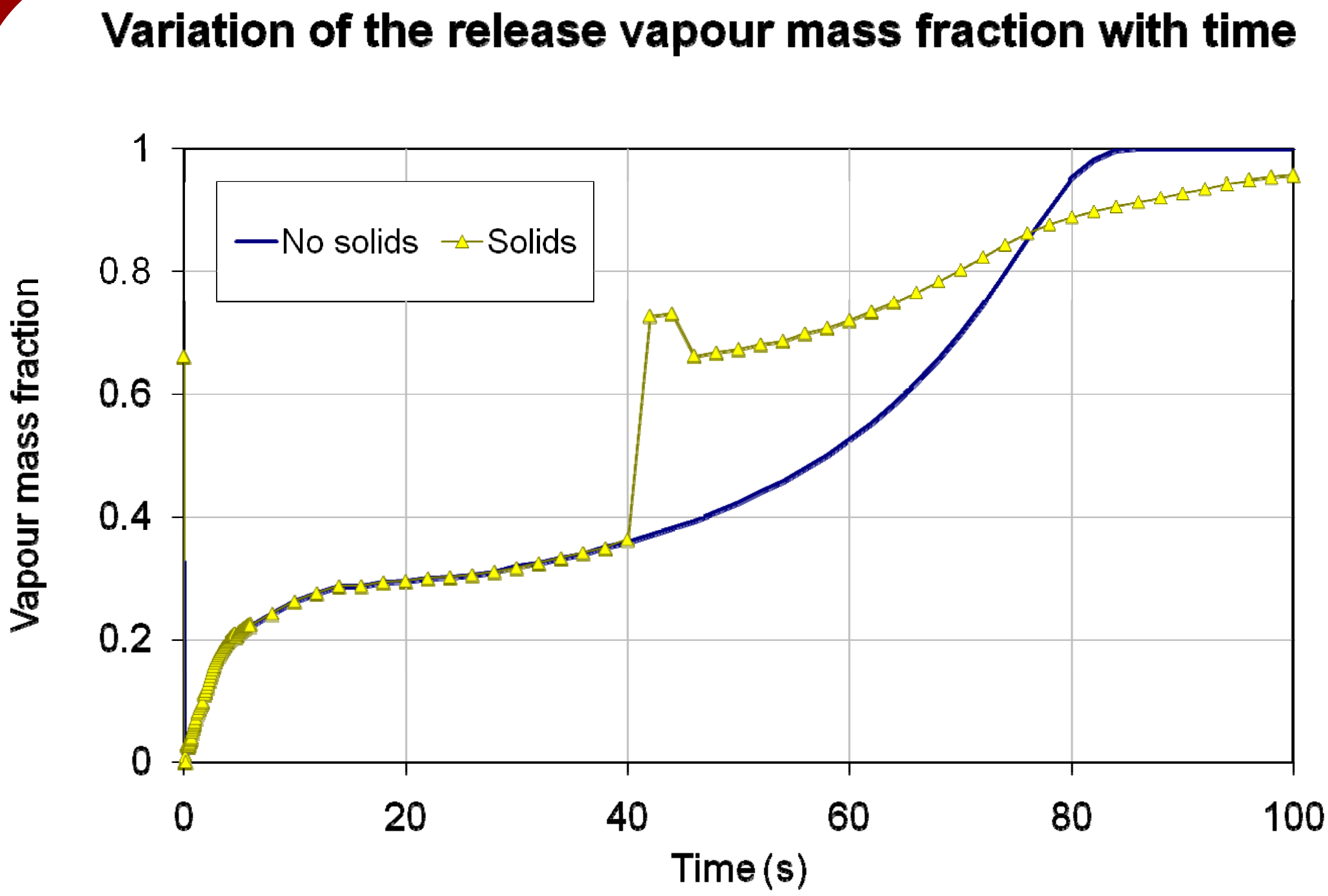
HEM results: Initial cond's: 140 bar, 20^{o}C



