# 3. THE SPILL MODEL

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## 3.1. Introduction

HGSYSTEM version 1.0 (or NOV90 version) already contained a module HFSPILL to simulate the transient release of liquid hydrogen fluoride (HF) from a pressurised reservoir. This chapter describes the implementation of a new HGSYSTEM module, SPILL, a general transient release model for two-phase multi-compound mixtures in a pressurised reservoir. SPILL is available in HGSYSTEM version 3.0. HFSPILL is the HF-specific version of SPILL and uses similar correlations to calculate discharge rates. HFSPILL is therefore not discussed in the Technical Reference Manual.

Although SPILL's main use will be the simulation of pure *liquid* phase releases, it can also deal with releases that are pure vapour phase initially and SPILL will also simulate the vapour-only discharge after liquid exhaustion has occurred in a reservoir that initially contained a two-phase fluid.

A complication in describing a multi-compound release from a two-phase reservoir mixture, is that as long as there is a multi-compound liquid in the reservoir, *the composition of the liquid and vapour phase changes with time*. With decreasing reservoir pressure, the more volatile components in the liquid will vaporise more easily than less volatile compounds. Once the liquid is exhausted the reservoir mixture is vapour-only and the composition will no longer change with time. The SPILL program takes these effects into account, but to be able to do so it has to calculate the *number of kilomoles of each compound* in the reservoir as a function of time, which adds to the complexity of the model. Increasing the number of compounds in the reservoir mixture will increase the model run-time accordingly.

SPILL uses the standard HGSYSTEM non-reactive, multi-compound, two-phase thermodynamical model (AEROPLUME version) as described in Chapter 2.A. It is therefore intended to be run in combination with the physical properties database program DATAPROP, which will prepare a link file for SPILL containing all physical compound properties.

SPILL can be used as a front-end to the HGSYSTEM model AEROPLUME and it will generate the necessary link file.

The liquid discharge rates used in SPILL are based on literature correlations [2] and they are completely identical to the one used in AEROPLUME.

In this chapter, a detailed discussion of the SPILL model equations will be given. A detailed discussion of SPILL input parameters is given in the SPILL chapter in the User's Manual.
A sensitivity analysis for the SPILL model is described in [4].

## 3.2. The model equations

The basic *time-dependent* variables that are used in the SPILL algorithm are: **P(t)** (in Pa), the (absolute) pressure in the reservoir, **M(t)** (in kg), the total mass contained in the reservoir, **E(t)** (in J), the (internal) energy of the reservoir mixture, **h(t)** (in J/kg), the enthalpy of the reservoir mixture and **$N_\alpha$(t)** (-), the number of kmoles of chemical compound $\alpha$ present in the reservoir multi-compound mixture, $\alpha = 1, 2, ..., N$, where N is the total number of compounds in the mixture.

Thus there are N+4 variables which are all functions of time t (s) and N+4 equations are needed to define the problem completely.

For given values of the mixture enthalpy h and the reservoir pressure P, the *thermodynamical* state is fixed and using the thermodynamical model equations, values for the density $\rho(t)$ (kg/m$^3$) and the temperature T(t) (K) of the reservoir mixture can be calculated for every time t. Thus $\rho$ and T are not basic variables but they can be calculated from these at every moment in time.

The thermodynamical model used in SPILL is the HGSYSTEM two-phase non-reactive multi-compound model as described in Chapter 2.A.

The set of N+4 equations consists of 2 algebraic equations and N+2 first order ordinary differential equations. These equations are solved as one set using the same numerical solver, SPRINT [1], as employed in AEROPLUME and HFPLUME.

### 3.2.1. Algebraic equations

The two algebraic equations are given by:

$$V \cdot \rho(t) = M(t) \tag{1}$$

and

$$E(t) = \left( h(t) - \frac{P(t)}{\rho(t)} \right) \cdot M(t) \tag{2}$$

where V is the (constant) user-specified reservoir volume ($m^3$).

These two relations ensure *physical consistency* between the several model variables.

Please note that h, P and ρ also must satisfy the *thermodynamical equations* as dictated by the thermodynamical model being used.

### 3.2.2. Conservation of total reservoir mass

The first differential equation expresses *conservation of mass* and it governs the rate of change of the total reservoir mass content M:

$$\frac{dM(t)}{dt} = \dot{m}(t) \qquad (3)$$

where $\dot{m}(t)$ (kg/s) is the (instantaneous) mass flow rate leaving the reservoir at time t, the value of $\dot{m}(t)$ is taken negative here as it is an *outflowing* rate.

The value of $\dot{m}(t)$ is given by correlations from literature [2].

