

STAWaRS: A NEW SOURCE TERM MODEL FOR WATER REACTIVE SUBSTANCES[†]

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STAWaRS (Source Term Assessment of Water Reactive Substances) models the spreading and simultaneous vaporisation of liquid pools resulting from spillages of water reactive chemicals. The following substances can currently be modelled using STAWaRS: sulphur trioxide and oleum, anhydrous hydrogen fluoride, hydrofluoric acid, acetyl chloride, chlorosulphonic acid, phosphorus oxychloride, phosphorus trichloride, silicon tetrachloride and titanium tetrachloride.

The major hazard associated with these substances arises from their reaction with water (in the form of free molecules and in some cases also chemical hydrates), vaporisation from the surface of any pool that forms, and subsequent fume formation in the atmosphere. After the initial release a violent and exothermic reaction with any water present (such as ground water or atmospheric water vapour) occurs, which liberates acidic vapour. The vapour release rate is largely determined by the availability of water in the vicinity of the spill, and as the pool of spilled liquid spreads, further vapour is released as more ground water is encountered. Once the pool reaches a limiting size, evolution of acidic vapour continues at a reduced rate as a result of wind-driven vaporisation and interaction with atmospheric moisture. The STAWaRS model quantifies the variation of the vapour release rate with time.

STAWaRS requires the user to define the nature of the liquid release, the ambient conditions, and the terrain onto which the liquid is spilt. It can then calculate the time evolution of many quantities, including the pool size, pool temperature, pool composition, vaporisation rate, and the total mass of vapour generated. The output from STAWaRS can be used to provide source terms for dispersion modelling.

STAWaRS was developed for the Health and Safety Executive (HSE) by ESR Technology and is based on the REACTPOOL model of Griffiths and Kapias (Kapias, 2001a). STAWaRS has been developed principally for use in land-use planning assessments, and provides a sound scientific basis for HSE advice.

This paper describes the STAWaRS mathematical model and outlines the software testing and mathematical model verification that has been undertaken. The behaviour predicted by STAWaRS has been examined in detail, and is compared to the output of other available models. Related experimental studies are to be undertaken and the experimental methodology is outlined. These studies will validate certain substance properties used by STAWaRS, such as the stoichiometry and enthalpy of the reaction with water.

INTRODUCTION

STAWaRS (Source Term Assessment of Water Reactive Substances) models the spreading and simultaneous vaporisation of liquid pools resulting from spillages of water reactive chemicals, and was developed in response to the Seveso II EU Directive (Seveso II, 1996). To comply with this legislation, the hazard posed by sites storing and processing water reactive substances must be assessed. Prior to the development of STAWaRS, the Health and Safety Executive (HSE) had only simple models for assessing releases of water reactive substances, and the methodology for assessing releases of sulphur trioxide and oleum was suspected of being overly cautious.

The vaporisation rates and pool dimensions calculated by STAWaRS can be used to provide source terms for dispersion modelling. The dispersion modelling output

is used as part of the quantified risk assessment process to determine the level of risk posed by a particular chemical site. From this information, 3-zone maps indicating criterion levels of risk around the site can be determined. Such maps are used to generate HSE's land-use planning (LUP) advice.

STAWaRS MATHEMATICAL MODEL

OVERVIEW

STAWaRS models either near-instantaneous or steady-continuous releases of water reactive liquid spilt over land. The possible sources of water in the model are:

- Free surface water: water lying on the ground surface;
- Substrate water: water both free and bound in the substrate below the ground surface;

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- Atmospheric water: water extracted from the moist air flowing over the pool due to the hygroscopic nature of the spilled substance; and
- User added water: addition of water at a constant rate.

Figure 1 is a schematic diagram of the mass exchanges included within the model.

STAWaRS is a one-dimensional integral pool model. It can be considered as a multi-component generalisation of the pool spreading and vaporisation model GASP (Webber, 1990), incorporating the water reactions of REACTPOOL (Kapias, 2001a, 2001b, 2001c, 2001d and 2005). Releases of sulphur trioxide (SO_3), oleum and hydrogen fluoride (HF) cannot be adequately modelled using the REACTPOOL chemical reaction and mixture models. Therefore, additional models have been implemented in STAWaRS. Specifically, STAWaRS incorporates:

- The solvation reactions adopted by Kapias and Griffiths in REACTPOOL (Kapias, 2001a, 2001b, 2001c, 2001d and 2005) for phosphorus trichloride (PCl_3), phosphorus oxychloride (POCl_3), silicon tetrachloride (SiCl_4), chlorosulphonic acid (HSO_3Cl), acetyl chloride (CH_3COCl) and titanium tetrachloride (TiCl_4);
- The solvation model of Nilges and Schrage (Nilges, 1991) and Bosen and Engels (Bosen, 1988) for SO_3 /oleum/sulphuric acid vapour pressure and heat of mixing;
- The binary interaction model of Wheatley (Wheatley, 1986; Raymond, 1994) for interaction of hydrogen fluoride with water;

Prior to the development of STAWaRS, the REACTPOOL model equations were reviewed by Tickle (2006) and a number of modelling recommendations were made. The following improvements have been implemented in STAWaRS:

- A unified model of wind-blown vaporisation and boiling based on the approach of Webber in GASP (Webber, 1988);

- A multi-component generalisation of Brighton's vaporisation model (Brighton, 1987), including coupling between vapour components;
- A radial liquid spread based on the model of Webber (1990), including allowance for the effect of liquid hold-up in puddles and restriction of spread due to bunding;
- A substrate permeation model based on the approach of Kapias and Griffiths (Kapias, 1998); and
- A simple ventilated enclosure model, which can be used for scoping the effects of the vaporising pool being indoors.

