VERIFICATION

UDM THERMODYNAMICS: CHAPTER 3

DATE: December 2023

Equilibrium model for HF

No.	Date	Reason for Issue	Prepared by	Verified by	Approved by
1	1999	6.0 version	Witlox		
2	Aug 2005	6.6 version (MC)	Witlox and Harper		
3	Jan 2021	8.4 version	Harper		
4	May 2021	Apply new template	D. Vatier		

Date: December 2023

Prepared by: Digital Solutions at DNV

ABSTRACT

This chapter contains a brief assessment of the HF thermodynamics model as implemented into the UDM:

1. The HF thermodynamics model is based on the HGSYSTEM thermodynamics model. Therefore the UDM thermodynamic predictions are compared against those of HGSYSTEM, and predictions are shown to be reasonably consistent. This also implies that good agreement is obtained against experiments by Schotte for mixing of HF with moist air. Some small oscillations do occur for the HF simulations, which may be explained by the lower accuracy adopted in the UDM (to reduce CPU time).

2. A limited sensitivity analysis is carried out for mixing of HF with moist air, whereby both humidity and initial liquid mass fraction are varied.

3. The UDM simulation against the Goldfish 3 experiments has been investigated in more detail, and also compared against the corresponding HGSYSTEM simulation. Good agreement is obtained against both the experimental data and the HGSYSTEM predictions.

As part of further work a cleaner implementation of the HF thermodynamics is recommended. This could also include extension of the algorithm to allow for the presence of inert gases and/or water in the released HF.

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3 EQUILIBRIUM MODEL FOR HF

3.1 Sensitivity analysis

This section describes the verification of the HF thermodynamics model, and illustrates the effect of polymerisation and fog formation. The chosen examples are taken from Witlox[i]. See the latter reference for further details.

The model is tested for mixing of HF with moist air excluding effects of heat and water-vapour transfer from the substrate. In the sensitivity analysis both humidity and the initial liquid mass fraction of the HF have been varied. Results are included in the figures below. The figures plot the mixture temperature (K) against the equivalent HF mole fraction (based on all HF monomer). The results of the following analyses are shown in these figures:

1. Mixing of HF vapour with moist air at 26^{0}C. Figure 3.1 includes temperature results corresponding to Schotte's experiments (humidity = 50%), for both the UDM thermodynamics testbed and HEGADAS.

2. Figure 3.2 includes results for the mass fractions (humidity = 70%). Figure 3.3 demonstrates the effect of variation of humidity on mixture temperature and mixture density[1].

3. Mixing of HF vapour/liquid with moist air (50% humidity) at the post-flash temperature of 19.55^{o}C. Figure 3.4 includes results for 0.8 post-flash liquid mass fraction of HF for both the UDM, the UDM thermodynamics test bed and HEGADAS. Figure 3.5 demonstrates the effect of variation of liquid mass fraction.

The above figures demonstrate the mechanisms for mixture heating and cooling:

- Upon mixing of HF vapour with the air, the HF depolymerises. This requires energy and therefore leads to mixture cooling.

- Upon mixing of HF vapour with moist air, a liquid aqueous fog forms, which gradually disappears if the HF is further diluted with the air. Fog formation leads to mixture heating, while fog disappearance leads to mixture cooling. Figure 3.3a. demonstrates that the increasing amount of fog formation for increasing humidity leads to increasing temperatures. Figure 3.5 demonstrates that for increasing amount of initial liquid HF mass fraction more fog disappearance will occur and therefore more mixture cooling.

- Mixing of air causes a heating effect for cloud temperature below ambient, and a cooling effect for cloud temperature above ambient.

[1] Results for the mixture density should ideally be checked against HGSYSTEM as well.

