PROSIM DAC APPLICATION EXAMPLE

CRYOSORPTION OF A MIXTURE OF HYDROGEN ISOTOPES

EXAMPLE PURPOSE
This example deals with the cryosorption of mixtures of hydrogen isotopes for the recycling of the tritium generated in the blanket a deuterium-tritium fusion reactor. The IAS adsorption thermodynamic model is used to take into account the competition between isotopes to access the adsorption sites of a 5A molecular sieve. This process is modeled in *ProSim DAC*, Fives ProSim's dynamic simulation software dedicated to gas-solid adsorption columns

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CORRESPONDING PROSIM DAC FILES	*PSPDYN_EX_EN-H2-D2-cryosorption.pmp3*

Energy

Fives ProSim

Siège social : Immeuble Stratège A - 51 rue Ampère - 31670 Labège - FRANCE

Tél. : +33 (0)5 62 88 24 30

S.A.S. au capital de 147 800 € - 350 476 487 R.C.S. Toulouse - Siret 350 476 487 00037 - APE 5829C - N° TVA FR 10 350 476 487

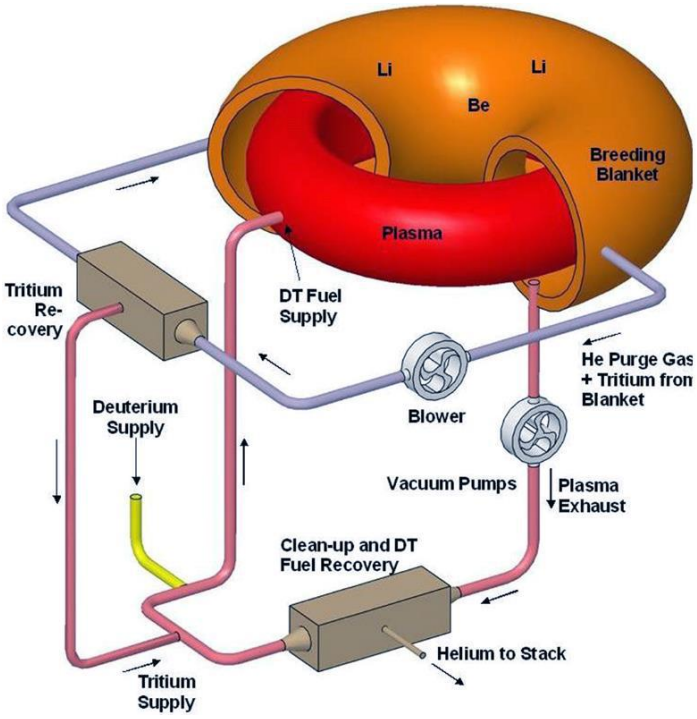
www.fivesgroup.com / www.fives-prosim.com

CONTENTS

1. PROCESS MODELING

1.1. Process description

The following figure shows a diagram of a deuterium-tritium fusion reactor (DT reactor) [HOS21]. One of the technological aspects is the retreatment of the helium and tritium purge of the blanket of the reactor in order to recover the gaseous tritium and reinject it as fuel into the blanket.



To use it as fuel, the tritium generated in the blanket must be extracted from the breeder reactor materials and transferred to the sweeping gas. 4 methods exist to recover tritium from the sweep helium:

- ✓ Adsorption after oxidation: the sweep gas is introduced into a catalytic bed to convert the gaseous tritium into tritiated water vapor. This vapor is then trapped by a porous adsorbent bed.
- ✓ Isotope exchange fixation: the sweep gas is introduced into a packed bed with a precious metal-based catalyst on a hydrophilic porous substrate, such as activated alumina, molecular sieves, silica gel, etc. An isotope exchange reaction occurs between the tritium present in the gas stream and the hydrogen present in the substrate. The tritium present in the gas stream is then fixed in the catalyst substrate, thus releasing hydrogen. In addition, tritiated water in the gas phase is trapped by adsorption on the surface of the substrate. Thus, tritium, in its two chemical forms, is trapped in the same bed.
- ✓ Absorption: the sweeping gas is introduced into a bed of metal pellets (uranium, porous titanium, porous zirconium, zirconium-cobalt, etc.). Only gaseous tritium is trapped by absorption in these metals.
- ✓ Cryosorption: the sweeping gas is introduced into a porous adsorbent bed, such as molecular sieves, activated carbon, etc., cooled with liquid nitrogen or helium. The gaseous tritium and tritiated water vapor in the gas phase are trapped by adsorption on the adsorbent.

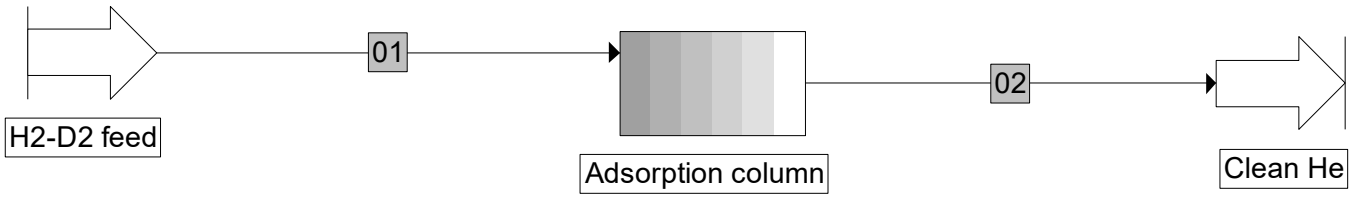
[NIS94] investigated the feasibility of cryosorption using porous adsorbents such as molecular sieves or activated carbon. [NIS94] found that cryosorption was interesting for the recovery of gaseous tritium from hydrogen-saturated sweeping helium. [WIL93] and [WIL95] showed that the liquid nitrogen-cooled 5A molecular sieve has a high affinity and adsorption capacity for hydrogen isotopes. When hydrogen-swamped helium is used as a sweep gas, it is assumed that about a hundred Pascals of hydrogen and a few Pascals of tritium in the helium must be processed.

For the design of the cryosorption process, a simulation tool is useful to go from the laboratory scale (simulation of adsorption experiments, validation of isotherms, validation of adsorption thermodynamics model, etc.) to the industrial scale. This is one of the possible applications of *ProSim DAC*, Fives ProSim's dynamic simulation software dedicated to gas-solid adsorption columns.

This example is based on the publication [NIS95]. This publication describes the adsorption in a laboratory column of H2 – D2, H2 – HD, HD – D2 and H2 – HT mixtures in helium-4 streams and on three adsorbents: 4A and 5A molecular sieves and one activated carbon. The experiments relating to the H2 – D2 mixtures on a 5A molecular sieve are retained in this example because they show a very visible effect of the competition of these two compounds with respect to the adsorption sites. The simulation set up to model this is simple. The "H2-D2 feed" is used to describe the helium-4 flow to be purified. The parameters of the adsorption column are used to represent the experimental conditions of [NIS95]. The "Clean He" outlet collects the gas outlet from the adsorption column.