The mathematical model equations implemented by STAWaRS are reported in detail in Tickle (2008). The equations are written as a set of coupled ordinary differential equations which are integrated using a variable order, variable step Gears method as implemented in the DDRIV3 package (part of the SLATEC library from the National Institute of Standards and Technology).

VERIFICATION TESTS

Verification testing has been undertaken on the model and is detailed in the STAWaRS software test report (Carlisle, 2007). The purpose of verification testing is to check the correct coding and numerical solution of the mathematical model equations. Verification is considered distinct from validation, which addresses the adequacy/validity of the model equations (Witlox, 2008). In outline the verification testing covers:

- Comparisons with results from other models for specific substances;
- Substance property checks; and
- Numerical integration checks.

A comparison with GASP results allowed the single component limit of vaporisation in the absence of water reaction and the liquid spreading to be checked. Close agreement was found between the two models. A comparison with REACTPOOL results allowed trends to be

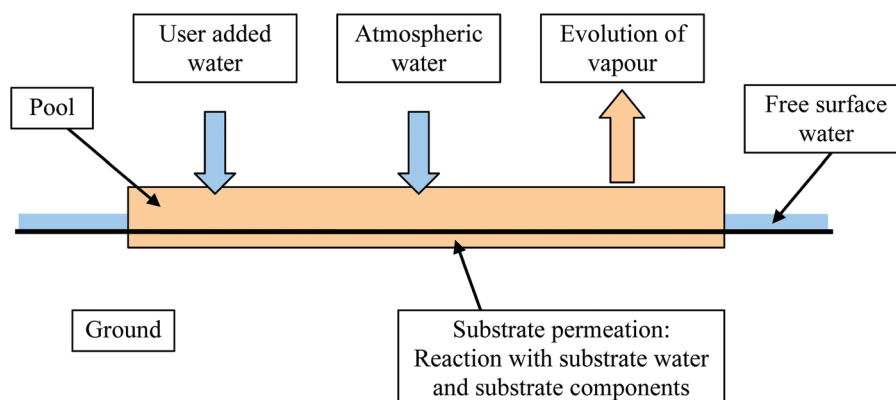


Figure 1. Schematic diagram of mass exchanges in the STAWaRS model

compared for water reactive substances. General broad agreement on the trends was found, although STAWaRS tends to evolve less total vapour from the pool than REACTPOOL. The observed differences between STAWaRS and REACTPOOL predictions appear mainly to be due to the coupling between vapour components in the STAWaRS vaporisation model, which is not present in REACTPOOL. This coupling effectively lowers the boiling point of the pool due to the evolution of a gaseous product (e.g. hydrogen chloride). It would be useful to have independent experimental validation of this theoretical result.

Partial pressures were compared with data from other sources and were generally found to be in close agreement. Spot-checks on other properties did not reveal any errors.

The mathematical model equations involve constraint equations in differential form (e.g. for vapour-liquid equilibrium), the numerically integrated values of which were compared with values from the exact constraint equations. Close agreement was found between the two sets of values.

The verification test results provide support for the model equations being correctly coded and solved to the requested numerical tolerance.

EXPERIMENTAL VALIDATION STUDIES

For some of the water-reactive chlorides modelled in STAWaRS, the mechanism of the reaction with water is not fully understood (Kapias, 2001d and 2005). Experimental studies are therefore required to validate the reaction parameters assumed in STAWaRS, such as the enthalpy and stoichiometry of the reaction with water. Experimental studies of the TiCl_4 hydrolysis reaction have been carried out at the Health and Safety Laboratory (HSL) and are reported elsewhere in these proceedings (Véchet, 2011). The experimentally validated stoichiometry and enthalpy of reaction proposed for TiCl_4 are different to those previously assumed, which were based on thermodynamic calculations (Kapias, 2005). Further experimental studies are planned on acetyl chloride and other water-reactive chlorides modelled in STAWaRS.

The hydrolysis reactions will be performed in a Dewar calorimeter and the enthalpy of reaction derived from the measured temperature increase. The reactions will be studied under both excess-water and excess-reactant conditions. For some of the substances of interest, the water-reactant balance is known to affect the reaction mechanism (Kapias, 2001d).

Hydrogen chloride (HCl) formed during the hydrolysis reaction is either evolved directly to the atmosphere as a gas or remains dissolved in solution. The HCl gas will be bubbled through caustic traps containing dilute sodium hydroxide (NaOH), which will be weighed before and after to determine the mass of HCl evolved. From the experimental data, the stoichiometry of the reaction can be determined.

In the longer term, spill tests are planned, in which the reaction with water of a spreading pool of water-reactive chloride will be studied.

SENSITIVITY STUDIES

Sensitivity studies on selected STAWaRS inputs were carried out to ensure that STAWaRS operates reliably and produces scientifically sound results over the range of input conditions typically used by HSE for LUP purposes.

Three sources of water are considered within STAWaRS: water present on the ground, water within the substrate, and atmospheric water. Particular emphasis was placed on determining the relative sensitivity of the vaporisation rate to variations in these inputs.

FREE SURFACE WATER DEPTH

The free surface water depth is defined in STAWaRS as the free surface water volume per unit area (Tickle, 2008). If the free surface water depth is increased, there is a concomitant increase in the rate at which a spreading pool encounters water. The puddle depth is defined as the volume per unit area of liquid (excluding the free surface water) held up in puddles. Increasing the puddle depth decreases the rate at which the pool spreads, which in turn decreases the rate at which the reactant encounters water. Therefore, there is a delicate balance between the puddle depth and the free surface water depth and the relative values of these inputs can strongly influence the model output.