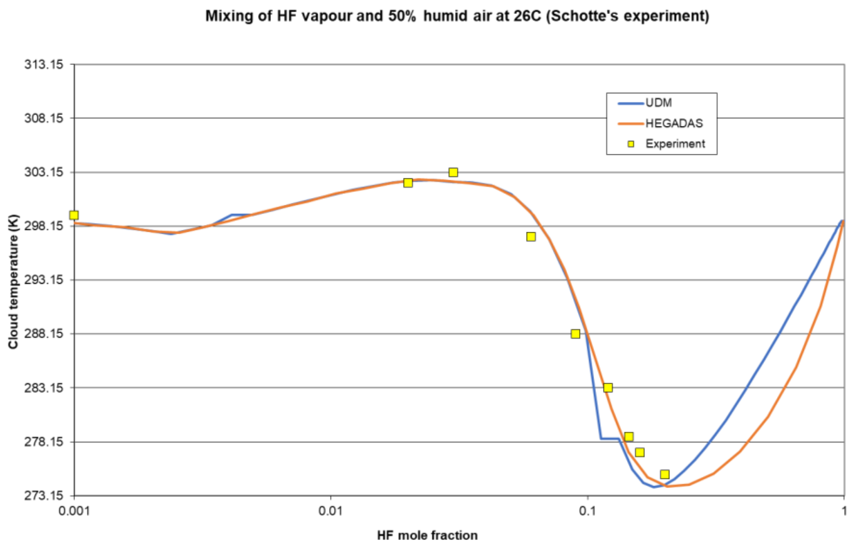


Figure 3.1. **Mixing at 26C of HF vapour with moist air (humidity = 50%); HEGADAS and UDM thermodynamic test-bed predictions, and experimental data by Schotte**

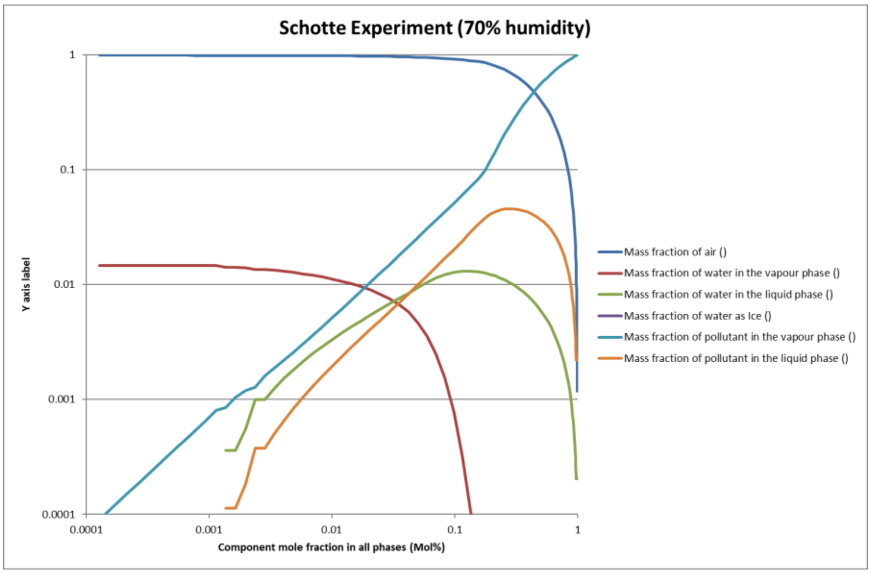
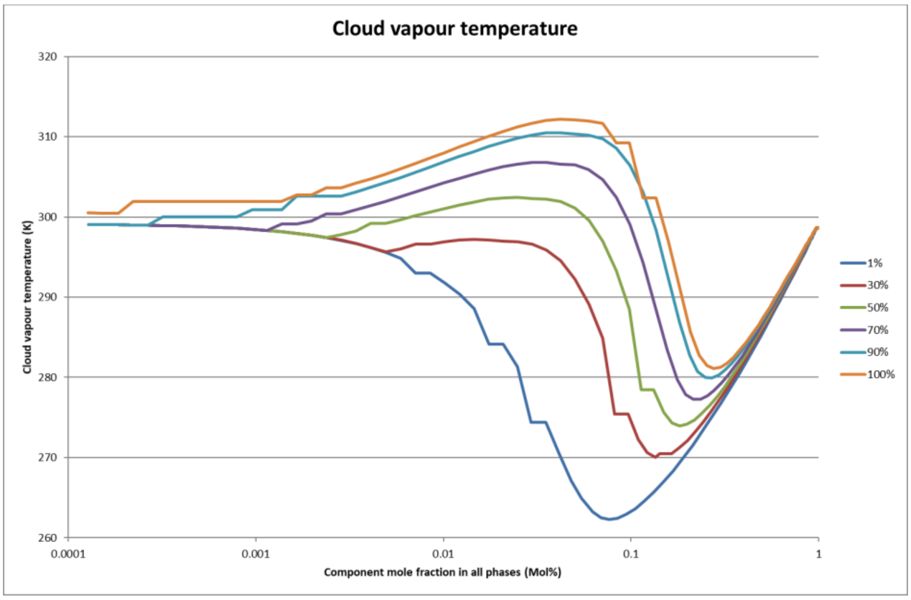
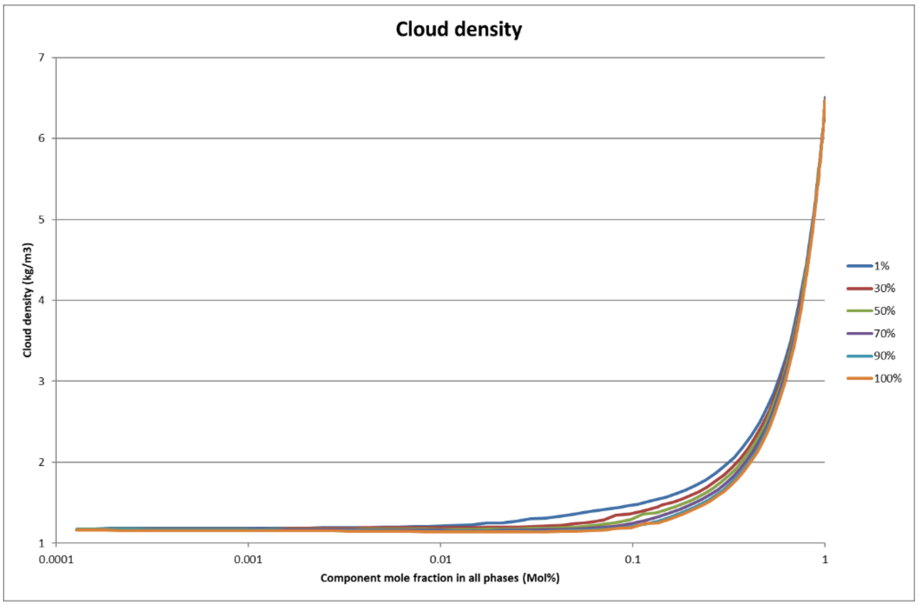