1.2. Simulation flowsheet

The simulation flowsheet is shown in the following figure.



1.3. Compounds

The compounds considered in the simulation, their chemical formulae and CAS® numbers[1] are presented in the table below. Their pure compound properties are extracted from the standard database provided with *ProSim DAC* [ROW24].

Compound	Chemical formula	CAS number
Hydrogen	H_2	1333-74-0
Deuterium	D_2	7782-39-0
Helium-4	He	7440-59-7

1.4. Thermodynamic model

The adsorption is done at atmospheric pressure and at a cryogenic temperature (77.4 K). Thus, the "Ideal" thermodynamic profile is selected in the Simulis Thermodynamics calculator.

[1] *CAS Registry Numbers® are the intellectual property of the American Chemical Society and are used by Fives ProSim SAS with the express permission of ACS. CAS Registry Numbers® have not been verified by ACS and may be inaccurate.*

1.5. Operating parameters

1.5.1. Process feeds

The characteristics of the process feed are described in the table below.

	H2-D2 feed
Temperature (K)	77.4
Pressure (atm)	1
Total flow rate (Nm^3/h)	0.012
Molar fractions	
Hydrogen	0.005856
Deuterium	0.005607
Helium-4	0.988537

1.5.2. Simulation duration

The "Final time" is the actual operating time of the adsorption. The "Final time" is entered in the *ProSim DAC* icon bars:

Simulation duration	Value
Final time	6.25 h

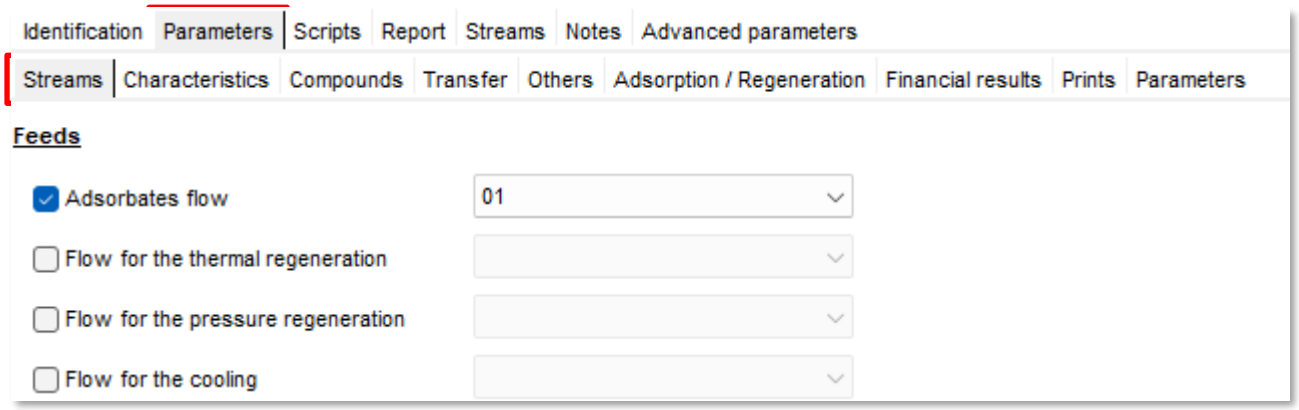
1.5.3. Adsorption column

1.5.3.1. Feeds

Four feeds can be used in *ProSim DAC*:

- ✓ Adsorbates flow: Flux to be purified during the adsorption step
- ✓ Flow for the thermal regeneration: Flow used during the temperature regeneration (hot inert, water vapor, etc.)
- ✓ Flow for the pressure regeneration: Flow used during the pressure regeneration (inert at pressure lower than the one of adsorption, etc.)
- ✓ Flow for the cooling: Flow used to cool the column at the end of the temperature regeneration step

Only the first feed is used in this example as shown in the screenshot below.

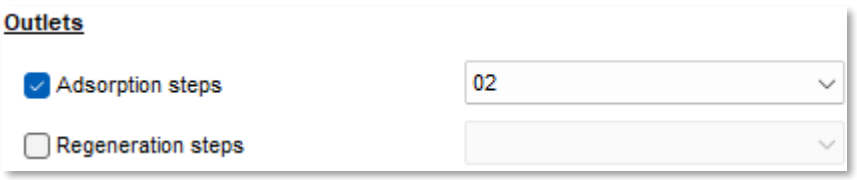


1.5.3.2. Outlets

Two outlets can be used in *ProSim DAC*:

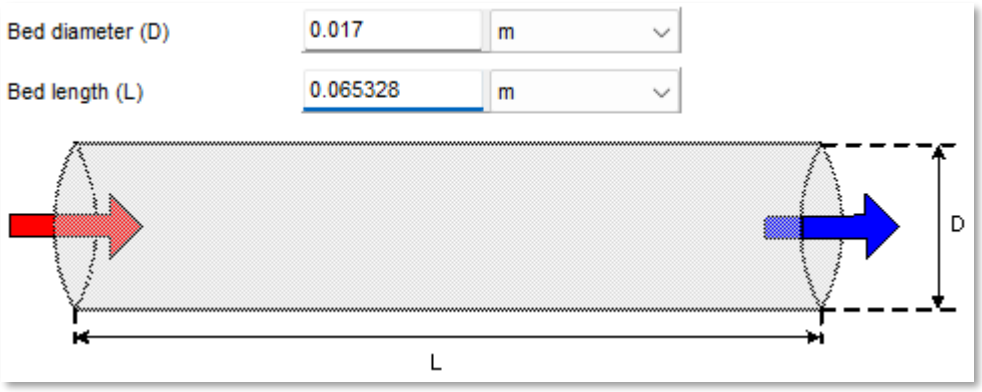
- ✓ Adsorption steps: Outlet during the adsorption steps
- ✓ Regeneration steps: Outlet during the regeneration steps

The screenshot below shows the outlet used.



1.5.3.3. Column characteristics

The column used is a lengthwise flow column. Its characteristics are shown in the screenshot below. The dimensions to be provided are those of the adsorbent bed. It should be noted that *ProSim DAC* also allows to model a transverse flow column.



The length of the adsorbent bed, L, is not specified in [NIS95]. It is calculated from three quantities specified in [NIS95], the adsorbent weight, $m_{ads} = 9.49\ g$, the bed density, $\rho_{bed} = 640\ kg/m^3$ and the bed diameter $d_{bed} = 0.017\ m$, using the following relation:

$$L = m_{ads} \frac{1}{\rho_{bed}} \frac{4}{\pi d_{bed}}$$

1.5.3.4. Thermal behavior

ProSim DAC allows you to model the following heat exchange modes:

- ✓ Heat exchange in the bed: "Given heat duty without wall transfer"
  This possibility allows to model an adiabatic operation or an operation at given amount of heat duty for each step (exchanger within the adsorbent bed).
- ✓ Transfer through the wall + heat exchange in the bed: "Given heat duty and wall transfer "
  Heat exchange takes place through the column wall. The wall temperature is by default constant over time and along the column. To overcome this hypothesis, it is necessary to activate the "Take into account thermal inertia of the column wall" option. It is possible to add to this transfer mode a given amount of heat in the adsorption bed for each step (by default zero).