Releases of Sulphur Trioxide and Oleum

A 25 kg/s release of 1800 s duration was modelled in STAWaRS for SO_3 , 65% oleum, 30% oleum and 20% oleum. Runs were carried out using a range of free surface water depths and puddle depths. For LUP assessments of SO_3 and oleum sites, the toxic substance that is considered is H_2SO_4 mist, and it is assumed that any SO_3 in the air is converted to H_2SO_4 when it encounters a person. Therefore, the total mass of H_2SO_4 vaporised within 1800 s was recorded in each case, using the assumption that all vaporised SO_3 is converted to H_2SO_4 . The results obtained for releases of 30% oleum and SO_3 are shown in Figure 2 and Figure 3, respectively. The mass of H_2SO_4 vaporised is strongly dependent on the relative values of the puddle depth and the free surface water depth.

Consider in more detail a release of 30% oleum on to a wet substrate (4 mm free surface water depth). At low puddle depths the pool of oleum spreads quickly so encounters enough water for all SO_3 to be converted to an aqueous solution of H_2SO_4 . At the pool temperatures predicted by STAWaRS H_2SO_4 is not very volatile, so predominantly wind-driven vaporisation of H_2SO_4 occurs. In this region, STAWaRS calculates that after a certain time (which is dependent on the input conditions) the pool ceases to contain reactant (in this case, SO_3) and the reaction rate equals the spill rate. At larger puddle depths the volume of reactant held up in puddles increases and the radial velocity of the pool decreases. The spreading pool encounters water at a lower rate, resulting in less SO_3 being converted to H_2SO_4 and a corresponding reduction in the wind-driven vaporisation rate. However, as the SO_3 content of the pool increases, the vaporisation rate of SO_3 begins to increase, leading to an increase in the total mass

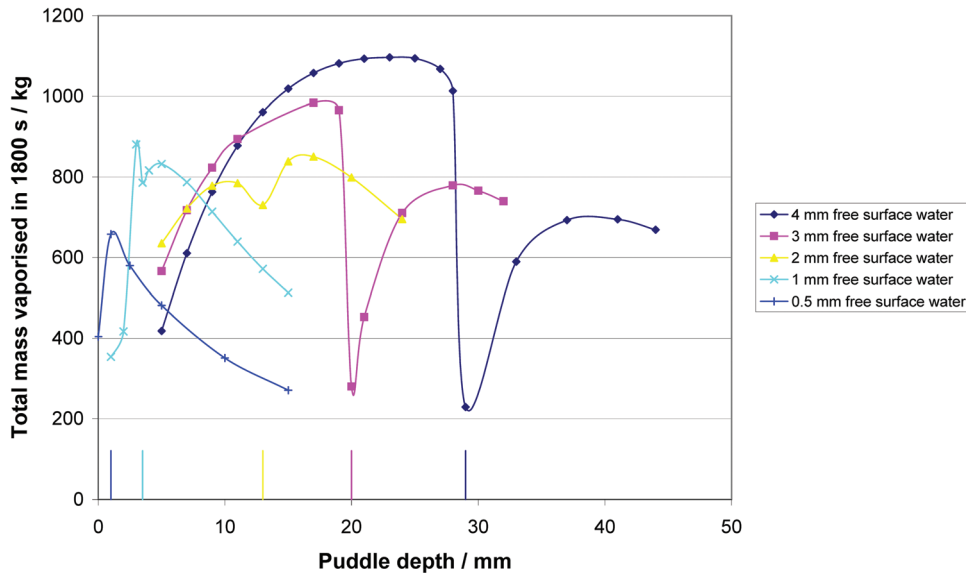


Figure 2. The total mass of SO₃/H₂SO₄ vaporised during a 25 kg/s release of 30% oleum of 1800 s duration in D5 weather conditions

vaporised at larger puddle depths. The minimum puddle depth for which there is always reactant in the pool is marked as a vertical line on the graph for each free surface water depth. For releases of 30% oleum, this is the point at which the lowest mass of SO₃/H₂SO₄ is vaporised as the ‘switch’ between wind-driven vaporisation of H₂SO₄ and direct vaporisation of SO₃ is occurring.

The trends observed for 30% oleum are typical of the results obtained for releases of lower strength oleums. However, as the proportion of SO₃ in the spill substance increases, the minimum puddle depth at which there is

always reactant in the pool decreases and therefore the puddle depth at which significant vaporisation of SO₃ commences also decreases. The data relating to releases of SO₃ are shown in Figure 3, and for each free surface water depth considered here, the predominant vaporisation mechanism at all puddle depths is direct vaporisation of SO₃.

Ten tonne instantaneous releases of SO₃, 65% oleum, 30% oleum and 20% oleum were also modelled in STAWaRS. The results for releases of 30% oleum are shown in Figure 4, for a range of free surface water depths. The minimum puddle depth for which there is