Figure 3.2. **Mixing at 26C of HF vapour with moist air (70% humidity); UDM thermodynamics test-bed predictions for mass fractions**

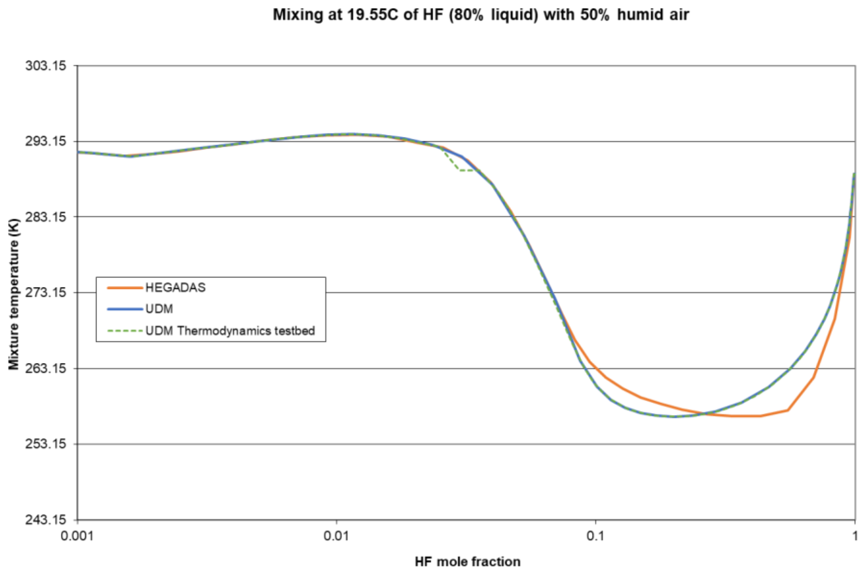


(a) cloud temperature (K)

