



Specification of a Mathematical Model of a Water Reactive Pool based upon REACTPOOL

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Specification of a Mathematical Model of a Water Reactive Pool based upon REACTPOOL

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The work presented in this report concerns reviewing the published REACTPOOL reports and deriving a mathematical model as input to the specification for a new computational model.

During the course of the review a number of mainly minor omissions have been identified and noted. Areas where the modelling might be improved have also been suggested. Based upon the review findings, a new pool model has been specified. This new model is closely based upon REACTPOOL, but differs in several respects, including:

- improvement on the REACTPOOL computational approach,
- use of a better founded spreading model,
- simplification of the sub-models for heat transfer from the ground and net radiation.

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EXECUTIVE SUMMARY

REACTPOOL is a mathematical model of the spreading and vaporisation of liquid pools resulting from accidental spillages of water reactive chemicals. REACTPOOL was developed on behalf of the Health and Safety Executive by researchers at UMIST. The basis of the model is described in a series of openly published reports.

The work presented in this report concerns reviewing the published REACTPOOL reports and deriving a mathematical model as input to the specification for a new computational model.

During the course of the review a number of mainly minor omissions have been identified and noted. Areas where the modelling might be improved have also been suggested. Based upon the review findings, a new pool model has been specified. This new model is closely based upon REACTPOOL, but differs in several respects, including:

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1 INTRODUCTION

REACTPOOL is a mathematical model of the spreading and vaporisation behaviour of liquid pools resulting from accidental spillages of water reactive chemicals. The chemical reactions considered are:

- Hydrolysis with water from the atmosphere, water within the substrate and free-water lying on the ground.
- Reaction with certain components of the substrate.

REACTPOOL was developed by researchers at UMIST on behalf of the Health and Safety Executive (HSE). The basis of the model has been openly published in series of reports [1], [2], [3], [4] and [5].

This report concerns a review of the information in the REACTPOOL reports and, based on the findings of this review, the specification of a mathematical model of a water reactive spill. The aim of the mathematical model specification is to provide input to the development of a new software implementation, so as to provide a robust tool for major accident analysis.

The scope of work is:

- Review of publicly available information regarding the existing REACTPOOL pool model.
- Recast the existing REACTPOOL equations into ordinary differential equation (ODE) form suitable for solution by an appropriate ODE solver.
- Prepare a mathematical model specification for the recast REACTPOOL model.

The water-reactive substances covered are those considered in [1] and [5], namely sulphur trioxide, oleum, chlorosulphonic acid, silicon tetrachloride, phosphorus trichloride, phosphorus oxychloride, acetyl chloride and titanium tetrachloride. However, an aim of the specification is to maintain a generic approach so as to facilitate adding new substances in the future.

2 REVIEW OF THE REACTPOOL MODEL

The REACTPOOL model is published in the open literature and has been subject to peer review. The review of the current study is motivated by the need to identify gaps in the model specification and to draw attention to any areas that may cause implementation problems or that might be better treated differently in a new software model.

2.1 OVERVIEW

The REACTPOOL model is described in the HSE contract research report [1]. The model is generalisation of an earlier model for accidental releases of SO₃ and oleum [6] (see also [7], [8], [9] and [10]), modified to account for substances that react with water in a different way to SO₃ and oleum. The model is for either the near-instantaneous or continuous release of water reactive liquid over land. Water is supplied to the pool from three sources: free water lying on the ground, moisture from the atmosphere and water within the substrate. These components of the model are shown schematically in Figure 1.

The model described in [1] incorporates the following water reactive substances:

- Sulphur trioxide (SO₃) and oleum (SO₃ in H₂SO₄)
- Phosphorus trichloride (PCl₃)
- Phosphorus oxychloride (POCl₃)
- Silicon tetrachloride (SiCl₄)
- Chlorosulphonic acid (HSO₃Cl)
- Acetyl chloride (CH₃COCl)

Subsequently, the model has been extended [5] to include titanium tetrachloride (TiCl₄).

