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**UNDERSTANDING THE DISPERSION OF INDUSTRIAL
RELASES OF ANHYDROUS HYDROGEN FLUORIDE
AND THE ASSOCIATED RISKS TO THE ENVIRONMENT
AND PEOPLE (URAHFREP)**

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TITLE:

**Work Package 5- HF Thermodynamic Data
& Work Package 7- Model Development and Validation**

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Introduction

Anhydrous hydrogen fluoride (AHF) is widely used in the petroleum and chemical industries, most notably as a catalyst in alkylation plants. A typical accidental release of HF will form a dense cloud of HF aerosol and vapour, in the case of alkylation plants possibly including isobutane as an immiscible component. HF droplets are hygroscopic reacting exothermically with liquid water, whereas in the vapour phase HF molecules form associations to form simple polymers called oligomers. Simple HF thermodynamic models indicate that, under sufficiently humid conditions, the heat generated by the interaction of HF with condensed atmospheric water can lead to the cloud, or at least parts of the cloud, becoming positively buoyant. The initially dense nature of the cloud means that it is quite likely to be dispersing at ground level before sufficient heat is generated to make the cloud positively buoyant.

The URAHFREP project is focused on improving understanding of the behaviour of HF clouds, however, buoyant lift-off is of much wider interest, being relevant to many areas including the dispersion of:

- fire plumes,
- intrinsically lighter than air gases released at ground level,
- gas clouds which may become buoyant due to heat transfer from the ground, latent heat, radioactive decay or chemical reaction processes and even volcanic flows.

Work Package 5 of the URAHFREP project consists of laboratory-scale thermodynamics experiments to check the validity of existing data on HF/water systems, and provide new data on HF/water/isobutane systems. One deliverable has been produced under Work Package 5 [1].

Work Package 7 of the URAHFREP project deals with the development of models to predict the thermodynamic and dispersion behaviour of AHF releases (with or without isobutane), and their validation against experimental data, including three sets of data produced under the URAHFREP project namely:

- HF Thermodynamics Tests [1]
- Wind Tunnel Tests investigating plume lift off [2]
- HF dispersion Field Trials [3]

Four deliverables have been produced under Work Package 7:

- Review of existing Plume Lift-off Models [4]
- Modelling of Lift off and Validation against Wind Tunnel Experiments [5]
- Thermodynamic Modelling of Anhydrous HF/Moist Air/Immiscible Component Mixtures and Validation against Experimental Data [6]
- Comparison of Model Predictions with URAHFREP Field Trial Data [7]

All five AEA Technology deliverables are briefly summarised below; the reader is referred to the reports themselves for more detail.

HF Thermodynamics Tests

Given the pivotal role of the thermodynamics on the dispersion of Anhydrous Hydrogen Fluoride (AHF) in the environment, the purpose of Work Package 5 [1] was to check the validity of previous experimental data and extend measurements to a wider range of compositions. Isobutane, which could be released with AHF, was also included in the test matrix to study its influence on the thermodynamics of mixing of HF with air.

The programme of work for Work Package 5 was divided into 4 stages:

- Review of requirements to focus experiments on gas mixtures and conditions that would be of most value in terms of validating or enhancing current databases on HF/water/isobutane/air systems.
- Design and set up of experimental apparatus to provide the necessary data.
- Measurements of HF/water systems, with at least five measurements intended to verify the general trend of results obtained in Schotte's tests on dry and humid air.
- Measurements of HF systems including isobutane, with at least 25 measurements to extend the database to wider ranges of components and concentrations.

The matrix of tests was intended to be flexible and was adapted to take account of the results from commissioning and main tests as they became available. For example, the maximum number of measurements per test was established and enabled a significant expansion of the range of conditions and compositions to be studied. It was also possible to conduct more tests than planned, which enabled duplicate runs to be included and less successful runs to be repeated.

The main conclusions of the work are:

1. The reliability of previous work conducted by Schotte has been verified.
2. Measurements have been extended to areas of the HF-water-air system not previously studied.
3. The impact of isobutane has been studied and found only to suppress the extent of temperature increase/decrease generated on mixing HF with humid or dry air.

The experimental results are to be included by Risoe within the REDIPHEM dense gas dispersion database. The implications and discussion of these results in terms of the treatment of atmospheric dispersion of HF and impact on risk assessments is addressed in other work packages within the URAHFREP programme, in particular Work Package 7.

Review of Existing Lift off Models

Models for the lift-off of ground based buoyant clouds have been reviewed [4] with the aim of providing a basis for enhancing existing hydrogen fluoride dispersion models to deal with possible plume lift-off in humid conditions. This requires that the models must ultimately apply to non-buoyancy conserving flows.

Few models exist which claim to deal with lift-off of ground based buoyant releases. Much of the published modelling work relates directly to experimental studies and therefore these studies are also discussed in the report.