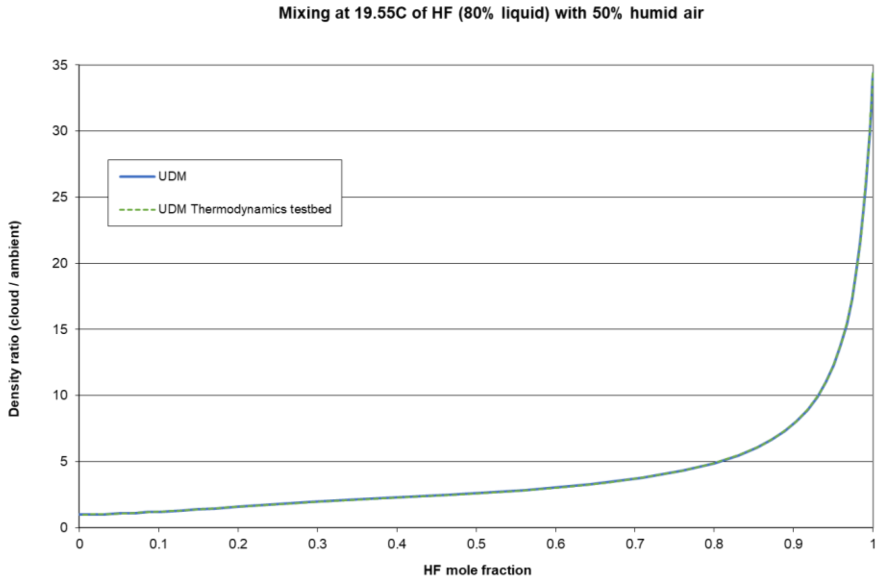


(b) cloud density (kg/m^3)

Figure 3.3. Mixing of HF vapour with moist air (varying humidity) at 26°C; UDM thermodynamic test-bed predictions for mixture density



(a) **HEGADAS, UDM and UDM thermodynamics test-bed predictions for mixture temperature**



(b) **UDM and UDM thermodynamics test-bed predictions for ratio of mixture and ambient density**

Figure 3.4. Mixing at 19.55C of air (50% humidity) with HF vapour/liquid (80% liquid mass fraction)

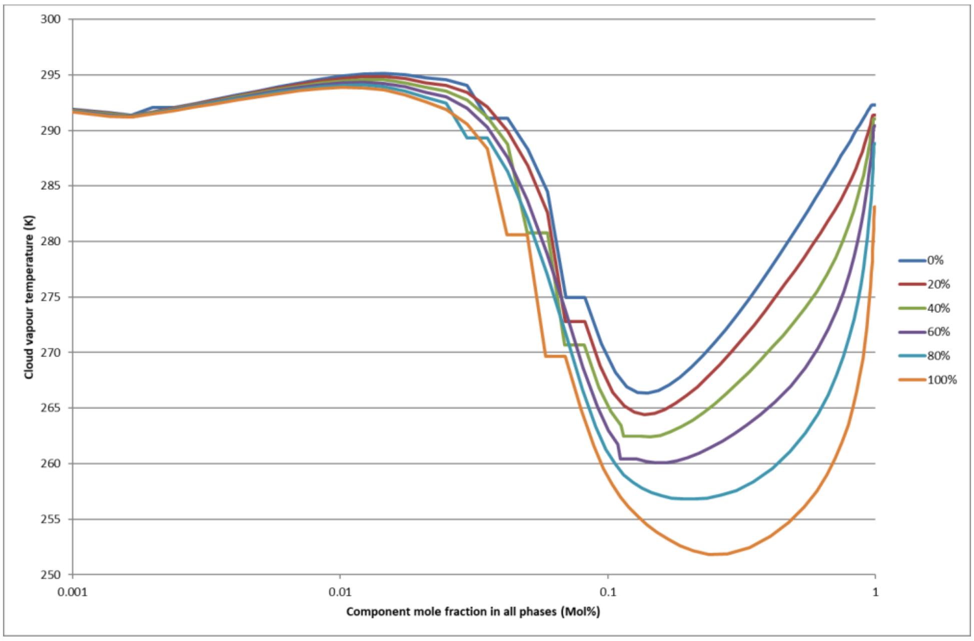


Figure 3.5. **Mixing at 19.55C of air (50% humidity) with HF vapour/liquid (varying liquid mass fraction); UDM thermodynamics test-bed predictions**

3.2 Comparison against Goldfish experiments

The UDM simulation against the Goldfish 3 experiments is investigated in detail, and also compared against the corresponding HGSYSTEM simulation. The columns in Table 3.1 include an overview of the adopted input data and the observed or calculated output data. The columns correspond to the following:

1. The first column included the input parameters for the Goldfish 3 experiment and the observed maximum concentrations[2] as explained in Chapter 9 of the HGSYSTEM 1.0 Technical Reference Manual[ii]. Note that the input data differ from those used by Hanna[iii], which adopts a lower value for the humidity and a larger value for the surface roughness[3].

2. The second column includes the HGSYSTEM input parameters and output data for Goldfish 3 as described in the HGSYSTEM 1.0 Technical Reference Manual[ii].