In this example, the heat transfer takes place through the column wall and without direct heat input into the adsorbent bed. The wall temperature specified in the "Characteristics" tab is the temperature of the wall during the adsorption.

Thermal behavior	
Thermal transfer	Given heat duty and wall transfer
Wall temperature	77.4 K

1.5.3.5. Bed adsorbent characteristic

Bed adsorbent characteristic	
Bed void ratio	0.36 m^3/m^3

The bed void ratio, ε_{bed}, has been calculated from the bed density, $\rho_{bed} = 640\ kg/m^3$ [NIS95] and assuming a particles ratio $\rho_p = 1000\ kg/m^3$ using the following relation:

$$\rho_{bed} = \rho_p(1 - \varepsilon_{bed})$$

1.5.3.6. Adsorbent characteristics

The density of the particles takes into account the intra-particle porosity. The surface-to-volume ratio is the ratio between the geometric surface and the geometric volume of one of the particles. The density and specific heat of the particles are not specified in [NIS95]. Assumptions are made in this example.

Particles characteristics	
Diameter	0.0625 in
Density	1 000 kg/m^3
Specific heat	945 J/kg/K
Surface/volume ratio	3 780 m^2/m^3

1.5.3.7. Measures conditions for concentration results

The user can specify the temperature and pressure conditions that he wants to use to calculate the volume concentrations in the gas phase. Indeed, density is then necessary and, particularly in the case of a gas, is sensitive to temperature and pressure. In this example, the volume concentrations in the gas phase are evaluated under normal temperature and pressure conditions.

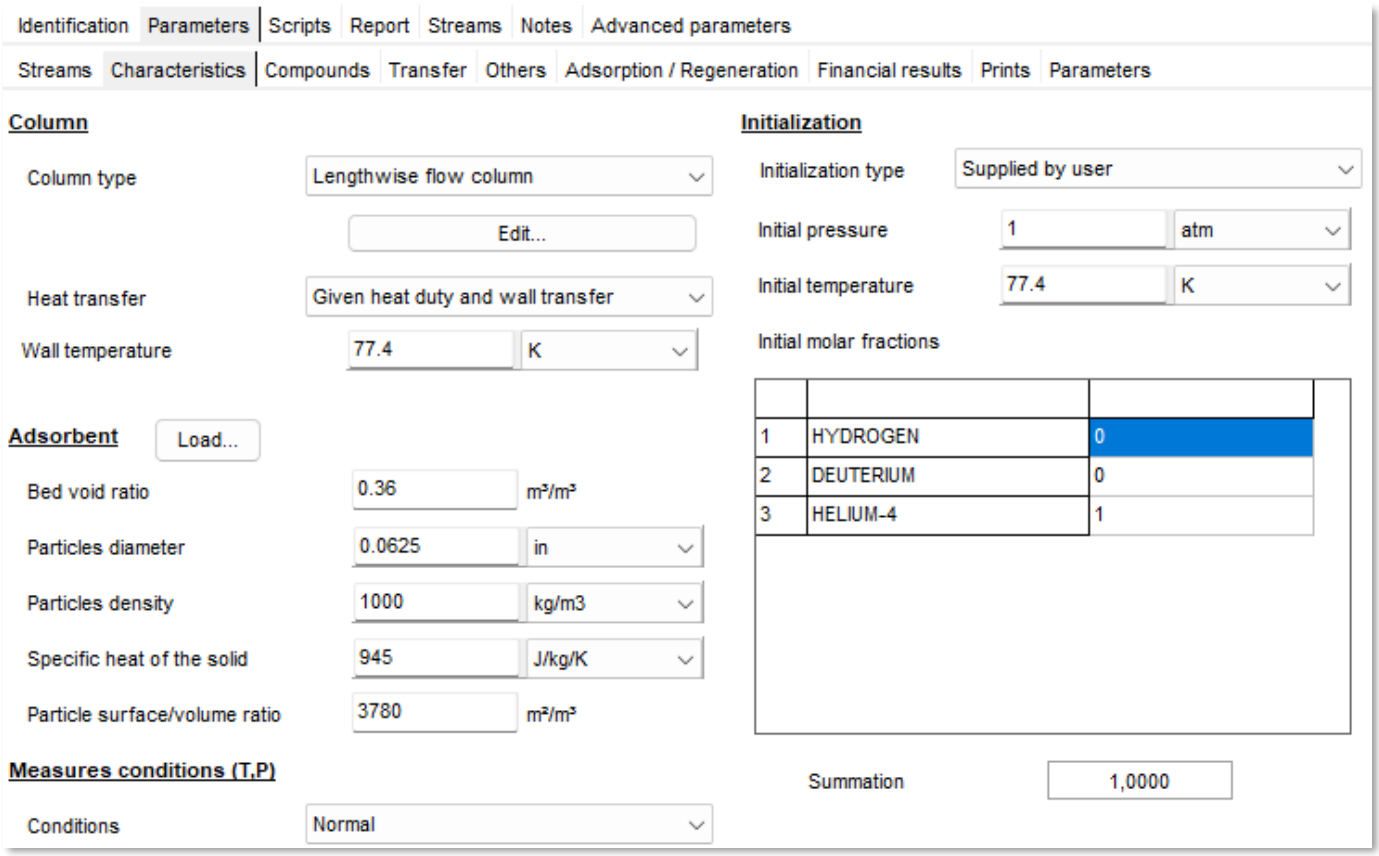
Measures conditions	Value
Conditions	Normal

1.5.3.8. Initialization

It is necessary to set the state of the column at startup. In this example, it is assumed that the column is filled with pure helium-4 at the temperature and the pressure of the gas to be purified.

Initialization	Value
Type	Supplied by suer
Pressure	1 atm
Temperature	120°C
Molar factions Air Carbon dioxide Water	 0.9881 0.0004 0.0115

The screenshot below shows the information from the previous paragraphs (from paragraph 1.5.3.3. to paragraph 1.5.3.8. included) entered into the module interface: "Parameters" tab, "Characteristics" sub-tab.