For a *vapour-only* release, the discharge rate used is simply the well-known (maximum) discharge rate found for an ideal gas release, either *choked* or *unchoked*. For a choked vapour-only release the result is

$$\dot{m} = -C_D^g \cdot A \cdot \left(\frac{2}{1+\gamma}\right)^{1/(\gamma-1)} \cdot \left(\frac{\gamma}{1+\gamma}\right) \cdot \sqrt{2 \cdot \rho(t) \cdot P(t)} \qquad (4)$$

and for unchoked vapour-only flow the result is

$$\dot{m}(t) = -C_D^g \cdot A \cdot \sqrt{\frac{\gamma}{\gamma - 1}} \cdot \sqrt{2 \cdot \rho(t) \cdot P(t) \cdot \left\{ \left(\frac{P_{atm}}{P(t)}\right)^{\frac{2}{\gamma}} - \left(\frac{P_{atm}}{P(t)}\right)^{\frac{\gamma+1}{\gamma}} \right\}} \qquad (5)$$

where $P_{atm}$ (Pa) is the atmospheric pressure, A ($m^2$) is the area of the discharge opening, $\gamma$ (-) is the ratio of specific heats ($c_p/c_v$) and $C_D^g$ (-) is the vapour discharge coefficient. $C_D^g$ has a default value of 1.0, but the user of SPILL can override this value if necessary.

For a *liquid* release, first the mixture saturation pressure $P_{sat}$ is calculated as

$$P_{sat} = \frac{\sum_{\alpha=1}^{N} y_{\alpha\ell} \cdot P_{sat,\alpha}(T)}{\sum_{\alpha=1}^{N} y_{\alpha\ell}} \tag{6}$$

where $y_{\alpha\ell}$ is the molar fraction *within the total mixture* of liquid compound $\alpha$ and $P_{sat,\alpha}(t)$ is the saturation pressure of compound $\alpha$ at temperature T. Note that this definition of $P_{sat}$ is inspired by Raoult's law as discussed in Chapter 2.A.

If $P_{sat}$ is less than $P_{atm}$ then the liquid mixture is *subcooled* even at atmospheric conditions and no flashing will occur at the exit. In SPILL the flow regime is then called *unchoked liquid flow*. From Fauske and Epstein [2] a Bernoulli-like expression for the discharge rate is found

$$\dot{m}(t) = -C_D^\ell \cdot A \cdot \sqrt{2 \cdot \rho_\ell(t) \cdot \left(P(t) - P_{atm}\right)} \tag{7}$$

where $\rho_\ell$ is the density of the *liquid* in the reservoir. The liquid discharge coefficient $C_D^\ell$ has a default value of 0.61 [2], but again the user can override this value by setting the relevant SPILL input parameter (see the SPILL chapter in the User's Manual).

When $P_{sat}$ exceeds $P_{atm}$, the flow regime is called *choked liquid flow* in SPILL. If this occurs, i.e. the liquid mixture in the reservoir, which is subcooled at reservoir conditions, is *not* subcooled at atmospheric conditions, then a distinction must be made between reservoir conditions that are *near the saturation point* and those that are not.

If $\left|P(t) - P_{sat}\right| > 10 \cdot P_{sat}$ (reservoir conditions far from the saturation point) then following [2]

$$\dot{m}(t) = -C_D^\ell \cdot A \cdot \sqrt{2 \cdot \rho_\ell \cdot \left|P(t) - P_{sat}\right|} \tag{8}$$

If $\left|P(t) - P_{sat}\right| < 0.1 \cdot P_{sat}$ (reservoir conditions near the saturation point), [2] gives

$$\dot{m}(t) = -C_D^\ell \cdot A \cdot \sqrt{\left|\frac{1}{dv/dP}\right|} \tag{9}$$

where v = 1/ρ (m³/kg) is the specific volume of the mixture. The term $\left|\frac{1}{dv/dP}\right|$ is estimated, following [2], by

$$\left|\frac{1}{dv/dP}\right| = \left(\frac{h_{vap}}{\Delta v_{vap}}\right)^2 / \left(T \cdot C_{p,\ell}\right) \tag{10}$$

where $h_{vap}$ (J/kg) is the heat of vaporisation, $\Delta v_{vap}$ ($m^3$/kg) the change in specific volume going from the liquid to the vapour state, $C_{p,\ell}$ (J/(kg·K)) is the specific heat of the liquid mixture and T (K) is the reservoir temperature.