3. The third column includes input and output data that are calculated using the more recent version HGSYSTEM 3.0. Note in the run the default Briggs formula for the ambient cross-wind dispersion coefficient σ_{ya} is adopted.

4. The fourth column includes UDM results with heat transfer (switching it off has little effect). The UDM input data are based on the HGSYSTEM 1.0 Technical Reference Manual[ii]. The post-flash calculations are carried out using the PHAST 6.0 model using an isenthalpic flash assumption.

The results of the UDM and HGSYSTEM 3.0 (HFPLUME/HEGADAS) simulations can be summarised as follows:

1. Figure 3.6 shows that the predicted maximum concentrations are in close agreement with the experimental data prior to the passive transition. Downwind of the passive transition the under-prediction increases, because the passive spreading predicted by UDM is larger than that observed. This has been verified by comparing the UDM concentration profiles against those observed; see **Error! Reference source not found.**.

2. Figure 3.7 compares the predicted temperatures against the observed temperatures. Note that generally good agreement is obtained with the experimental data, though the model does under-predict in the 20 – 60m region.

[2] Concentrations given by McFarlane are in fact the mean concentration over the steady-state period. Hanna uses maximum observed concentration. We use McFarlane mean concentrations for all UDM Goldfish simulations.

[3] Webber et al. (1984) state humidities were converted by Hanna from dew point values to relative humidity, though McFarlane does appear to report relative humidity. The significant difference for the surface roughness (Hanna uses 3e-3m) is unknown, though McFarlane does give some detail on their reasoning behind the 2e-4m figure. Again, we use McFarlane data throughout

Table 3.1. Model parameters for Goldfish 3

Model input parameters are reservoir, pipe-exit plane, release data, inclusion of heat transfer from the ground and adopted formula for passive dispersion coefficient σ_{ya}. Model output parameters (or observed experimental data) are post-flash data and maximum concentrations.

Parameter	Shell report experiment	Shell report HGSYSTEM	UDM
RESERVOIR			
- temperature (C)	39.4	39.4	39.4
- pressure (atm)	8.96	8.96	8.96
PIPE EXIT-PLANE			
- orifice diameter (m)	0.0242	0.0242	0.0242
- orifice height (m)	1.263	1.263	1.263
RELEASE DATA			
- HF release rate (kg/s)	10.07	10.07	10.07
- release duration (s)	360	∞ (steady)	360
AMBIENT			
- temperature (C)	36.5	36.5	36.5
- pressure (atm)	1	1	1
- relative humidity (%)	35	35	35
- wind speed at 2m (m/s)	5.4	5.4	5.4
- surface roughness (m)	0.0002	0.0002	0.0002
- stability class	D	D	D
- averaging time (s)	60	60	60
HEAT TRANSFER	Yes	Yes	Yes
passive $\sigma_{ya}(x)$, m	$0.17\ x^{0.79}$	$0.17\ x^{0.79}$	Mullen
POST-FLASH data	(unknown)	(calculated)	(i/o)
- temperature (C)	?	19.55	19.35 (o)
- velocity (m/s)	?	45.84	42.2 (i)
- diameter (m)	?	0.13	0.082 (o)
- liquid HF mass fraction	?	0.842	0.867 (i)
MAX.CONC. @ 1m (%mol.fr.)			
- 300 m	1.6	1.02	1.13
- 1000 m	0.23	0.16	0.099
- 3000 m	0.02	0.0277	0.0073