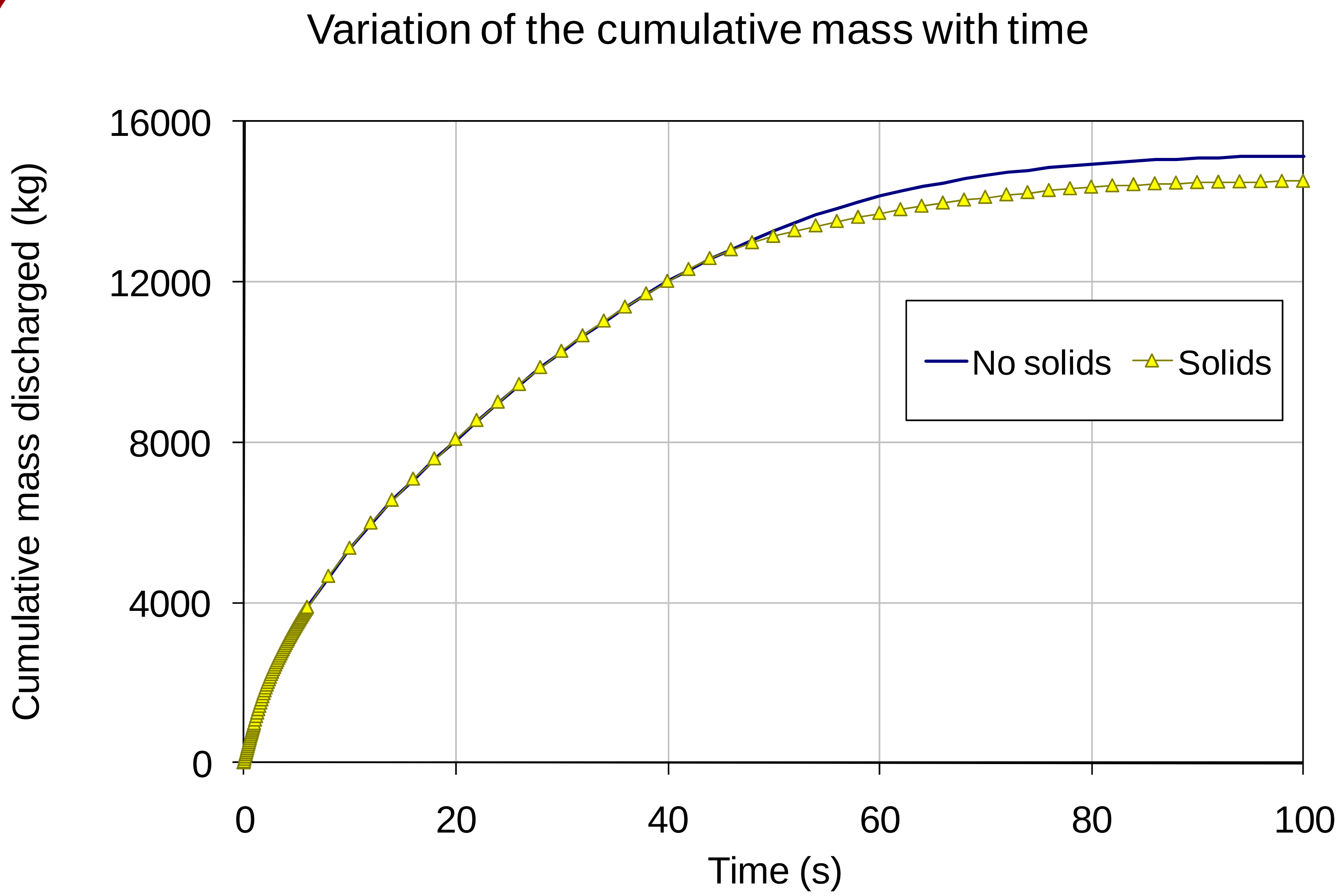
HEM results: Initial cond's: 140 bar, 20ºC



HEM results: Initial cond’s: 140 bar, 20ºC



HEM results: Initial cond's: 140 bar, 20ºC



HEM results: Base-line case

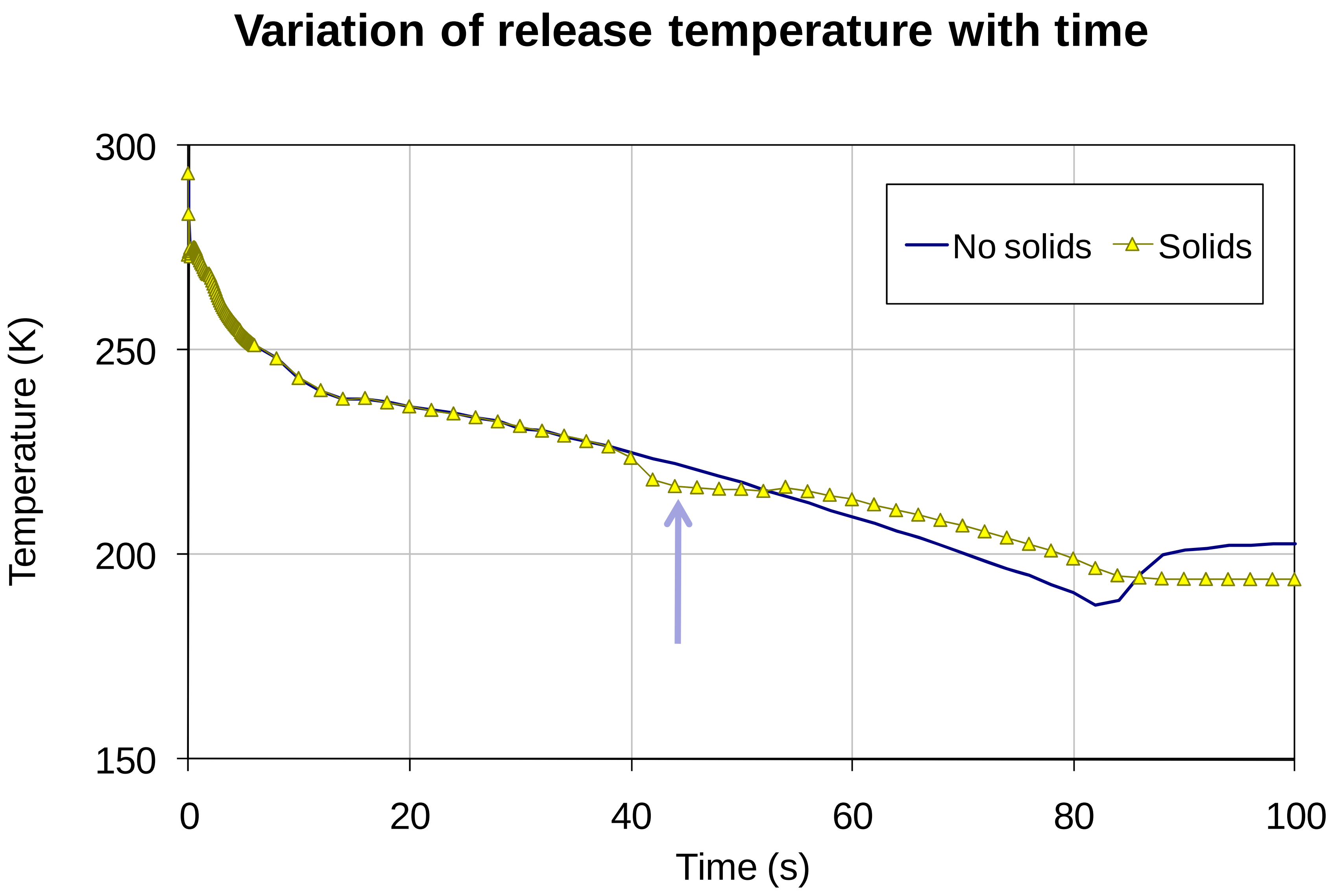
- EoS modified for solid-phase region: dP/dT_{subl} > dP/dT_{sat} affecting the decompression path
- The solid formation is accompanied by:
  - An increase in the mass fraction of the vapour phase
  - Rapid decrease and temporary stabilisation of the temperature and pressure in the flow
  - Decrease in the mass flow rate