1.5.3.9. Adsorption isotherm

The Langmuir extended isotherm with [NIS95] parameters was for the hydrogen and the deuterium:

$$q_i = \frac{q_{m0}^{(1)} exp\left(\frac{q_{m1}^{(1)}}{T}\right) K_0^{(1)} exp\left(\frac{K_1^{(1)}}{T}\right) P_i}{1 + K_0^{(1)} exp\left(\frac{K_1^{(1)}}{T}\right) P_i} + \frac{q_{m0}^{(2)} exp\left(\frac{q_{m1}^{(2)}}{T}\right) K_0^{(2)} exp\left(\frac{K_1^{(2)}}{T}\right) P_i}{1 + K_0^{(2)} exp\left(\frac{K_1^{(2)}}{T}\right) P_i}$$

	Hydrogen	**Deuterium**
$q_{m0}^{(1)}$ **(mol/kg)**	1,518519	1,348315
$K_0^{(1)}$ **(atm-1)**	270	890
$q_{m1}^{(1)}$ **(K)**	0	0
$K_1^{(1)}$ **(K)**	0	0
$q_{m0}^{(2)}$ **(mol/kg)**	1,692308	3,166667
$K_0^{(2)}$ **(atm^{-1})**	13	12
$q_{m1}^{(2)}$ **(K)**	0	0
$K_1^{(2)}$ **(K)**	0	0

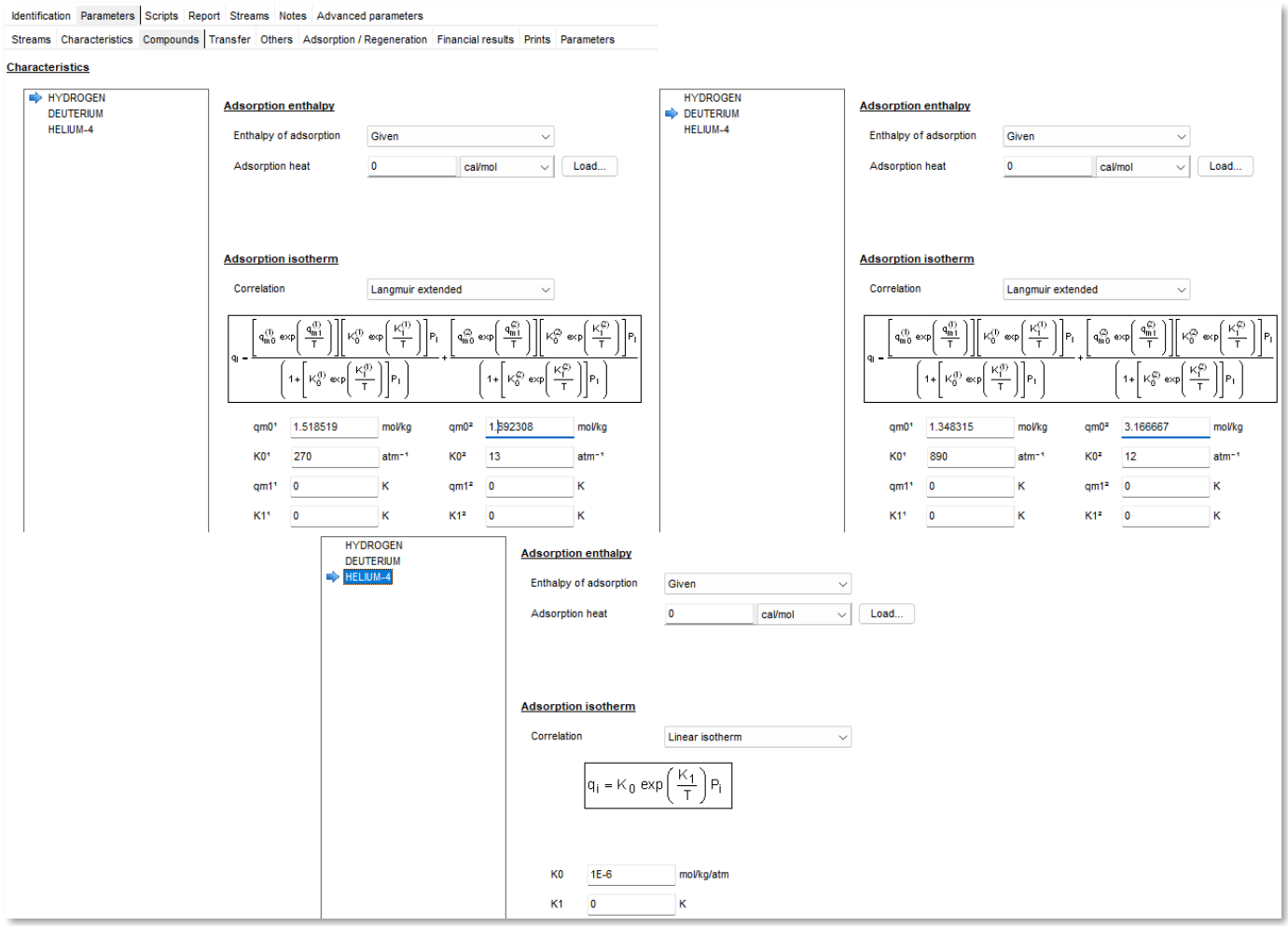
It is assumed that the helium-4 is only weakly adsorbed. It is represented by a linear isotherm with the parameters of the table below.

$$q_i = K_0 exp\left(\frac{K_1}{T}\right) P_i$$

K_0 (mol/kg/atm)	10^{-6}
K_1 (K)	0

The simulation is isothermal. The adsorption enthalpies are set to zero.

This information must be provided in the Compounds" sub-tab of the "Parameters" tab:



1.5.3.10. Mass transfer

The following options are available for mass transfer:

- ✓ Coupled gas and solid phase transfer
- ✓ Mass transfer resistance ("Linear Driving Force") in the gas and/or the solid phase, the necessary mass transfer coefficients can be provided by the user or calculated by *ProSim DAC*. It is also possible to neglect the transfer resistances.

In this example, the mass transfer resistance has been considered only in the solid phase. The mass transfer coefficients are specified.