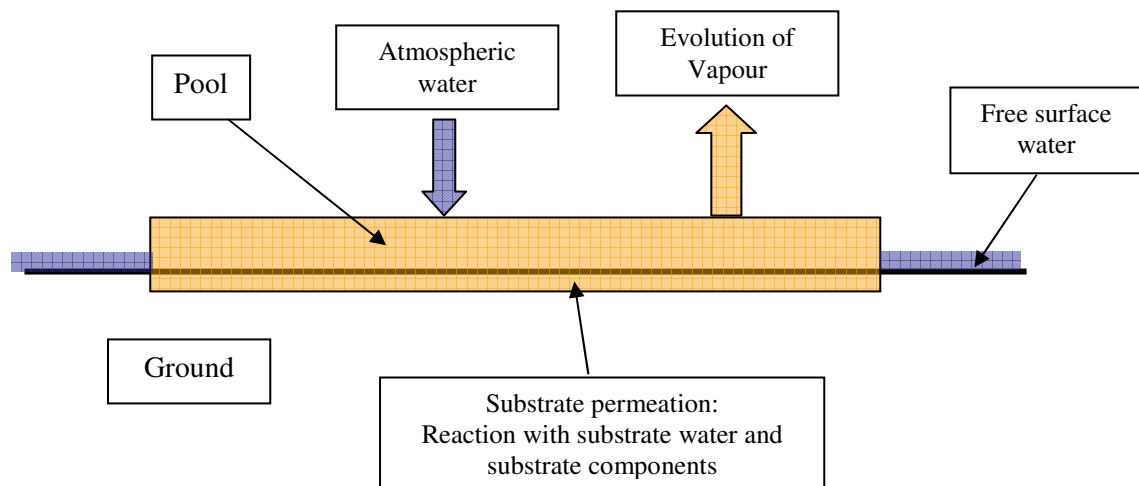


Figure 1 Schematic Diagram of Mass Exchanges in the REACTPOOL Model

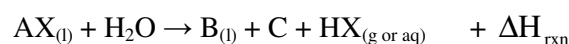
Following [1], it is convenient to consider the parts of the model under the following headings:

- Reaction with water
- Reaction with substrate
- Pool spreading
- Permeation through substrate
- Availability of water
- Energy balance
- Evaporation
- Boiling
- Solidification
- Computational procedure

These aspects are discussed in the following sections.

2.2 REACTION WITH WATER

The model considers reactions with water of the general form:



where

- AX is the water reactive chemical
- B is a possible liquid product
- C is a possible solid product (soluble or insoluble)
- HX is the acid generated
- ΔH_{rxn} is the enthalpy of hydrolysis

In the cases where at least one of the hydrolysis products is liquid, then the pool will contain at least two liquids AX and B. The pool composition and properties vary as AX continuously reacts with water forming product B.

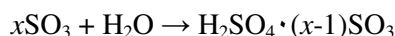
When product C is formed, the model allows for C either being soluble or insoluble in the liquid.

Where the water reactive chemical contains a halogen bond, acid HX is formed. If water is in excess then a liquid aqueous solution of the acid is usually formed. If the water reactive chemical AX is in excess then the acid may be directly evolved to the atmosphere as gas.

Reactions of the spilled substance with water are assumed to be rapid, complete and exothermic.

2.2.1 Sulphur Trioxide (SO₃) and Oleum (SO₃ in H₂SO₄)

In the case of the reaction of sulphur trioxide (SO₃) and oleum (SO₃ solution in H₂SO₄) with water, REACTPOOL adopts the model of [6], [8], [10]. In this model the reaction with water is given by



where x depends upon the percentage (by mass), p , of free SO₃ in the pool. No experimental data exists for pure SO₃, the parameterisation $x(p)$ in [8] suggests a value of $x = 21.5$ for pure

SO₃, although it should be noted that this is based on an extrapolation of experimental data. The heat of reaction between SO₃ and water is also parameterised in terms of p :

$$\Delta H_{\text{rxn}} = A + Bp + Cp^2 + Dp^3 + Ep^4 \quad \text{kJ kg}^{-1} \text{ water reacted}$$

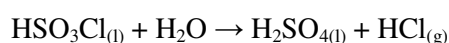
where $A = 4921.8$, $B = 14.225$, $C = 0.195$, $D = -0.399 \times 10^{-2}$ and $E = 3.4 \times 10^{-5}$ (also with units kJ kg^{-1} water). [8] states that this heat of reaction formula is only valid when $p > 0$ and when $p = 0$ (corresponding to pure sulphuric acid) $\Delta H_{\text{rxn}} = 0$. This implies a discontinuous change in going from very small p to zero p . No other terms are included in REACTPOOL for the heat of solution of pure H₂SO₄ with water. We therefore conclude that the model is incapable of accounting for the thermodynamic behaviour of mixing pure H₂SO₄ with water.