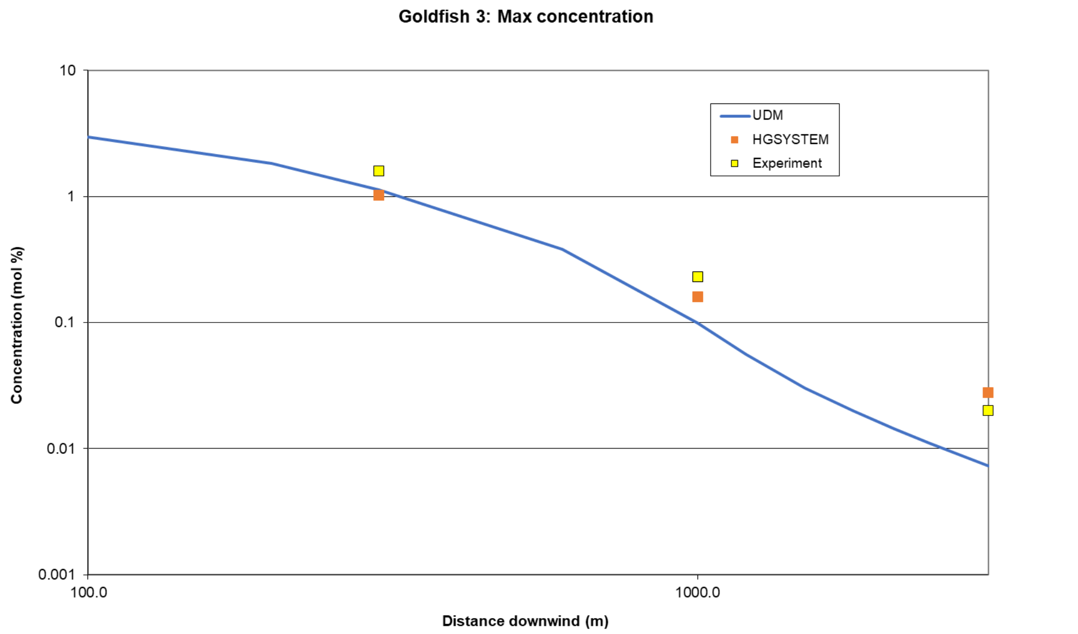


Figure 3.6. **Goldfish 3 simulations for HGSYSTEM and UDM; averaged maximum concentration versus downwind distance**

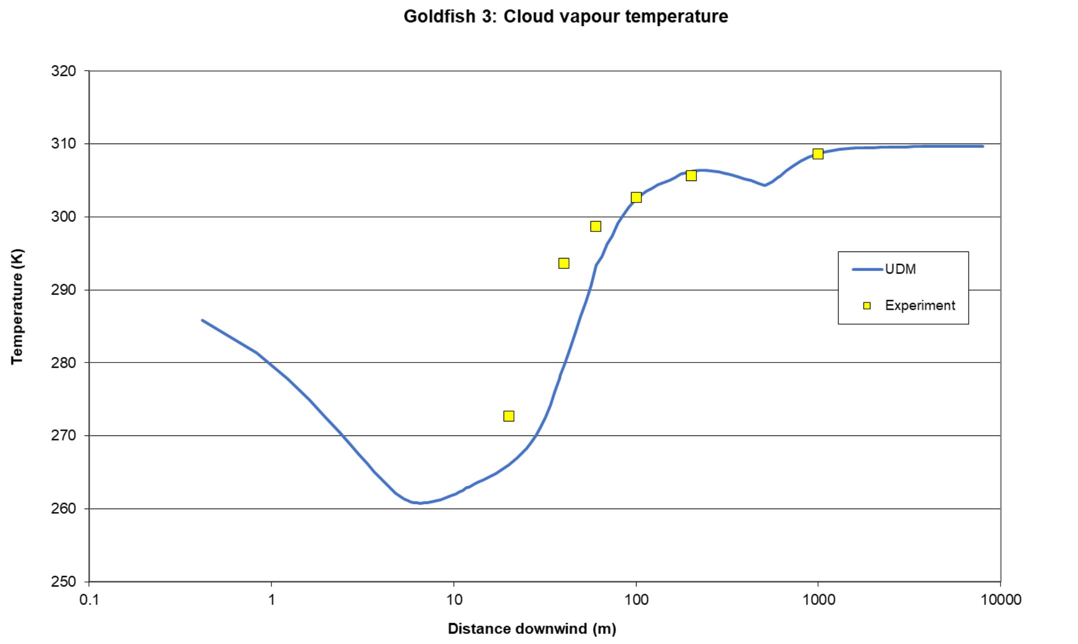


Figure 3.7. **Goldfish 3 simulations for the UDM; temperature versus downwind distance**

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REFERENCES

[i] Witlox, H.W.M., “Thermodynamics model for mixing of moist air with pollutant consisting of HF, ideal gas and water”, Report TNER.93.021 (non-confidential), Thornton Research Centre, Shell Research, Chester, England (1993)

[ii] McFarlane, K., Prothero, A., Puttock, J.S., Roberts, P.T., and Witlox, H.W.M., “Development and validation of atmospheric dispersion models for ideal gases and hydrogen fluoride”, Part I: Technical Reference Manual, Shell Report TNER.90.015, Thornton Research Centre (1990)

[iii] Hanna, S.R., D.G.Strimaitis, and J.C.Chang, “Hazard response modeling uncertainty (A quantitative method)”, Sigma Research Corp. report, Westford, MA for the API (1991)