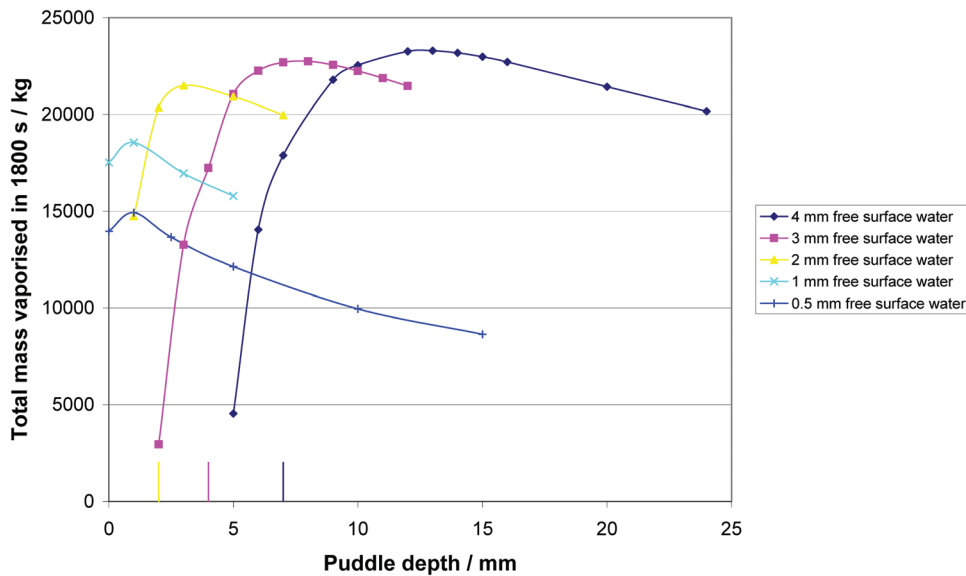


Figure 3. The total mass of SO₃/H₂SO₄ vaporised during a 25 kg/s release of SO₃ of 1800 s duration in D5 weather conditions

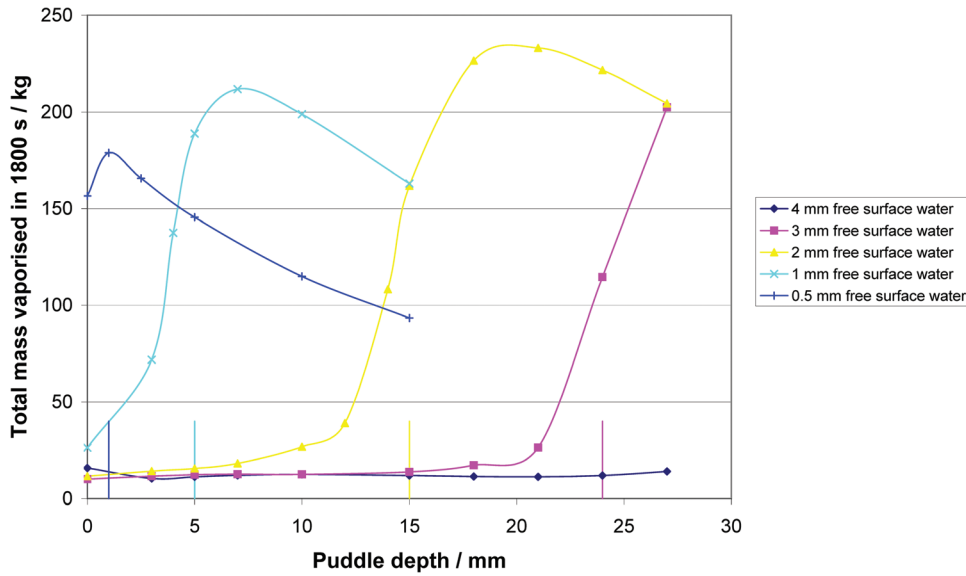


Figure 4. The total mass of SO₃/H₂SO₄ vaporised in 1800 s following a 10 tonne release of 30% oleum in D5 weather conditions

always reactant in the pool is marked as a vertical line on the graph for each free surface water depth. (The reactant in the pool was exhausted during each 30% oleum run with a free surface water depth of 4 mm.) Under conditions where the reactant in the pool is rapidly exhausted little direct vaporisation of SO₃ occurs, and the rate of wind-driven vaporisation of H₂SO₄ is also low. Above the minimum puddle depths indicated on the graph, the vaporisation is dominated by direct vaporisation of SO₃. In contrast, for each SO₃ release shown in Figure 5, the predominant vaporisation

mechanism at all puddle depths (both above and below the minimum puddle depths marked on the graph) is direct vaporisation of SO₃. The variation in the total mass vaporised with puddle depth is small compared to that observed for releases of 30% oleum.

Releases of Water-Reactive Chlorides

The reaction of a water-reactive chloride with water produces hydrogen chloride (HCl) vapour and, in some cases, a second, less volatile, acid. Furthermore, due to their

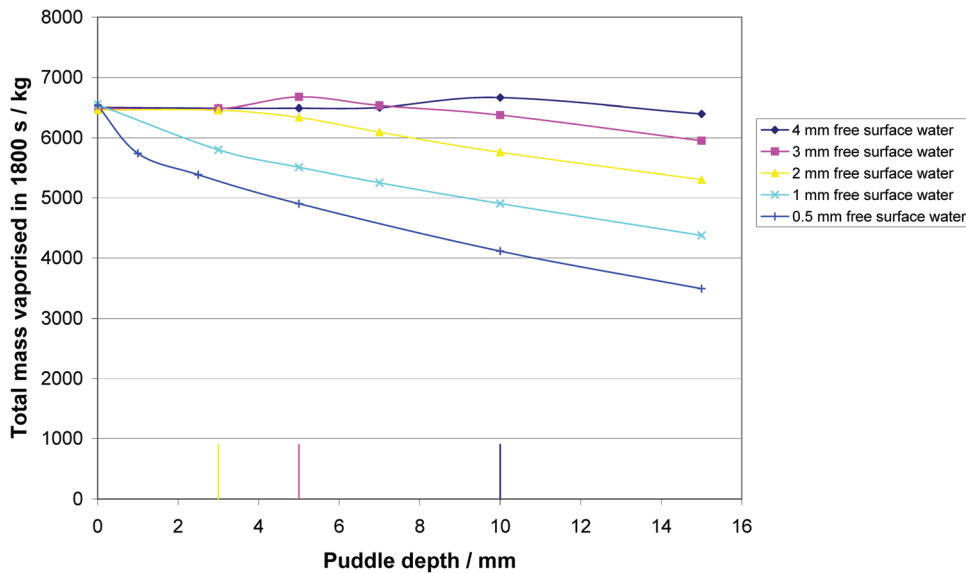


Figure 5. The total mass of SO₃/H₂SO₄ vaporised in 1800 s following a 10 tonne release of SO₃ in D5 weather conditions