Physical properties of the pool are parameterised in [8], [10] as functions of the pool composition, p and temperature. The form of the property correlations appear to be piecewise fits to experimental data and in many cases there are small discontinuities in property values. Even small discontinuous changes such as these will be seen by and cause problems for an ODE solver with adaptive step size based on error control.

REACTPOOL also includes the reaction of H₂SO₄ with calcium hydroxide in a concrete substrate – see Section 2.3.

2.2.2 Chlorosulphonic Acid (HSO₃Cl)

The reaction of chlorosulphonic acid with water is discussed in [11]. In REACTPOOL the reaction is represented by



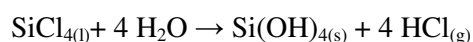
REACTPOOL assumes that HCl is evolved directly as gas rather than going into aqueous solution. The heat of reaction for the above is -1115 kJ kg^{-1} water reacted. The simplification that HCl is generated directly in gaseous, rather than aqueous form, is due to the difficulty in determining the degree of solvation of HCl in the mixture. This is discussed further in [11].

In addition to HCl, HSO₃Cl vapour will also evolve to the atmosphere due to its high volatility. Although H₂SO₄ is less volatile, it may also be evolved as vapour in cases where the pool temperature is sufficiently high ($>333 \text{ K}$).

As for SO₃/oleum case, REACTPOOL includes the reaction of H₂SO₄ with calcium hydroxide in a concrete substrate – see Section 2.3.

2.2.3 Silicon Tetrachloride (SiCl₄)

The reaction of SiCl₄ with water is discussed in [3]. In REACTPOOL the reaction is represented by



The reaction product Si(OH)₄ (*ortho*-silicic acid) is assumed to be an insoluble solid. As discussed in [3], *ortho*-silicic acid is actually expected to be produced in hydrate form ($n\text{SiO}_2 \cdot m\text{H}_2\text{O}$ with $m < n$) as silica gel, which may then undergo condensation in air, changing its molecular weight. This condensation behaviour is complex and ignored in REACTPOOL which simply assumes that Si(OH)₄ is insoluble in the liquid. Examples in [3] indicate that

the model results are generally not sensitive to whether the solid is assumed to settle or be suspended in the liquid.

Based on the assumption that for accidental spills there is unlikely to be excess water, the HCl product is assumed to be evolved directly as gas into the atmosphere. The heat of reaction in this is given as -4050 kJ kg^{-1} water reacted [3]. Due to its volatile nature, SiCl_4 vapour will also be generated from the spill.

2.2.4 Phosphorous Trichloride (PCl_3)

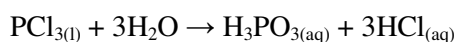
The reaction of PCl_3 with water is discussed and reviewed in [4]. Reactions both with PCl_3 in excess and with water in excess are considered.

In excess PCl_3 ($<0.393\text{kg}$ water per kg PCl_3), the reaction is



The heat of reaction for the above is given in [4] as $-47.5 \text{ kJ mol}^{-1} \text{ PCl}_3$. In the absence of data on the solubility of red phosphorus, $\text{P}_{(s)}$ in mixtures of PCl_3 and H_3PO_4 it is assumed in REACTPOOL that the red phosphorous is insoluble. In the case that the pool boils, the phosphorous particles are assumed to be suspended, otherwise they are assumed to settle at the bottom of the pool. HCl gas is assumed to be directly evolved into the atmosphere. REACTPOOL neglects the vaporisation of H_3PO_4 due to its low volatility at the temperatures expected to be encountered for accidental spills.

In the excess or balanced water case ($\geq 0.393\text{kg}$ water per kg PCl_3)

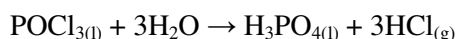


A heat of reaction of $-272.1\text{kJ mol}^{-1} \text{ PCl}_3$ is given in [4] - this is assumed to apply to the water balanced case. For excess water, it is not clear from the REACTPOOL reports how the heat of reaction variation with degree of solvation is determined. [4] indicates also that HCl vapour is evolved from the solution due to its volatility, but the vapour pressure of HCl over a mixture of H_3PO_3 , HCl and water is not explicitly given. It is stated that the vaporisation of H_3PO_3 is neglected due to its low volatility. [4] indicates that excess water conditions are considered very unlikely for an accidental spillage unless there is a large external source of water.

2.2.5 Phosphorous Oxychloride (POCl_3)

The reaction of POCl_3 with water is discussed and reviewed in [4]. Reactions both with POCl_3 in excess and with water in excess are considered.