HEM results: the effect of solids

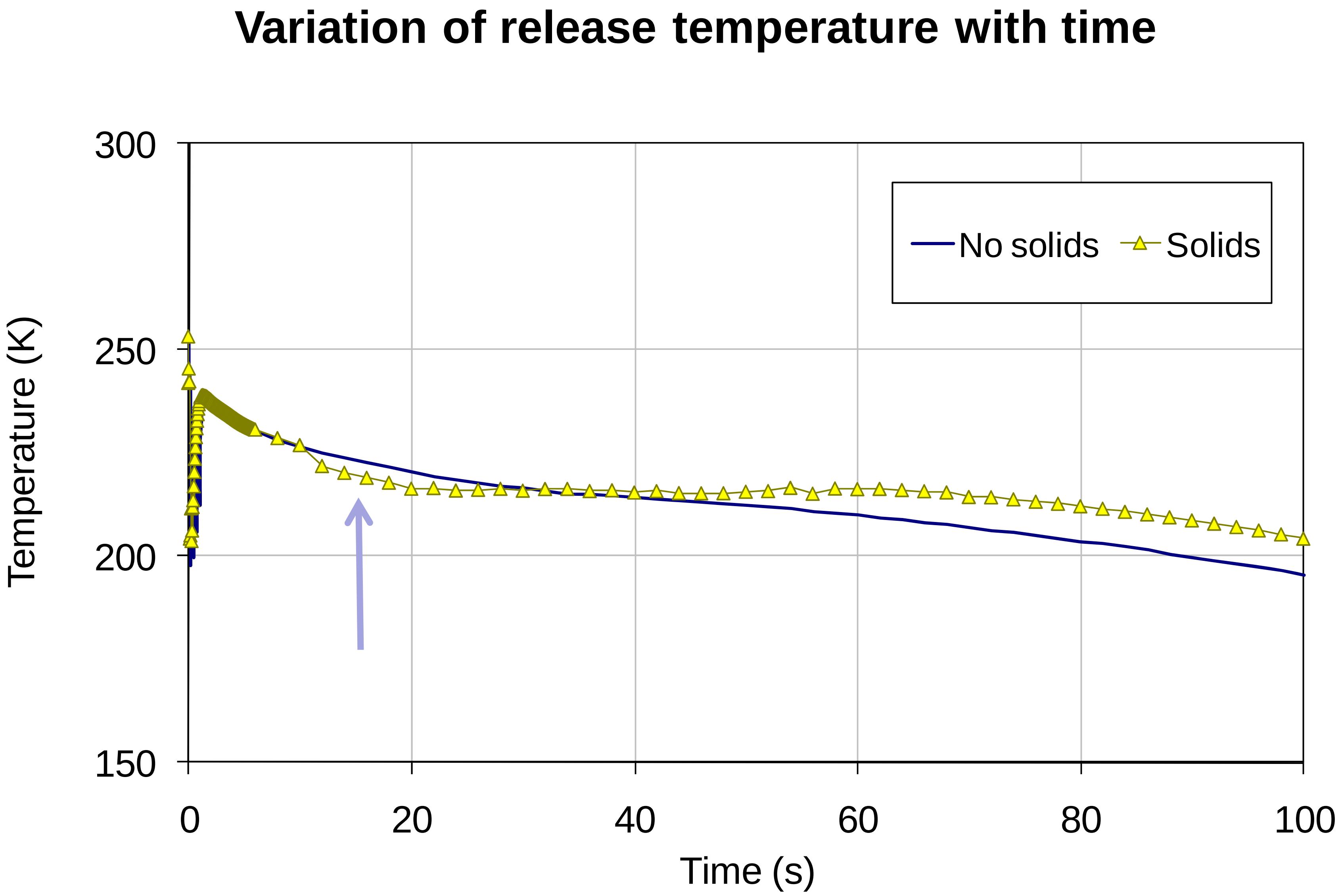
Impact of the fluid temperature:

Initial pressure = 240 bar
Initial temperature = –20 deg C
Ambient temperature = 0 deg C

HEM results: Initial cond's: 140 bar, 20^{o}C

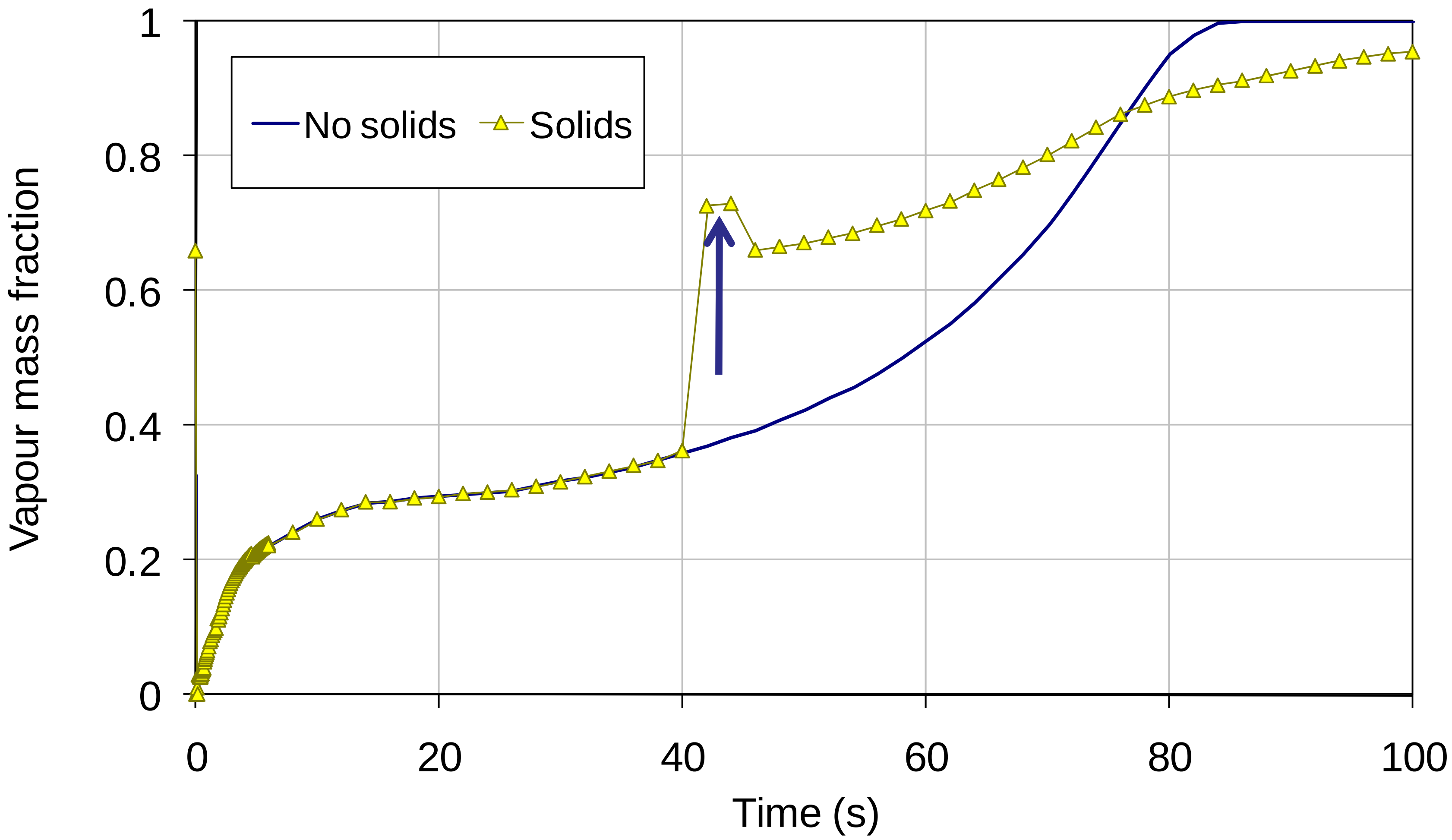


HEM results: Initial cond’s: 140 bar, - 20ºC



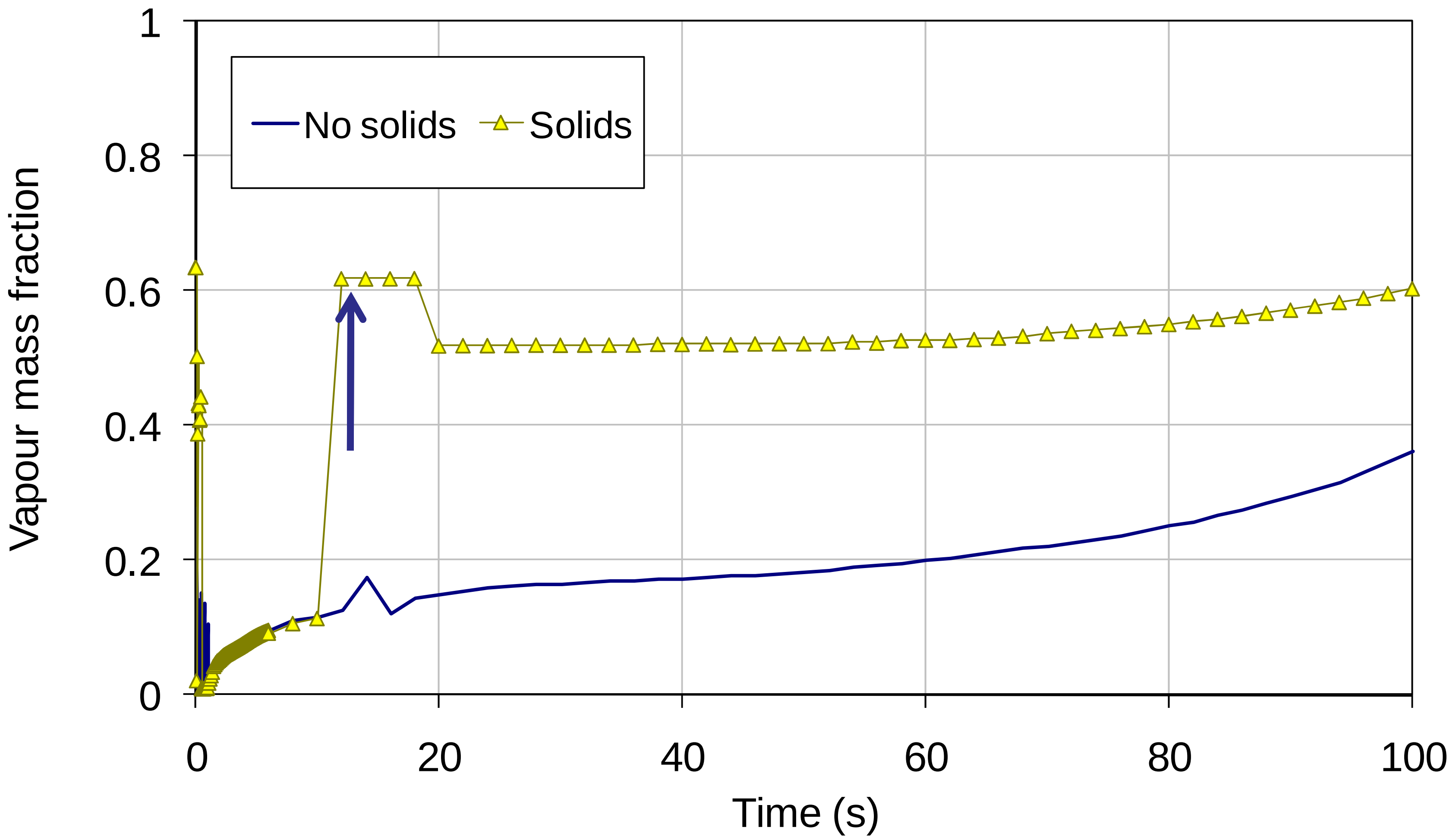
HEM results: Initial cond’s: 140 bar, 20°C