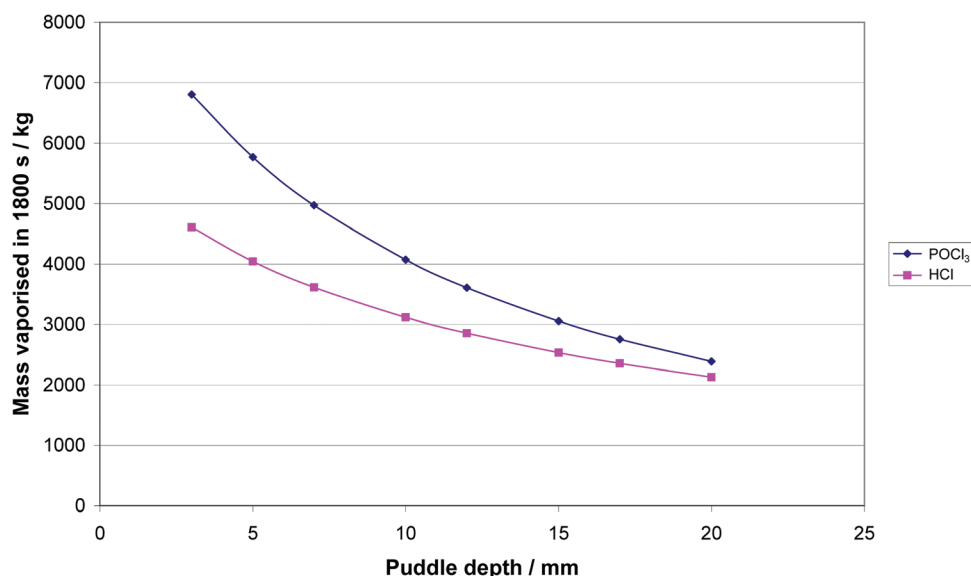


Figure 6. The mass of POCl₃ and HCl vaporised during a 25 kg/s release of POCl₃ of duration 1800 s on to a substrate with 1 mm free surface water depth in D5 weather conditions

volatility, these chlorides will evolve directly from the pool formed. Therefore, at least two toxic vapours will be produced in each case.

Puddle depth sensitivity studies have been carried out for each of the water-reactive chlorides listed on page 288. Similar trends were observed for most of these substances, which is consistent with the fact that they are all modelled using the same solvation model. The POCl₃ results presented here are typical of those obtained. The mass of POCl₃ and HCl evolved during a 25 kg/s release of POCl₃ of 1800 s duration in dry conditions (1mm free

surface water depth) is shown in Figure 6. It can be seen that the mass of toxic products released decreases smoothly as the puddle depth increases and the rate at which the reactant encounters water decreases. The same behaviour is observed for continuous releases in wet conditions (4 mm free surface water depth), and for instantaneous releases in both dry and wet conditions.

Releases of Hydrogen Fluoride

For continuous releases of HF on to a wet substrate, the mass of HF vaporised increases rapidly with puddle depth,

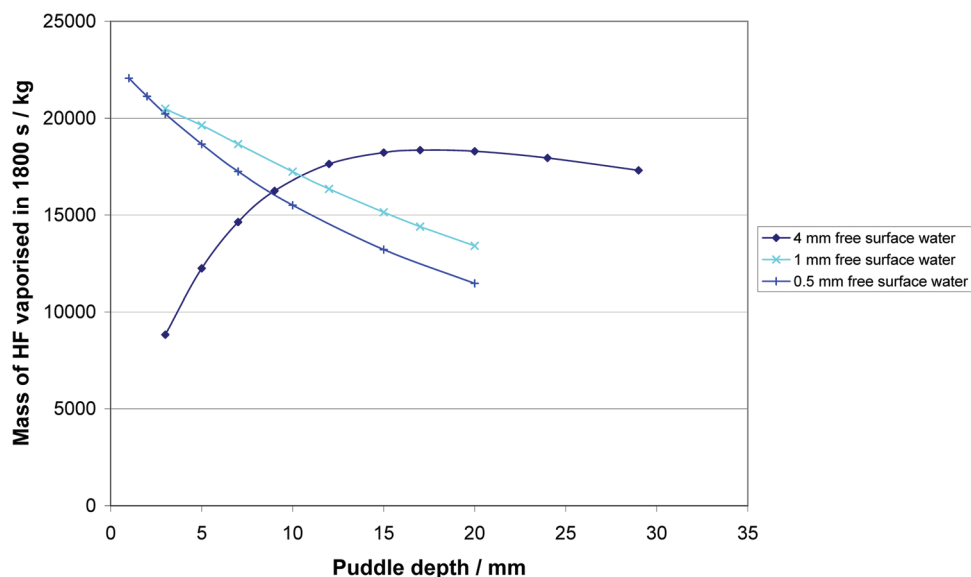


Figure 7. The total mass of HF vaporised during a 25 kg/s release of 100% HF of 1800 s duration in D5 weather conditions

until a maximum is reached at a puddle depth of around 15 to 20 mm. Beyond this maximum the mass vaporised decreases slowly with increasing puddle depth. This behaviour is illustrated in Figure 7 for a 25 kg/s release of 100% HF. Similar trends are observed for instantaneous releases of HF on to wet substrates, but the variation in the mass vaporised with puddle depth is much smaller. For continuous and instantaneous releases of HF on to a dry substrate, the mass of HF vaporised decreases with puddle depth, as is shown in Figure 7 for a continuous release of 100% HF. Similar results are obtained for releases of 70% HF and 86% HF.