For the intermediate stage, $0.1 \cdot P_{sat} \leq |P(t) - P_{sat}| \leq 10 \cdot P_{sat}$, *linear interpolation* between the two previous cases is used. Let FACTOR, TERM1 and TERM2 be defined by

$$\mathrm{FACTOR} = \frac{|P(t) - P_{sat}|}{P_{sat}} \tag{11}$$

$$\mathrm{TERM1} = 2 \cdot \rho_\ell \cdot |P(t) - P_{sat}| \tag{12}$$

$$\mathrm{TERM2} = \left| \frac{1}{dv / dP} \right| \tag{13}$$

Define the variable TERM3 by using linear interpolation between TERM1 and TERM2 using FACTOR, that is

$$\mathrm{TERM3} = \mathrm{TERM2} + (\mathrm{FACTOR} - 0.1) \cdot \frac{\mathrm{TERM1} - \mathrm{TERM2}}{10.0 - 0.1} \tag{14}$$

and the reservoir mass discharge rate when $0.1 \cdot P_{sat} \leq |P(t) - P_{sat}| \leq 10 \cdot P_{sat}$, is given by

$$\dot{m}(t) = -C_D^\ell \cdot A \cdot \sqrt{\mathrm{TERM3}} \tag{15}$$

This linear interpolation procedure for the case where $0.1 \cdot P_{sat} \leq |P(t) - P_{sat}| \leq 10 \cdot P_{sat}$ is found to give more satisfactory results than the recommendation in [2] , the latter being equivalent to taking TERM3 = TERM1 + TERM2.

Please note that the mass discharge literature correlations and the definition of $P_{sat}$ used in SPILL and AEROPLUME (HGSYSTEM version 3.0) are completely identical.

### 3.2.3. Conservation of energy

The second differential equation expresses *conservation of energy*

$$\frac{dE(t)}{dt} = h_{exit}(t) \cdot \dot{m}(t) + Q_{atm}(t) \tag{16}$$

where $h_{exit}$ (J/kg) is the enthalpy of the discharged fluid and $Q_{atm}$ (W) is the total heat exchange with the atmosphere surrounding the reservoir. For a pure liquid release $h_{exit}$ is equal to the enthalpy of the liquid phase in the reservoir which is *not* equal to the mixture enthalpy h. For vapour-only situations this difference does not occur.

$Q_{atm}$ can be calculated as

$$Q_{atm} = A_{heat} \cdot (\Phi_{rad} + \Phi_{conv} + \Phi_{solar}) \qquad (17)$$

where $A_{heat}$ ($m^2$) is the user-specified total reservoir area over which heat transfer with the surrounding atmosphere takes place, $\Phi_{rad}$ ($W/m^2$) is the radiative heat flux given by

$$\Phi_{rad} = \sigma \cdot \varepsilon \cdot (T_{atm}^4 - T^4) \qquad (18)$$

where $\sigma$ is the Stefan-Boltzmann constant ($5.67 \cdot 10^{-8}$ $W/(m^2 \cdot K)$), $\varepsilon$ (-) the user-specified emissivity of the reservoir outside wall material and $T_{atm}$ (K) the user-specified temperature of the surrounding air.

$\Phi_{conv}$ ($W/m^2$) is the convective heat flux, given by [3]

$$\Phi_{conv} = 1.97 \cdot (T_{atm} - T) \cdot \left|T_{atm} - T\right|^{0.25} \qquad (19)$$

$\Phi_{solar}$ ($W/m^2$) is a user-specified direct solar heat flux on the reservoir.

Note that a user-specified value for $A_{heat}$ of 0.0, effectively sets the heat transfer between the reservoir and the ambient atmosphere to 0.0.

### 3.2.4 Conservation of mixture compound $\alpha$

The final N differential equations express *conservation of each compound* $\alpha$ in the mixture.

For a *vapour-only release* (after liquid exhaustion or for a vapour-filled reservoir), the *total* number of kmoles leaving the reservoir is equal to $\dot{m}/M$, where $M$ (kg/kmole) is the molar mass of the reservoir vapour, which is constant once the release is vapour-only. The number of kmoles of compound $\alpha$ leaving the reservoir per second is then simply $y_\alpha \cdot \dot{m}(t)/M$ (kmole/s), where $y_\alpha$ is the molar fraction of compound $\alpha$ in the mixture. Again, $y_\alpha$ does not change with time for vapour-only releases. So in this case for all compounds $\alpha$ the following equation holds

$$\frac{dN_\alpha(t)}{dt} = y_\alpha \cdot \dot{m}(t) / M \qquad \alpha = 1, 2, ..., N \qquad (20)$$

For a *multi-compound liquid-only release*, where the reservoir contains a real two-phase multi-compound mixture, the situation is more complicated, as the mixture composition both in the vapour and the liquid phase changes with time.