Variation of the release vapour mass fraction with time

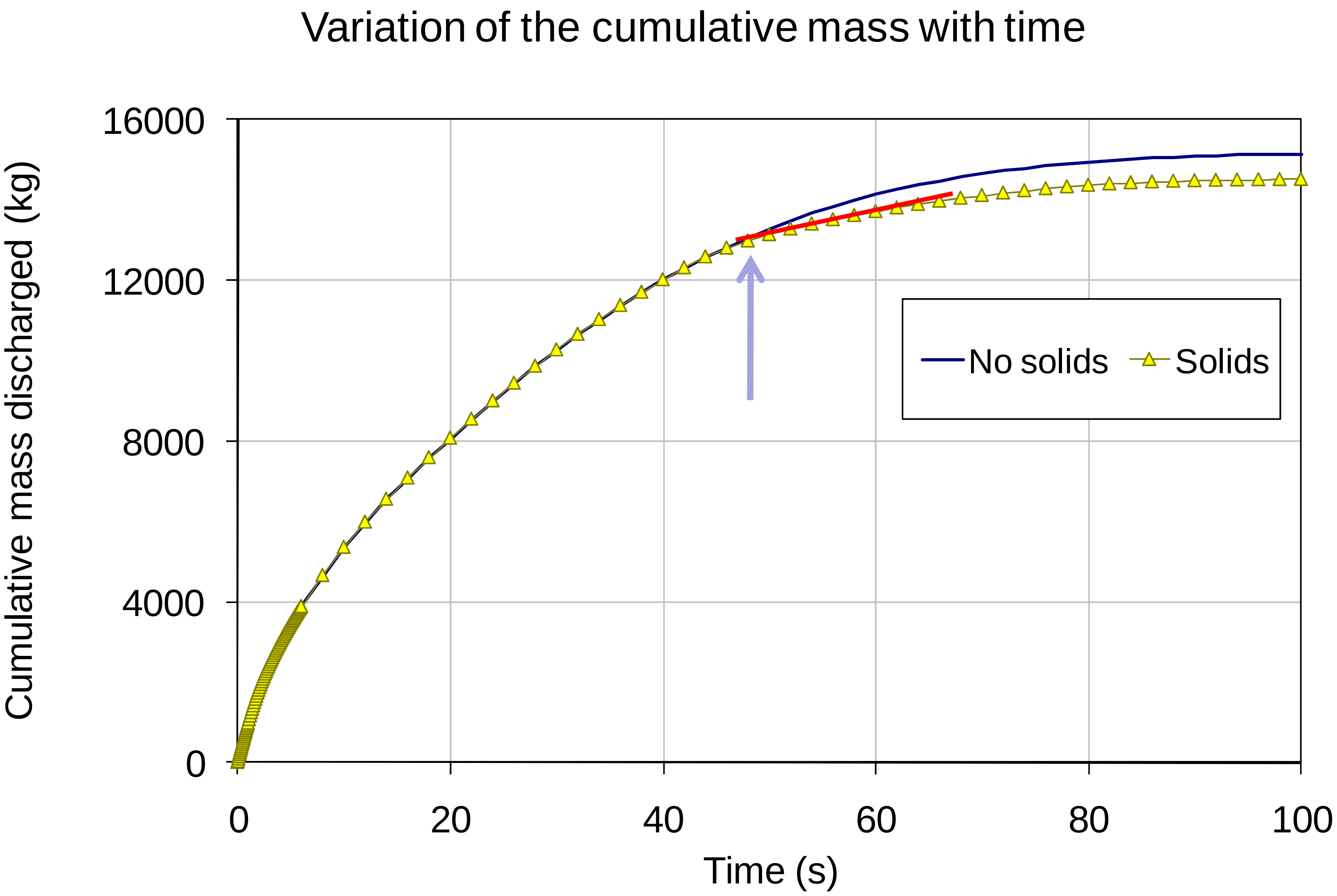


HEM results: Initial cond's: 140 bar, - 20^{o}C

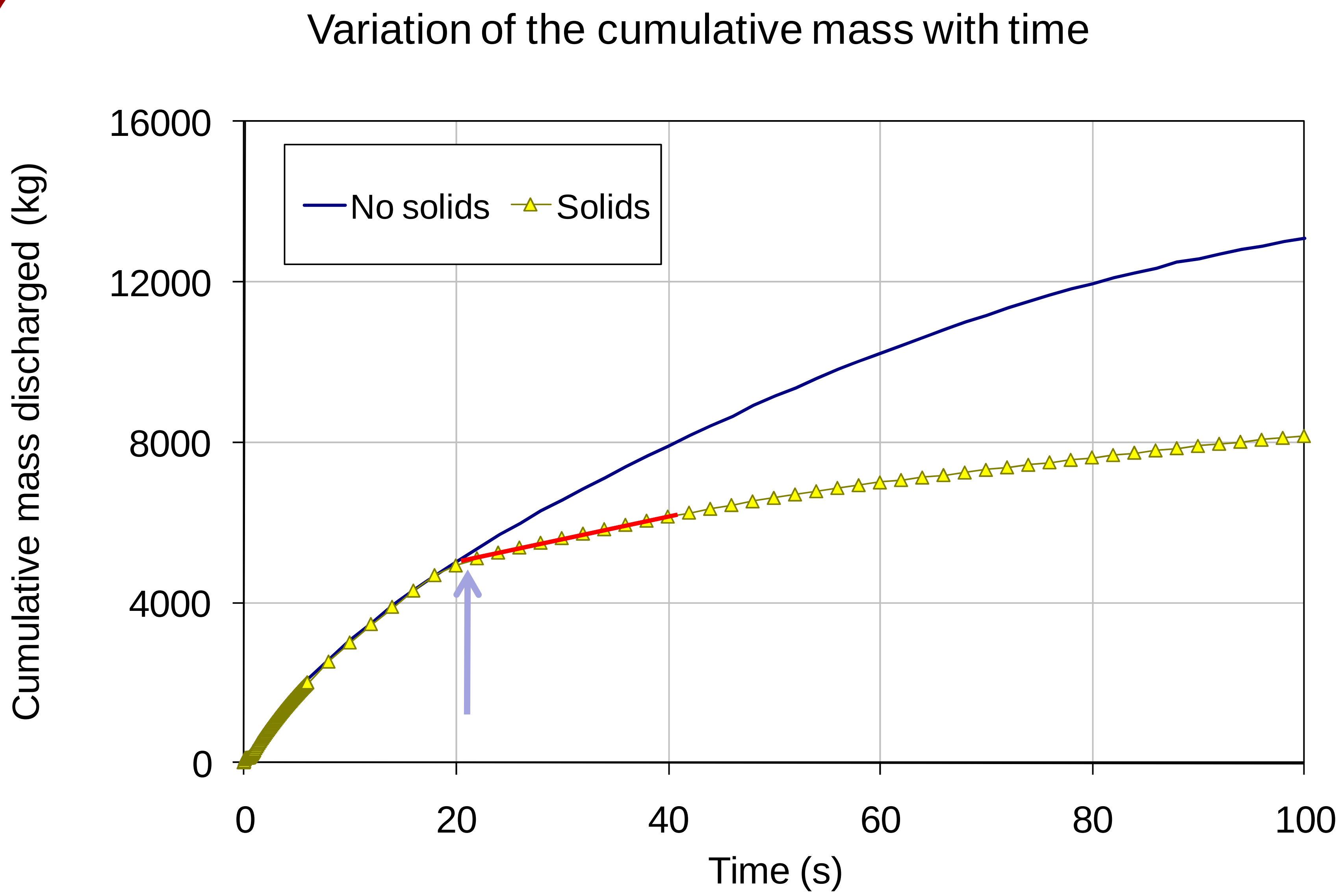
Variation of the release vapour mass fraction with time