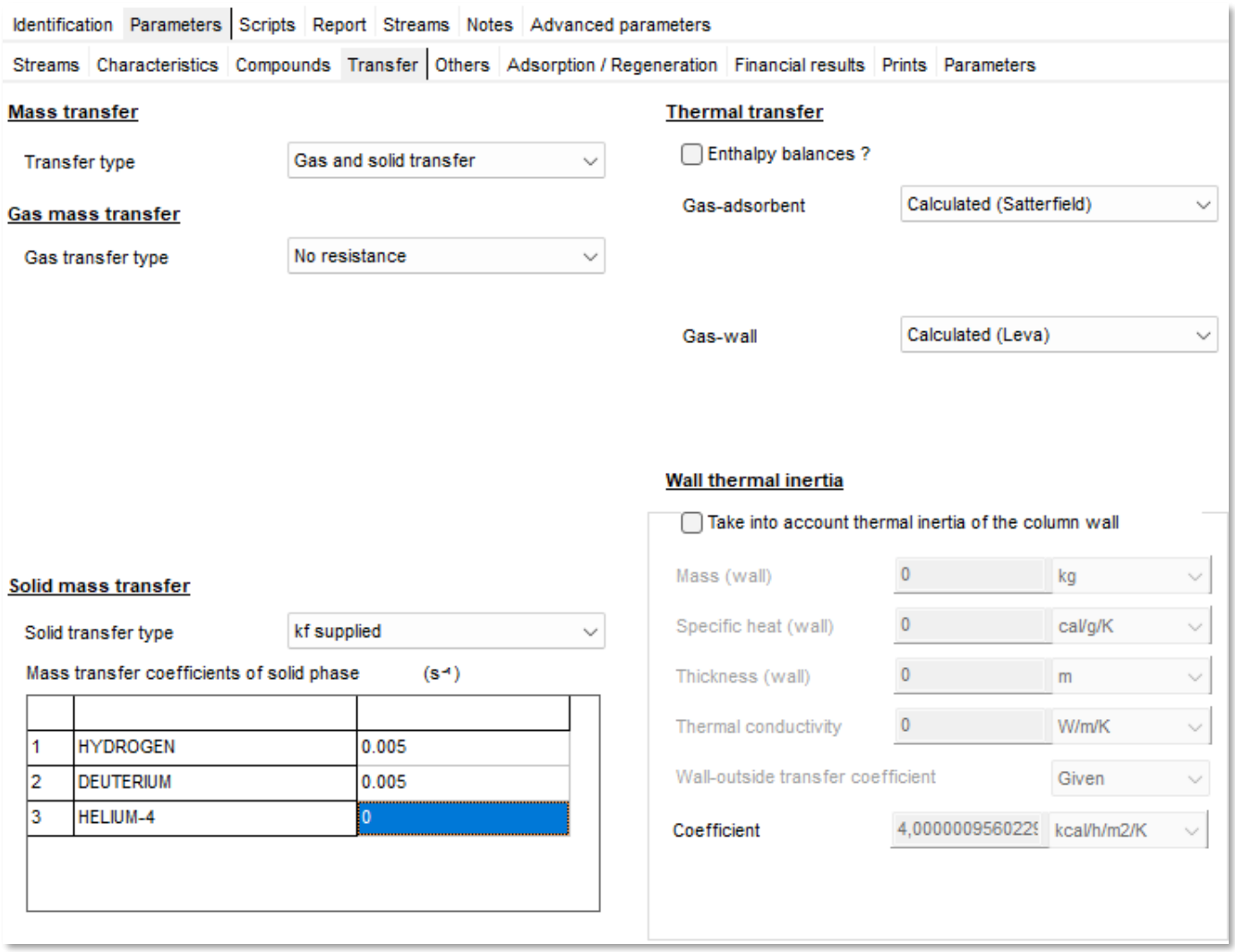
	Value
Mass transfer	
Type	Gas and solid transfer
Gas mass transfer	
Type	No resistance
Solid mass transfer	
Type	kf supplied
Hydrogen	0.005 s^{-1}
Deuterium	0.005 s^{-1}
Helium-4	0 s^{-1}

1.5.3.11. Thermal transfer

It's possible to take into account or to ignore the enthalpy balance in *ProSim DAC*. Not taking into account the enthalpy balance makes possible to simulate isothermal operation. When enthalpy balances are taken into account, the calculations require the knowledge of the gas-adsorbent and gas-wall heat transfer coefficients. These can be calculated or provided, as in this example. The simulation of this example is isothermal at the temperature of the gas to be purified (77.4 K) according to the work of [NIS95].

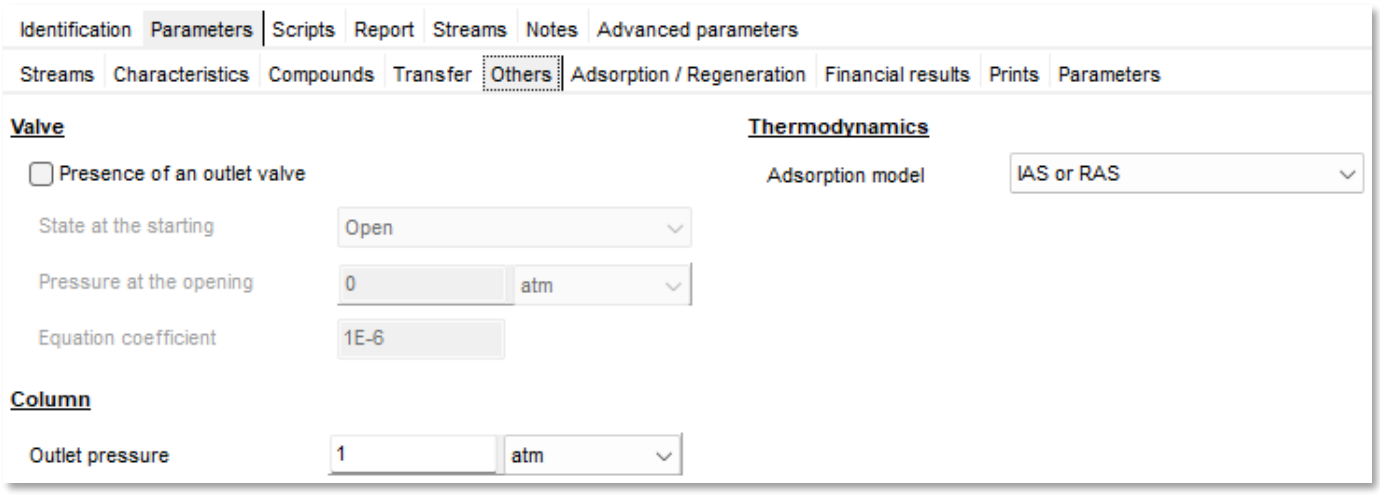
Thermal transfer	**Value**
Enthalpy balances	Not taken into account

The screenshot below shows the information of paragraphs 1.5.3.10. and 1.5.3.11. entered in the module's interface: "Parameters" tab, "Transfer" sub-tab.



1.5.3.12. Adsorption thermodynamic model

For this example, the IAS (Ideal Adsorption Solution) thermodynamic adsorption model [MYE65] is used. This model allows to take into account the competition between compounds regarding adsorption sites.