These results demonstrate that for sufficiently rapid initial rates of water mixing into the pool (i.e. at high free surface water depths and low puddle depths), the vaporisation of HF is suppressed. A possible explanation is that, for rapid initial water addition, the vaporisation is enhanced whilst the pool area is smaller, with subsequent spreading of the pool occurring during the less volatile dilute phase, resulting in an overall reduction of total HF vaporised.

Dependence on the Release Size

Further sensitivity studies were carried out on instantaneous releases up to 100 tonnes in size and continuous releases with spill rates between 10 and 50 kg/s. Releases of sulphur trioxide, 30% oleum, hydrogen fluoride and acetyl chloride were studied. In each case, the variation in the total mass of vapour evolved with free surface water depth and puddle depth was not significantly affected by the size of the release. This is because as the size of the release increases, the pool-spreading rate does too, so the reactant-to-water ratio at a given time does not change greatly with release size.

SUBSTRATE WATER SATURATION

The porosity of a material is a measure of the fraction of void space that it contains. The porosity is material specific and is preset for each STAWaRS substrate. The percentage of the void space that is occupied by water is determined by the water saturation parameter, which may be set by the user. Sensitivity studies were carried out to determine the effect of the substrate water saturation on the STAWaRS output, and the results are summarised in Table 1.

For spills of SO₃ on to concrete or limestone, the mass of vapour produced is insensitive to the substrate water saturation. However, when a porous asphalt substrate is used, a significant increase in the mass of vapour produced is observed when the substrate water saturation is increased. The porosity of asphalt is not significantly higher than that of the other substrates considered, but its permeability (a measure of how rapidly liquid can be transmitted through the substrate) is several orders of magnitude higher. Therefore, a higher proportion of the spilt SO₃ will permeate into the substrate and react with the water contained there, leading to an increase in the SO₃ vaporisation rate.

The mass of vapour produced following a spill of PCl₃ or 86% HF on to limestone does not depend on the substrate water saturation chosen. For spills of these substances on to concrete, the mass of vapour produced does vary with substrate water saturation, but the percentage change in the mass vaporised on going from 0% saturation to 100% saturation is small.

In general, 100% substrate water saturation produces the most conservative STAWaRS output, and varying the water saturation does not lead to large changes in the mass of vapour produced.

Table 1. The mass of vapour evolved as a function of the substrate water saturation. Ten tonne releases on to dry (1 mm free surface water) substrates in D5 weather conditions were modelled. A release temperature of 308 K was used for SO₃

Release substance	Substrate	Substrate permeability (m/s)	Substrate porosity (%)	Water saturation (%)	Mass of vapour produced in 1800 s (kg)	Average pool diameter over 1800 s (m)
SO ₃	Concrete	7.8×10^{-7}	13	100	SO ₃ : 4507	17.3
				0	SO ₃ : 4498	17.3
SO ₃	Porous asphalt	0.003	20	100	SO ₃ : 4629	13.0
				20	SO ₃ : 3826	14.3
				0	SO ₃ : 2901	14.8
SO ₃	Limestone	1×10^{-9}	17	100	SO ₃ : 4477	17.3
				0	SO ₃ : 4477	17.3
PCl ₃	Concrete	7.8×10^{-7}	13	100	PCl ₃ : 4334 HCl: 1719	22.5
				0	PCl ₃ : 4180 HCl: 1451	22.5
PCl ₃	Limestone	1×10^{-9}	17	100	PCl ₃ : 3656 HCl: 1471	22.5
				0	PCl ₃ : 3656 HCl: 1471	22.5
86% HF	Concrete	7.8×10^{-7}	13	100	HF: 2601	38.8
				0	HF: 2765	38.6
86% HF	Limestone	1×10^{-9}	17	100	HF: 2762	39.5
				0	HF: 2762	39.5

Table . The mass of vapour produced during a continuous release, as a function of the release temperature. 10 kg/s releases of 1800 s duration on to a dry concrete substrate were modelled

Spill substance	Weather	Ambient temperature (K)	Release temperature (K)	Mass of vapour evolved in 1800 s (kg)	Average pool diameter over 1800 s (m)
HF	F2	278.15	278.15	HF: 4968	12.4
			288.15	HF: 5374	11.4
POCl ₃	F2	278.15	278.15	POCl ₃ : 1182 HCl: 1817	11.0
			288.15	POCl ₃ : 1345 HCl: 1813	10.7
SiCl ₄	F2	278.15	278.15	SiCl ₄ : 3723 HCl: 1927	10.7
			288.15	SiCl ₄ : 3989 HCl: 1899	10.2

RELATIVE HUMIDITY

A third source of water considered in STAWaRS is atmospheric water extracted from moist air flowing over the pool. The mass of vapour produced increases linearly with humidity, but the rate of increase is small: increasing the relative humidity from 50% to 90% produces only a 1% rise in the mass of vapour evolved following a 10 tonne release of SO₃.

RELEASE TEMPERATURE

If a liquid is stored outdoors, for LUP purposes HSE usually assumes an ambient air temperature of 288.15 K for daytime, and 278.15 K for nighttime. The release temperature is the temperature of the liquid at the start of the release.

Table 2 compares the results obtained for nighttime releases at two different release temperatures. When the release temperature is increased from 278.15 K to 288.15 K, a greater mass of the spill substance is directly vaporised. For the spill substances tested, the magnitude of this increase ranges from 7% for SiCl₄ to 14% for POCl₃. As a result of the increase in direct vaporisation, less of the spill substance will react with water, so the mass of HCl produced following a release of POCl₃ or SiCl₄ is reduced. SO₃ and some oleums are stored above ambient temperature, so were not considered in this analysis.