HEM results: Initial cond's: 140 bar, 20^{o}C



HEM results: Initial cond’s: 140 bar, - 20°C



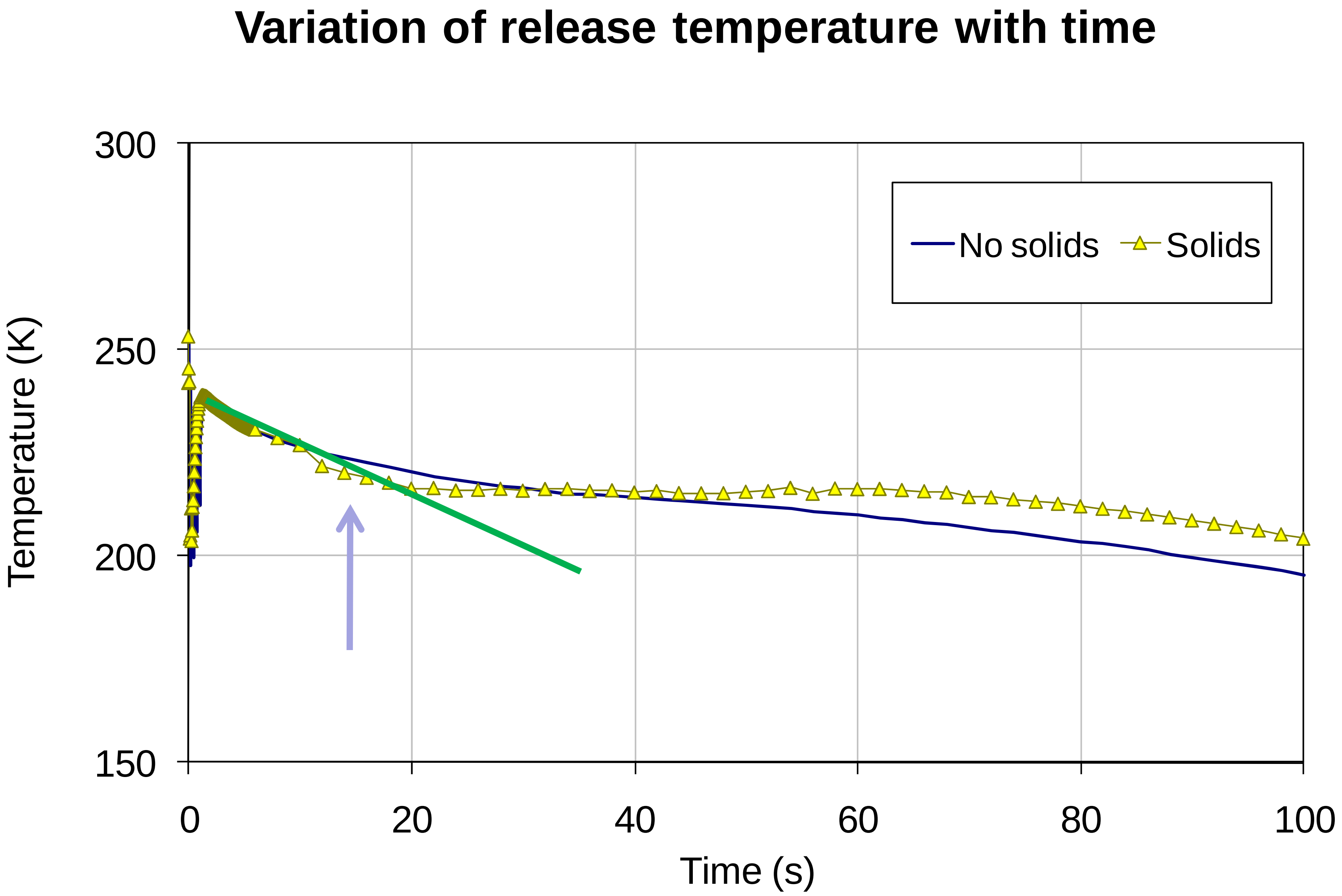
HEM results: the effect of solids

Impact of rupture diameter:

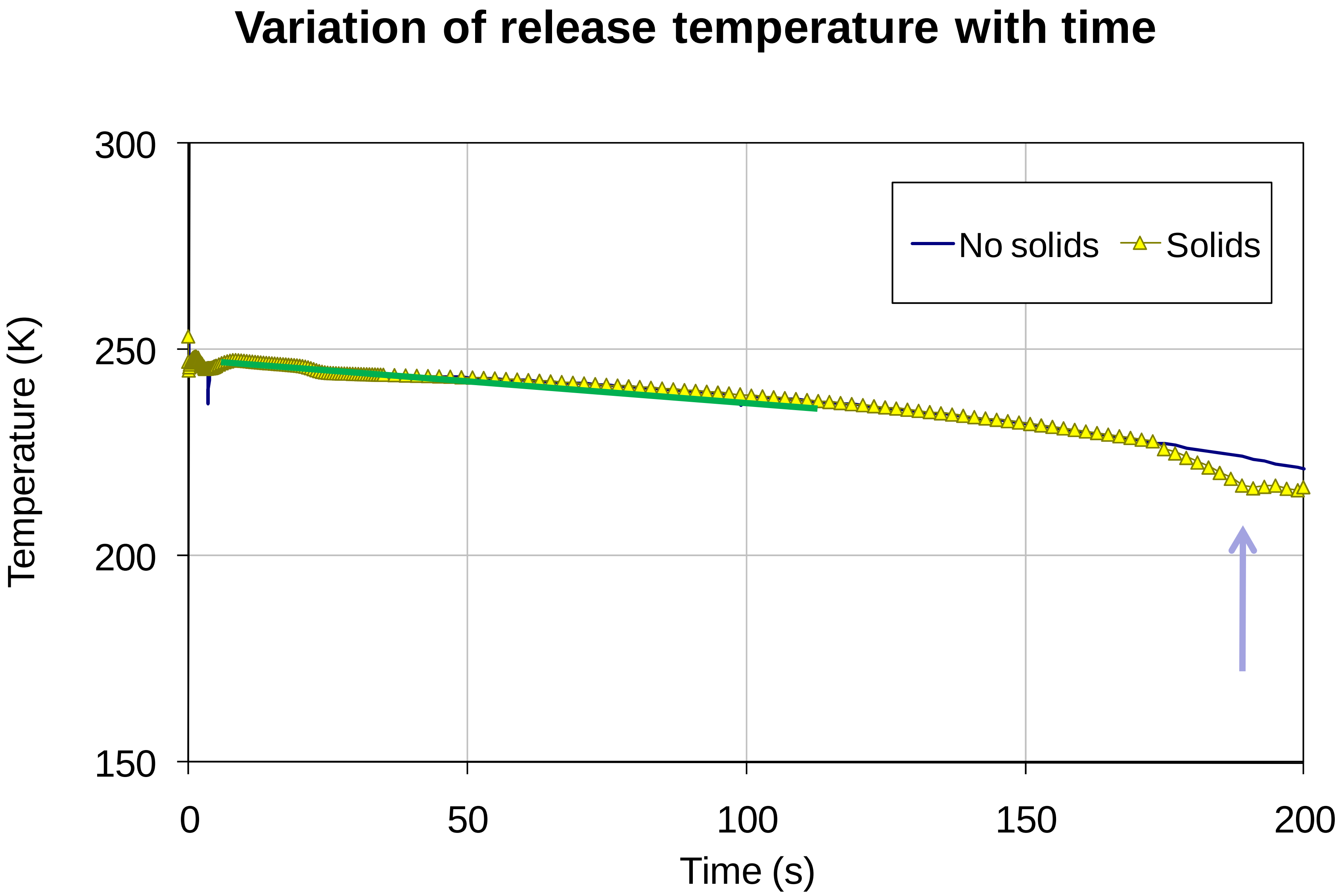
Initial pressure = 140 bar
Initial temperature = –20 deg C
Ambient temperature = 0 deg C

Rupture diameter = 100 mm

HEM results: 140 bar, - 20ºC, FBR



HEM results: 140 bar, - 20ºC, 100mm rupture



Conclusions

- Parameters of the Peng-Robinson EoS are modified for calculation of the thermodynamic properties of solid phase CO_2
- The effect of solids on the CO_2 releases from pipelines are examined by comparing the results of calculation of releases using the original P-R EOS and its modified version extended to the solid phase region
- The outflow model developed allows quantitative characterization of the amount of solid phase CO_2 formed inside the pipe and released into atmosphere

Conclusions

Results of the preliminary study indicate that:

- Solid CO_2 is formed when the triple point pressure and temperature are reached for the flow at the rupture plane. At this stage a significant amount of fluid can still remain in the pipeline
- The mass fraction of the solid phase can be as large as ~50%, although the volume fraction is small (~1%)
- For long pipelines and low initial temperatures of CO_2 fluid, a large amount of solid CO_2 can be formed and released from the pipeline

Publications

H. Mahgerefteh, S. Martynov and S. Brown

"Modelling Dry Ice Formation Following Rapid Decompression of CO_2 Pipelines" *The Second International Forum on the Transportation of CO_2 by Pipeline, 22-23 June, 2011, Newcastle, UK*

H. Mahgerefteh, S. Martynov and S. Brown

"A cubic equation of state for the solid-vapour equilibrium of carbon dioxide " *A manuscript submission to the AIChE Journal*

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Thank you

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