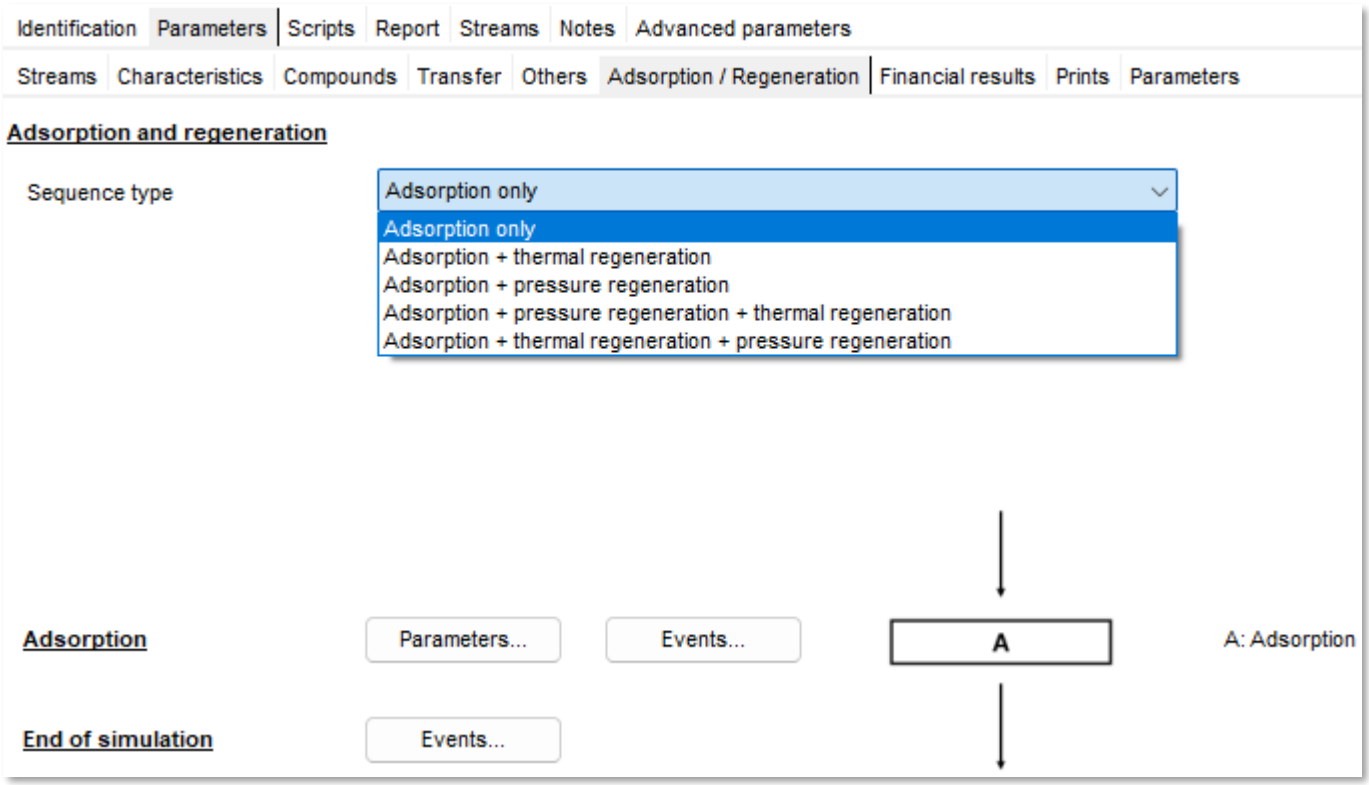


1.5.3.13. Sequence

The "Adsorption / Regeneration" sub-tab of the "Parameters" tab allows you to choose the type of cycle to simulate among the five available:

1. Adsorption only
2. Adsorption + thermal regeneration
3. Adsorption + pressure regeneration
4. Adsorption + pressure regeneration + thermal regeneration
5. Adsorption + thermal regeneration + pressure regeneration

The "Adsorption only" cycle is used in this example as shown in the screenshot below.



The parameters of the adsorption step are:

Adsorption	
Parameters	Default value
Event	Duration = 22 500 s

The simulation end event is:

End of simulation	
Event	End simulation time

1.5.3.14. Financial balance

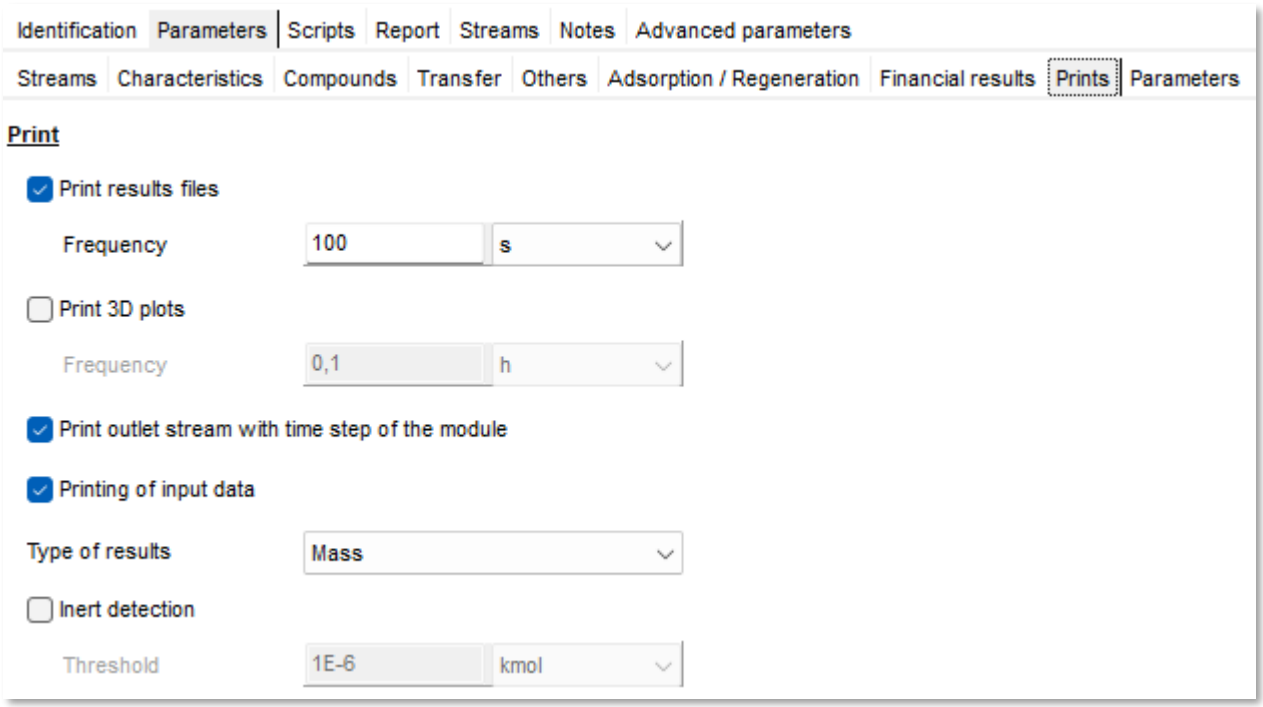
ProSim DAC carries out a financial balance on the regeneration steps. If the user is interested, it is possible to change the default parameters in the "Financial balance" sub-tab of the "Parameters" tab.