COMPARISON WITH MODELS PREVIOUSLY USED BY HSE

A further aim of this work was to determine the impact of the introduction of STAWaRS on HSE's LUP advice. This was investigated by making detailed comparisons between STAWaRS and models previously used by HSE to determine source terms for releases of water reactive substances.

RASP AND TOEM

RASP (Grint, 1990; Griffiths, 1996) was previously used by HSE to model releases of SO₃ and 65% oleum. RASP models both the rapid and violent reaction of SO₃ with surface water, and wind-driven vaporisation from the pool surface. The reaction of 20% oleum with water is much less violent and wind-driven vaporisation predominates.

Releases of 20% oleum were therefore modelled using TOEM (Twenty percent Oleum Evaporation Model), which considers wind-driven vaporisation only.

A hazardous substances consent application originally assessed using RASP, TOEM and GABLE (Gas Arising from Buildings, a program developed by HSE to model the mitigation provided by the building in the event of an indoor release) has been reassessed using STAWaRS. The release scenarios with the greatest hazard potential are discussed here.

Indoor Releases of Sulphur Trioxide

At the site of interest, liquid sulphur trioxide was stored indoors in three 100 tonne storage tanks. The release scenarios considered here are catastrophic failure of one of the storage tanks and guillotine failure of the pipework. In the original assessment the SO₃ release scenarios were modelled in RASP to obtain indoor source terms. The mitigation provided by the building was then calculated using GABLE. In the STAWaRS reassessment mitigation provided by the building was modelled within STAWaRS.

The results of the STAWaRS reassessment are given in Table 3, together with a summary of the results from the original assessment for comparison. All releases are expressed in terms of the mass of H₂SO₄ vaporised in 1800 s.

RASP does not have a separate facility to model instantaneous releases, so in the original assessment a catastrophic failure of one of the storage tanks was treated as a continuous release of duration 120 s. In the reassessment, catastrophic releases have been modelled using both the instantaneous and continuous options in STAWaRS. Despite the fact that the same mass of SO₃ is released in each case, the mass of vapour evolved is larger when the release is modelled as continuous. This difference is caused by the fact that there is a small bund present. Once the spreading liquid reaches the bund, the vaporisation rate starts to decrease, and this point is reached more quickly following an instantaneous release.

When the catastrophic failure of a storage tank is modelled in STAWaRS, the mass of H₂SO₄ vapour predicted is much smaller than that calculated using RASP and GABLE. If the instantaneous option is used, the mass of vapour is one third of that predicted in the original assessment; this

Table . Indoor releases of SO₃: Comparison of the RASP and GABLE outputs from the original assessment with the STAWaRS outputs from the reassessment

Scenario	Weather conditions	Description of run	Puddle depth (mm)	Mass of H ₂ SO ₄ equivalents evolved in 1800 s (kg)
Catastrophic failure of main SO ₃ storage tank (100 tonne)	D5	RASP/GABLE, 833 kg/s over 120 s	5	5388
		STAWaRS, 833 kg/s over 120 s	5	3391
		STAWaRS, 100 tonne release	5	1830
	F2	RASP/GABLE, 833 kg/s over 120 s	5	4424
		STAWaRS, 833 kg/s over 120 s	5	2683
		STAWaRS, 100 tonne release	5	1361
Guillotine failure of 80 mm SO ₃ pipework (remote isolation)	D5	RASP/GABLE, 25.2 kg/s over 300 s	5	4950
		STAWaRS, 25.2 kg/s over 300 s	5	2458
	F2	RASP/GABLE, 25.2 kg/s over 300 s	5	4050
		STAWaRS, 25.2 kg/s over 300 s	5	1893

fraction increases to two thirds when the continuous option is used. The enclosure mitigation calculated by GABLE and STAWaRS has been shown to be very similar, so the discrepancy between the two outputs is caused by differences between the RASP and STAWaRS models.

STAWaRS also predicts the vaporisation of a much lower mass of H₂SO₄ than RASP and GABLE when guillotine failure of the SO₃ pipework is considered. Sensitivity studies reveal that the mass of H₂SO₄ vapour obtained for the puddle depth and free surface water depth used here is close to the maximum value predicted by STAWaRS for this release. Therefore, it is unlikely that any physically realistic combination of STAWaRS inputs can be found which will produce results as conservative as the RASP and GABLE output.

Outdoor Releases of 35% Oleum

At the site under consideration, 35% oleum was stored and processed outside. The two release scenarios that have been reassessed are catastrophic failure of the oleum absorption tower and guillotine failure of the pipework to the oleum building. At the time of the original assessment, no spill model was available for 35% oleum, so each scenario was modelled in both RASP and TOEM, and the H₂SO₄ vaporisation rates calculated were assumed to correspond to releases of '100% oleum' and 20% oleum respectively. The rate of vaporisation of H₂SO₄ following a release of 35% oleum was then calculated by linear interpolation between the RASP and TOEM outputs. The interpolation method is known to overestimate release rates for low strength oleums and has not been validated by experimental data.