The simplest lift-off models are based on lift-off occurring when a suitable non-dimensional cloud parameter exceeds a given critical value. Cloud Richardson Number based on the atmospheric friction velocity is an appropriate lift-off parameter. Experimental studies indicate that lift-off depends on such a parameter, but in a continuous, rather than abrupt manner. Lift-off parameters based on local cloud scales are most appropriate for generalisation to HF clouds.

Correlations for distance to lift-off have been reported in the literature. Such distance to lift-off correlations are discussed in the report, but unfortunately are not directly suitable for generalisation to HF clouds.

A lift-off correlation based on wind tunnel data of buoyant releases from buildings has recently been published. This correlation and its suitability for describing HF clouds are discussed in the report.

Other models identified in the review include a three-dimensional computational fluid dynamic model for a buoyant wall jet. The empirical mixing length turbulence closure used in this model may provide insight for entrainment in an integral model.

A simple integral model due to Slawson is discussed in the report which has potential for further development. The model has similarities with the airborne plume model in HGSYSTEM 3.0. The enhanced mixing and lift-off modelling capability of this type of model is far from demonstrated. However, such integral models are the most readily generalisable to include HF thermodynamics.

The review concluded that there was scope to use the existing experimental data for further developing lift-off models for inclusion in integral dispersion models. However, new experimental data were also required, particularly relating to source conditions closer to those expected for HF releases. Additionally, data on real HF clouds in humid atmospheres were necessary, in order to check lift-off predictions of integral models using HF thermodynamics. The URAHFREP experiments later provided additional invaluable data in this respect.

Development of Lift off Model and Validation against Wind Tunnel Experiments

A simple integral plume model for plume lift-off is presented [5], based on traditional free plume models, modified to account for the reduced area for entrainment due to the presence of the ground. Apart from this modification of entrainment and also introduction of an algorithm to relate the plume centroid to plume concentration maximum, this simple model has no further modifications to account for dynamical effects of the ground on the plume. Comparisons have been made with existing and also new wind tunnel data on buoyancy conserving plumes collected by partners in the URAHFREP programme [2]. These comparisons indicate that the simple model is capable of adequately representing plume dilution and lift-off for plumes arising from sources which are not too wide compared with the conserved buoyancy length scale. For wide sources, the model significantly under-predicts the suppression of plume rise.

Further work has been undertaken to attempt to overcome the shortcomings of the simple model. Parametrisation of the buoyant contribution to dilution for the ground-based plume (prior to lift-off) has been investigated. Incorporating such buoyant entrainment in ground based models, such as DRIFT, may enable them to be applied up to the point of lift-off. Wind tunnel data [2] indicate possible critical lift-off parameter values which could be used as the transition point from a grounded to an elevated plume model. Improved modelling of the area sources in the wind tunnel experiments is also considered. However, difficulties in the modelling of the subsequent plume lift-off remain with regard to suppression of plume rise from wide sources, and more work is required in this area.

The behaviour of short duration buoyant releases has been studied in the wind-tunnel by Hall et al [8]. The detailed implications of these findings for mathematical models have yet to be assessed. It would be interesting to compare the new wind-tunnel results with mathematical models for instantaneously released thermals and continuous buoyant plumes. In such a study the scaling of the buoyant rise and dilution predicted by these limiting case models might be compared with the experimental data. The observed high levels of intermittency and high repeat variability may hinder such comparisons. In the mean time, the wind-tunnel study lends support to the statement that modelling releases as though they are steady and continuous is pessimistic in terms of concentration estimates.

Thermodynamic Modelling of Anhydrous HF / Moist Air / Immiscible Component Mixtures and Validation against Experimental Data

Thermodynamic experiments on the mixing of AHF with moist air and isobutane have been conducted under the URAHFREP project [1]. These extend the earlier fog chamber studies of Schotte to higher HF model fractions. In addition, releases of HF and isobutane have been undertaken in the URAHFREP Field Trials [3]. Reference [6] concerns the validation and extension of an existing HF thermodynamic equilibrium model against this new and existing data.

The model of Clough et al is extended to include an immiscible liquid phase. The main complication in extending the model is in evaluating the phase boundaries for the system. Phase tests for determining these boundaries are given. The extended thermodynamic model, incorporating isobutane as the immiscible phase, has been coded. The resultant computer model is called HFMIXTURE. During the course of this work, some errors in the thermodynamic model implementation in AEAT/HSE dispersion codes EJECT and DRIFT were found and corrected.

HFMIXTURE predictions for the pure HF-moist air system compare favourably with the original data of Schotte and also with the data from the new URAHFREP thermodynamic experiments [1]. It is concluded that a simple "126 model", with only HF monomers, dimers, hexamers and no HF.H₂O complex in the vapour phase, is sufficient for predicting the equilibrium temperature of HF-air mixtures over the range of conditions in the experiments.

Model predictions also compare favourably with the URAHFREP thermodynamic experiments for isobutane mixtures. The model indicates that for these experiments, under equilibrium conditions, no liquid isobutane is present. Isobutane is thus acting as an inert diluent with smaller temperature rise (and fall) attributable to the relatively large heat capacity of the isobutane vapour.