1.5.3.15. Printings

ProSim DAC offers various options for the printing of the calculation results. The parameters used in this example are listed in the table below.

Parameters	Value
Print result files	Frequency = 100 s
Print outlet stream with time step of the module	Yes
Printing of input data	Yes
Type of results	Mass
Other parameters	Default value

The screenshot below shows their specification in the "Parameters" tab, "Impressions" sub-tab.

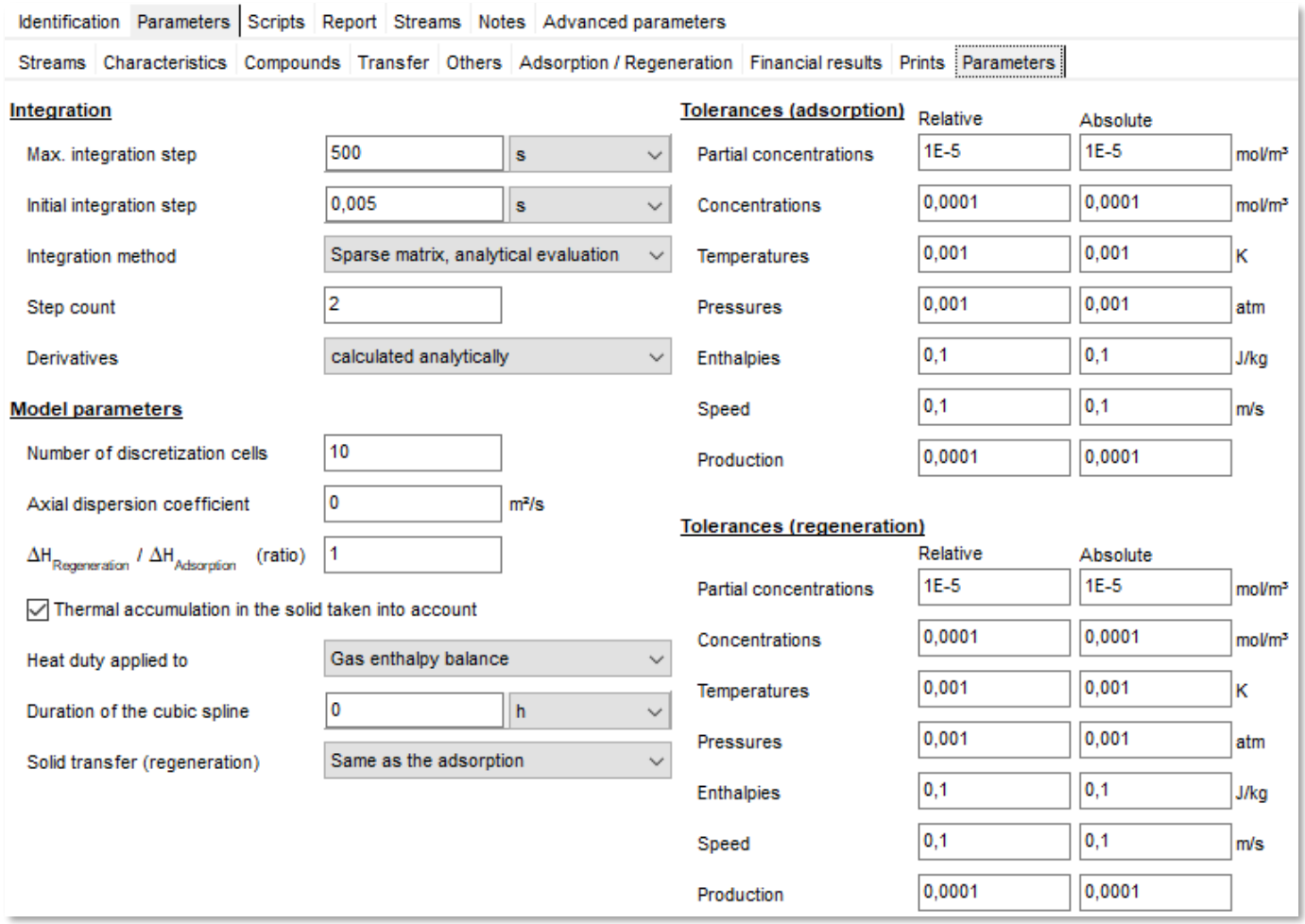


1.5.3.16. Parameters

ProSim DAC provides an access to a given number of numerical and models parameters. The model is based on time integration and spatial discretization. The column is here discretized into 10 cells in order to obtain a "fine" solution of the problem.

Model parameters	Value
Number of discretization cells	10
Other parameters	Default value

The screenshot below shows their specifications in the "Parameters" tab, "Parameters" sub-tab.



2. RESULTS

2.1. Adsorption column simulation report

The adsorption column simulation report ("Report") presents overall results (integrated over time), initial characteristics of the column, amount adsorbed, amount recovered during regeneration, etc.

The mass of adsorbent is not provided directly in the input data. It is calculated by *ProSim DAC* according to the geometric characteristics of the bed and the properties of the adsorbent. It is then interesting to check in the simulation report if the calculated mass of adsorbent corresponds to the one expected. For this example, the mass of adsorbent is 9.49 g.

COLUMN GENERAL CHARACTERISTICS

Adsorbent mass in the column:		9.49002	(g)
Column volume	:	14.8282	(cm3)
Solid volume	:	9.49002	(cm3)
Void volume	:	5.33814	(cm3)

With the selected operating parameters (see § 1.5.3. among others), 8.9 mg of hydrogen and 40 mg of deuterium are adsorbed. The adsorbed amount of helium-4 is the deviation to the mass balance due to the numerical resolution.

AMOUNT ADSORBED (g)

These values include the inventory of the gas phase of the column.