Table . Outdoor releases of 35% oleum: Comparison of the STAWaRS outputs with the results obtained from the RASP and TOEM outputs by interpolation

Scenario	Weather conditions	Description of run	Puddle depth (mm)	Mass of H ₂ SO ₄ equivalents evolved in 1800 s (kg)
Catastrophic failure of oleum absorption tower (46 tonne)	D5, dry	RASP/TOEM, 383 kg/s over 120 s	5	11063
		STAWaRS, 383 kg/s over 120 s	5	1632
			2	3313
		STAWaRS, 46 tonne release	5	1506
			3	1604
			35	1769
	D5, wet	RASP/TOEM, 383 kg/s over 120 s	5	11362
		STAWaRS, 383 kg/s over 120 s	5	4966
		STAWaRS, 46 tonne release	5	102
Guillotine failure of 100 mm pipework to oleum building (remote isolation)	D5, dry	RASP/TOEM, 39.3 kg/s over 300 s	5	3211
		STAWaRS, 39.3 kg/s over 300 s	5	419
	D5, wet	RASP/TOEM, 39.3 kg/s over 300 s	5	4338
		STAWaRS, 39.3 kg/s over 300 s	5	597
			13	925
			13	925

In the original assessment, catastrophic failures were modelled as continuous releases of duration 120 s. In the reassessment, catastrophic failures were modelled using both the instantaneous and continuous options within STAWaRS and the results were compared. The STAWaRS results for oleum releases in D5 weather conditions are listed in Table 4, together with a summary of the RASP and TOEM results for comparison.

When a release of a low strength oleum is modelled in STAWaRS, the mass of H₂SO₄ vaporised is strongly dependent on the puddle depth and the free surface water depth. To ensure that the most conservative results were obtained for each free surface water depth, brief sensitivity studies were carried out on the puddle depth. In each case, the maximum mass of H₂SO₄ evolved, and the puddle depth at which this occurred, were noted. These results are given in Table 4 together with the mass of H₂SO₄ vaporised at a puddle depth of 5 mm, which is a value typically used in LUP assessments. Even the most conservative STAWaRS results are not comparable with the RASP and TOEM output. At most, the mass of H₂SO₄ vapour predicted by STAWaRS is approximately half that predicted by interpolation between the RASP and TOEM outputs, and more typically the STAWaRS output is only 10% of the corresponding RASP and TOEM output. STAWaRS is known to be less conservative than many of the models previously used by HSE. However, the discrepancy between the two sets of results is largely due to approximations made during the interpolation procedure in the original assessment.

OTHER MODELS PREVIOUSLY USED BY HSE

Releases of aqueous HF (hydrofluoric acid) were previously modelled by HSE using an in-house model named SHAOL (Spillage of Hydrofluoric Acid on Land). STAWaRS predicts much lower HF vaporisation rates than SHAOL. For catastrophic releases, the STAWaRS vaporisation rate is generally between 25 and 60% of the SHAOL vaporisation rate. For continuous releases, the agreement between the two models is poorer, with the STAWaRS vaporisation rate being roughly 10 to 35% of the SHAOL vaporisation rate. There is no obvious explanation as to why the agreement is better for catastrophic releases. However, STAWaRS contains separate instantaneous and continuous release models, whereas instantaneous releases in SHAOL are approximated as continuous releases of duration 10 s, so a similar level of agreement should not necessarily be expected.

Two hydrofluoric acid consent applications were reassessed using STAWaRS. As a result of the reduction in the vaporisation rates, the LUP 3-zone map calculated in each case was significantly smaller than that calculated in the original assessment. At the first site, the outer risk zone decreased from 150 m to 95 m in radius when STAWaRS was used. At the second site, an even larger difference was observed, and the outer risk zone decreased from 260 m to 45 m in radius.

Releases of water-reactive chlorides were previously modelled by HSE using a simple spreadsheet model. The spreadsheet contains sets of parametric equations derived from the output of the REACTPOOL model (Kapias, 2001a). A consent application for PCl₃ and POCl₃ was reassessed using STAWaRS. Overall, the agreement between STAWaRS and HSE's spreadsheet model was good, which is to be expected, as both models are based on the REACTPOOL methodology. The HCl and PCl₃/POCl₃ vaporisation rates predicted by STAWaRS are generally between 80% and 120% of the spreadsheet vaporisation rates. Poorer agreement is obtained for catastrophic releases of PCl₃. This may be due in part to the fact that catastrophic releases are modelled as continuous releases of 1 s duration in the spreadsheet.

CONCLUSIONS

STAWaRS is a new model of the spreading and vaporisation of liquid pools resulting from spillages of water reactive chemicals. It contains a more rigorous scientific model than earlier codes used by HSE to model releases of water reactive substances. Experimental studies are planned to validate this model and certain substance properties used by STAWaRS.

Sensitivity studies were carried out on many of the STAWaRS input parameters. Three sources of water are considered within STAWaRS: water present on the ground, water within the substrate, and atmospheric water. Particular emphasis was placed on determining the relative sensitivity of the vaporisation rate to variations in these inputs. The substrate water saturation only becomes significant for spills that occur on to highly permeable substrates such as asphalt, and the relative humidity had a negligible effect on the STAWaRS output. By far the largest changes to the STAWaRS output were observed when the free surface water depth was varied. Furthermore, for a given free surface water depth the vaporisation rate is very sensitive to the puddle depth chosen. STAWaRS incorporates three different solvation models, and the effect of the puddle depth and free surface water depth on the STAWaRS output is strongly dependent on which of the three models is used.

None of the other inputs tested had a significant effect on the STAWaRS output when varied over a range of physically realistic values.

STAWaRS produces significantly less conservative results than the models previously used by HSE to model releases of sulphur trioxide, oleum and aqueous hydrogen fluoride. Furthermore, in most cases there is no physically sensible combination of STAWaRS inputs that produces an output as conservative as that from the older models. This discrepancy is due, at least in part, to inherent differences between the STAWaRS model and the scientific models on which the earlier codes are based. Approximations introduced into the original assessments when catastrophic failures were modelled as continuous releases may also contribute to the discrepancy. The agreement

between STAWaRS and HSE's spreadsheet model for water-reactive chlorides is better, as both models are based on the REACTPOOL methodology.

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