Comparisons with temperature measurements from the URAHFREP Field Trials [3] indicate good agreement for the maximum temperature rise. For the releases involving isobutane, the thermodynamic model predicts no rise above ambient temperature, whereas some rise may have been observed in the trials.

The effect on temperature and density of including increased amounts of immiscible isobutane liquid with HF has been investigated using the thermodynamic model. The results indicate that the inclusion of liquid isobutane as an immiscible component significantly reduces the magnitude of the temperature rise and decreases the region of positive buoyancy.

Comparison of Model Predictions with URAHFREP Field Trial Data

Field trials have been conducted under URAHFREP involving the medium scale ($\sim 0.1\text{kg/s}$) release and dispersion of AHF under normal European (humid) atmospheric conditions [3]. Reference [7] details comparison of data from these field trials with predictions of HF dispersion models. The dispersion models are the AEAT/HSE models EJECT and DRIFT. These models employ HF thermodynamic models which have been shown to adequately represent chamber mixing studies [6]. The dispersion models have also recently been enhanced in the light of URAHFREP wind-tunnel studies [5]. The findings of these wind-tunnel experiments are used in this study as a guide to assessing the possible lift-off implied by the model predictions.

Initial comparisons show many of the URAHFREP field trials to be dominated by passive dispersion. This is due to the combination of the low HF release rates and the atmospheric conditions pertaining during the trials. A review of the passive dispersion model in DRIFT for continuous sources has led to a modification to the lateral passive spreading model. A simple model to account for the effect of time averaging time on concentration has also been introduced. A selective re-validation of the model has been conducted, before going on to compare the new model predictions with the URAHFREP field trials.

The URAHFREP field trials indicate that plume lift-off may have occurred for only one trial (HF012) out of the 12 conducted. Dispersion model predictions and lift-off criteria based on wind-tunnel data are in accord with these findings. Only a selection of the trials have been modelled, but findings are expected to apply more widely due to the similarity of many of the release and ambient conditions. The influence on concentration of ambient conditions are predicted to be dominant over HF thermodynamics, except possibly for trial HF012. The models indicate that (due to low wind speed and high humidity) the generated buoyancy may be sufficient to lead to lift off for Trial HF012. Some caution is necessary since the lift-off criteria employed do not include the effect of ambient convection which may be the dominant mechanism for the lift-off which was observed for HF012. Downdrafts in ambient convection may also lead to clouds, which otherwise would be expected to lift-off, remaining ground based.

Modelling studies have also been undertaken for other release conditions. These are aimed at showing the effects of releasing larger quantities of HF and of releases under different atmospheric conditions. Not surprisingly, increasing the size of the release increases the importance of gravitational effects, including the potential for buoyant lift-off. Similarly more stable atmospheric conditions encourage lift-off, although stable ambient stratification may limit the ultimate plume rise height.

Concluding Remarks

Overall, we believe, the URAHFREP project has led to an improved understanding of the release and dispersion behaviour of HF clouds. The wind-tunnel studies show how (buoyancy conserving) buoyant clouds released into a neutrally stable boundary layer lift-off from the ground. The HF thermodynamic experiments support the existing HF models under equilibrium conditions and the suppression of positive buoyancy effects due to the presence of isobutane. The Campaign 2 field trials show the propensity for other influences (e.g. due to ambient convection) to dominate over the HF induced buoyancy effects. Our modelling studies indicate that simple models as used in risk assessment studies are able to represent many, but not all, of the observed features. Weaknesses include the modelling of the suppression of plume rise for wide sources, accounting for the influence of atmospheric stability on plume rise, uncertainties regarding the influence of non-buoyancy conservation on dispersion and the influence of plume meander and concentration fluctuations on toxic dose.

Factors other than those studied under URAHFREP may also act against plume rise, e.g. the influence of obstacles, termination of plume rise by break-up due to ambient turbulence, encountering an elevated inversion or stable density gradient. These factors are well known in the context of plume rise modelling and in most cases adequate methods of dealing with these probably already exist. They may, however, need transcribing into a framework permitting the plume buoyancy to change.

Our modelling studies indicate that under the usually considered worst case conditions for risk assessment, i.e. low windspeed stable conditions, that large pure AHF releases are expected to lift-off under ambient humidities commonly encountered in European climes. This does not necessarily mean that there will be no residual ground based hazard. The URAHFREP wind tunnel studies show that shreds of the cloud may remain and disperse (passively) at ground level. Also the thermodynamic nature of HF is such that the cloud is not expected to remain buoyant and may possibly become dense. It would also be prudent to consider within a risk assessment the likelihood of conditions less favourable to lift-off e.g. the occurrence of lower ambient humidity in combination with low windspeed.

Suggested areas for further study are:

- modelling the suppression of plume rise for wide sources,
- modelling lift-off in non-neutral atmospheric stabilities,
- use of the URAHFREP wind-tunnel data to develop mathematical models for short duration releases,
- modelling the residual ground based shreds of a lifted off cloud, and
- investigation of the effects on lift-off of the distribution of buoyancy generation in an HF cloud.

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