COMPONENT	Cycle N° 1
HYDROGEN	8.863256E-03
DEUTERIUM	3.991413E-02
HELIUM-4	-3.860674E-05

2.2. Adsorption column profiles

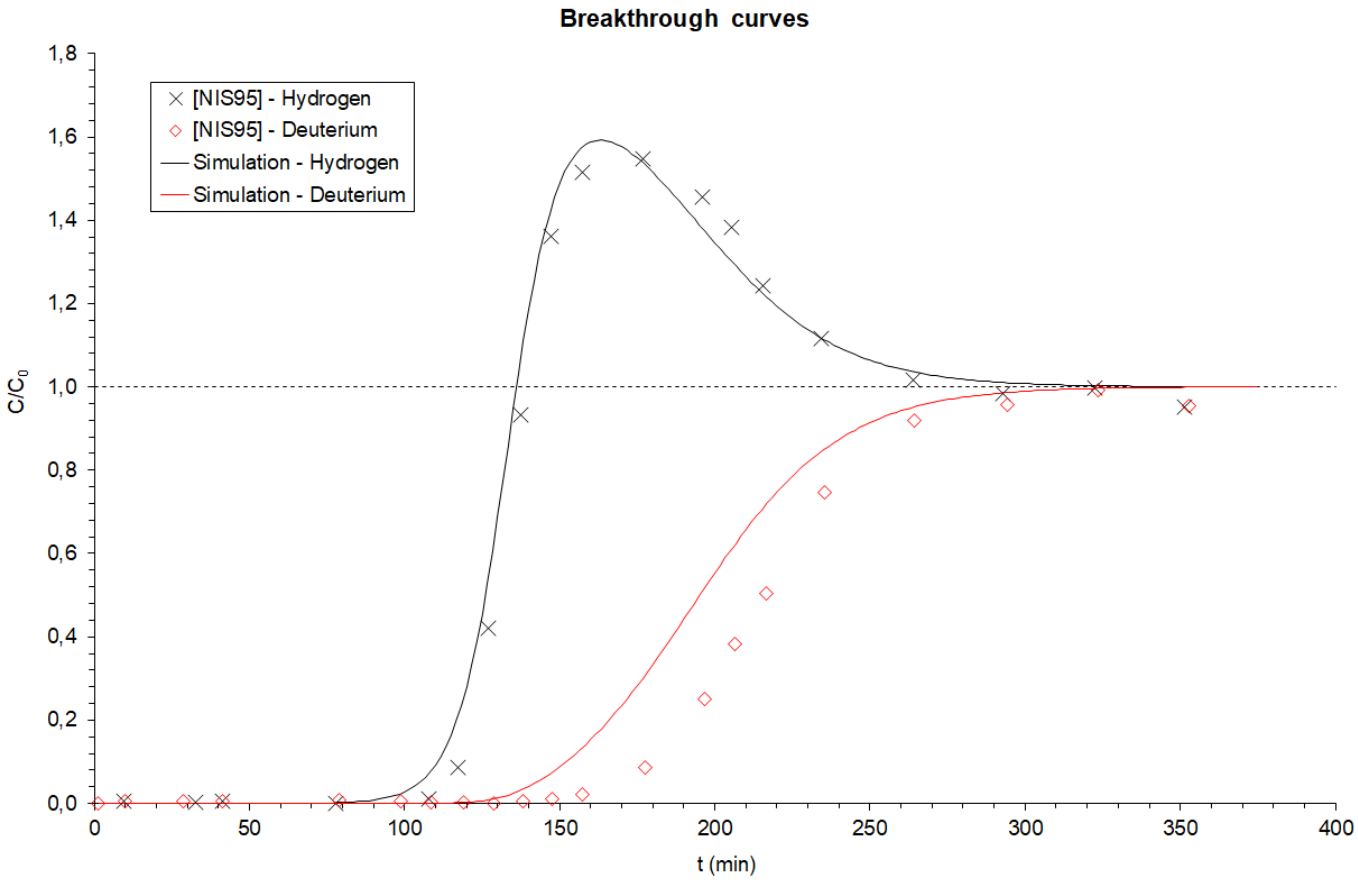
Several profiles in the adsorption column (temperatures, pressures, velocities, molar or mass concentrations, molar or mass fractions and breakthrough curves) are available at the end of the simulation in the editing window (tab "Profiles"). These profiles have two curves:

- ✓ “Fist cell”: Column inlet cell in the direction of adsorption flow
- ✓ “Last cell”: Column output cell in the direction of adsorption flow

If conter-current regeneration occurs:

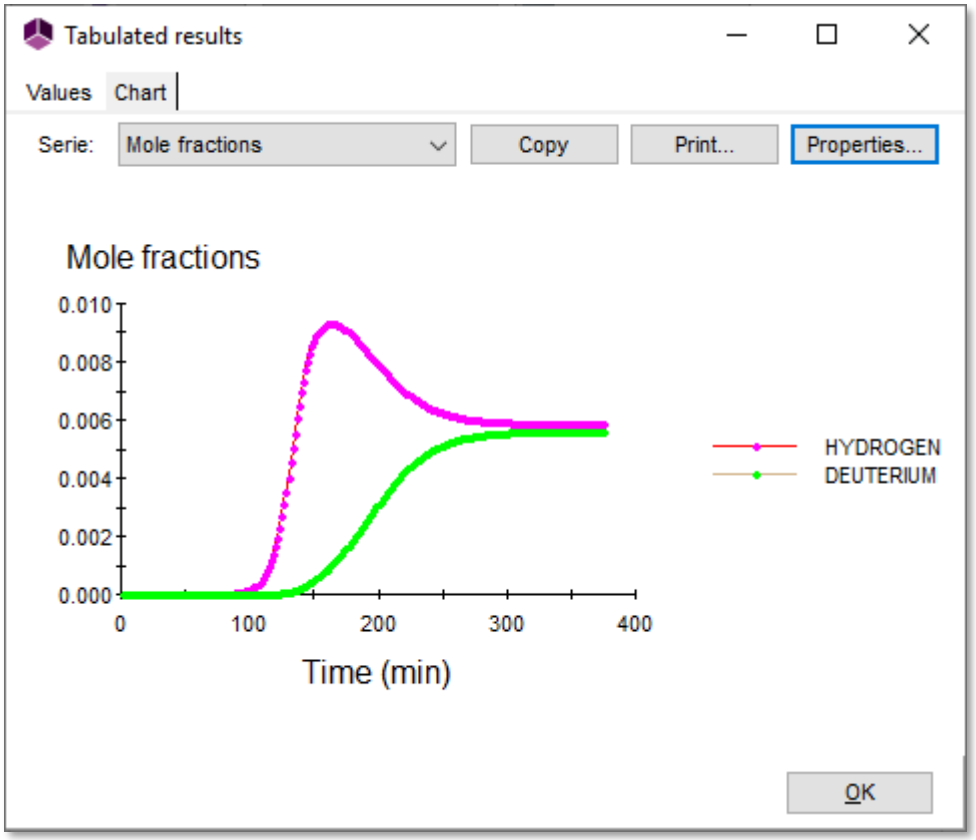
- ✓ “First cell”: Column outlet cell
- ✓ “Last cell”: Column inlet cell

The figure below shows the hydrogen and deuterium breakthrough curves obtained by simulation and the experimental data of [NIS95]. The simulation allows to find the values of [NIS95] for hydrogen both in breakthrough time and in maximum concentration. The breakthrough time of deuterium is somewhat underestimated by the simulation. The simulation makes it possible to represent the competition of the two compounds regarding the adsorption sites. The peak of hydrogen release due to the effect of deuterium adsorption is correctly reproduced.



2.3. Outlet streams profiles

Temperature, pressure, flow, enthalpy and composition profiles are also available for each adsorption column output streams at the end of the simulation. They can be accessed via the "Tabulated results..." button on the " Parameters" tab of the output stream editing window.



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