For a liquid-only release, the change per second in the number of kmoles of compound α, $\frac{dN_\alpha}{dt}$, is given by

$$\frac{dN_\alpha}{dt} = \frac{N_{\alpha,\ell}}{N_\ell} \cdot \frac{dN_\ell}{dt} \qquad \alpha = 1, 2, ..., N \qquad (21)$$

where $N_\ell$ is the total number of kmoles of liquid in the reservoir. In this expression $\frac{dN_\ell}{dt}$ is equal to $\frac{\dot{m}}{M_\ell}$, where $M_\ell$ is the (now time-dependent) molar mass (kg/kmole) of the total liquid phase fluid.

The term $\frac{N_{\alpha,\ell}}{N_\ell}$ in (21) can be interpreted as the mole fraction of liquid compound α in the total liquid phase of the reservoir mixture. The thermodynamic model uses as a basic variable $y_{\alpha,\ell}$, which is the molar fraction of compound α within the *total mixture*. Let L denote the total liquid mole fraction within the reservoir, then $\frac{N_{\alpha,\ell}}{N_\ell} = \frac{y_{\alpha,\ell}}{L}$.

Thus for a *liquid-only release* the equation expressing conservation of compound α will be

$$\frac{dN_\alpha(t)}{dt} = \frac{y_{\alpha,\ell}(t)}{L(t)} \cdot \frac{\dot{m}(t)}{M_\ell(t)} \qquad \alpha = 1, 2, ..., N \qquad (22)$$

### 3.2.5. Initial conditions

Initial conditions for the N+2 first order differential equations are needed. The initial values for the reservoir pressure P and temperature T are user-specified. The initial value for the reservoir mass contents M is either user-specified or calculated by SPILL as the maximum reservoir contents for given P and T.

Based on the initial P and T and the initial mixture composition, all user-specified, SPILL calculates the initial value for h, the reservoir enthalpy, ρ, the mixture density and the initial values of $N_\alpha$ for all compounds α. This is done using the thermodynamic model.

There is a slight complication when the user has specified an initial reservoir mass contents, M, lower than the maximum for the given initial P and T. In this case the value of $\rho$ given by relation (1) on one hand and the value of $\rho$ following from the thermodynamical relations will not be consistent. In other words, the correct value for P for the given mass M at the given temperature would be lower than specified by the user. In this case SPILL changes the initial mixture composition by adding *dry air* to the mixture. The needed amount is calculated using the solver NAESOL in such a way that finally all relevant relations (relation (1) plus thermodynamical relations) are satisfied. SPILL is actually pressurising the given amount of material to the required pressured using dry air.

If the user specifies a value of M larger than the maximum possible for the given P and T, SPILL simply resets M to the maximum value.

The input option of specifying the initial value of M is only effective if the SPECIES keyword in the GASDATA input block is being used *and* if the initial reservoir mixture is more dense than dry air. In all other cases, the initial value of M is calculated by the program based on mixture composition and reservoir pressure, temperature and volume.

The initial value for the total energy E is simply calculated by using relation (2) in which all other (initial) values are now known.

This completes the description of the N+4 equations of the SPILL mathematical model.

### 3.3. Notation

| | |
|---|---|
| A | surface area of release opening ($m^2$) |
| $C_D$ | discharge coefficient (-) |
| $C_p$ | specific heat (J/(kg·K)) |
| E | reservoir mixture (internal) energy (J) |
| h | reservoir mixture enthalpy (J/kg) |
| $\dot{m}$ | mass flow rate out of reservoir (kg/s) |
| M | reservoir total mass content (kg) |
| $M$ | molar mass (kg/kmole) |
| N | total number of chemical compounds in reservoir mixture |
| $N_\alpha$ | number of kmoles of compound $\alpha$ in reservoir (-) |
| P | reservoir pressure (Pa) |
| Q | total heat transfer reservoir-ambient atmosphere (W) |
| T | reservoir temperature (K) |

| | |
|---|---|
| t | time (s) |
| V | reservoir volume ($m^3$) |
| v | fluid specific volume ($m^3/kg$) |
| $y_\alpha$ | molar fraction of compound $\alpha$ (-) |
| | |
| $\alpha$ | chemical compound indicator |
| $\Delta v$ | change in specific volume liquid-vapour ($m^3/kg$) |
| $\gamma$ | ratio of specific heats ($c_p/c_v$) for ideal gas (-) |
| $\rho$ | reservoir mixture density ($kg/m^3$) |
| $\Phi$ | heat flux ($W/m^2$) |

Subscripts and superscripts

| | |
|---|---|
| atm | ambient atmosphere |
| $\alpha$ | chemical compound indicator |
| conv | convective heat transfer |
| g | vapour (gas) phase |
| $\ell$ | liquid phase |
| rad | radiative heat transfer |
| sat | saturation |
| vap | vaporisation |
| solar | solar heat |

## 3.4. References

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