In excess POCl_3 ($<1.585\text{kg}$ water per kg POCl_3), the assumed reaction is



The heat of reaction in this case is given as $-89.54 \text{ kJ mol}^{-1} \text{ POCl}_3$. H_3PO_4 liquid is produced and the pool composition continuously changes. HCl gas is assumed to be directly evolved as a reaction product. Due to its high volatility, POCl_3 vapour is assumed to evolve from the pool. Due to its low volatility the vaporisation of H_3PO_4 is neglected.

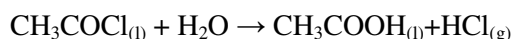
In excess or balanced water ($\geq 1.585\text{kg}$ water per kg POCl_3)



The heat of reaction is dependent upon the amount water in excess. In the case of a balanced reaction, the heat of reaction is stated in Section 4.3 of [4] to be $-286.19 \text{ kJ mol}^{-1} \text{ POCl}_3$. It is not clear from the REACTPOOL reports how the heat of solvation is accounted for in the excess water case. HCl vapour will evolve due to its high volatility. The vaporisation of H_3PO_4 is neglected due to its low volatility. Excess water conditions are considered very unlikely unless there is a large external source of water.

2.2.6 Acetyl Chloride (CH_3COCl)

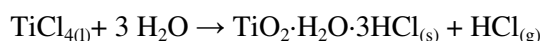
The reaction of acetyl chloride with water is given in [1] as



The heat of reaction is given in [1] as -5000 kJ kg^{-1} reacted water. It is assumed that HCl is evolved directly to the atmosphere in its gaseous phase. Both acetyl chloride (CH_3COCl) and CH_3COOH vapour will be evolved from the pool. [1] does not discuss separate cases for excess acetyl chloride and excess water.

2.2.7 Titanium Tetrachloride (TiCl_4)

The reaction of TiCl_4 with water is discussed and reviewed in [5]. In REACTPOOL the reaction is represented by

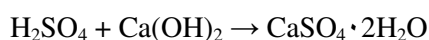


As discussed in [5], the above is based on the assumption that for accidental spills, water will be the limiting compound (i.e. TiCl_4 is present in excess). Heats of reaction are quoted separately for water in the liquid and vapour phases [5]. (This is different from the other water reactive substances which have a heat of reaction with water that appears to be independent of phase).

The complex solid product $\text{TiO}_2 \cdot \text{H}_2\text{O} \cdot 3\text{HCl}$ is assumed [5] to settle to the bottom of the pool forming a layer altering the conduction of heat from the ground. The physical properties of the solid complex are taken in [5] to be the same as TiO_2 , although these properties are not given. The pool contains only one liquid (TiCl_4). Apart from the HCl gas produced directly from the reaction, TiCl_4 vapour will also evolve due to its relatively high volatility.

2.3 REACTION WITH SUBSTRATE

Water reactive chemicals are usually highly aggressive and may react also with some of the other compounds of the substrate. Additionally, the liquid product B may react with the substrate. The only substrate reaction included within the referenced REACTPOOL reports is the exothermic reaction between H_2SO_4 (from SO_3 /oleum or chlorosulphonic acid spill) and calcium hydroxide ($\text{Ca}(\text{OH})_2$) in the cement of the concrete. The reaction assumed in [8] is the production of gypsum:



with a heat of reaction $-2278 \text{ kJ kg}^{-1} \text{ H}_2\text{SO}_4$ reacted. The mass of H_2SO_4 reacted is determined from the amount of cement encountered assuming a saturated reaction: 1.3 kg of H_2SO_4 being required for saturated reaction with 1 kg of cement. [8] indicates that the cement content of concrete can vary widely, but states that in most cases the range is 200-600 (kg cement)/(m^3 concrete).

[It is not clear what REACTPOOL assumes for its standard “concrete” substrate type, or whether calcium hydroxide is assumed to be present in the any of the other standard REACTPOOL substrates]

The amount of substrate encountered is calculated from the permeability as described in Section 2.5.

2.4 POOL SPREADING

Spreading of the pool is modelled in REACTPOOL as a radial spread according to:

Instantaneous release from initial an height h_0 :

$$\frac{dR}{dt} = \sqrt{1.08g(h_0 - h)}$$

Continuous release

$$\frac{dR}{dt} = \sqrt{2g(h - h_{min})}$$

where R is the pool radius, h the pool depth. h_{min} is the depth of the pool at which spreading ceases. The model assumes that the pool depth remains fixed when h_{min} is reached, leading to the possible shrinkage of the pool when the volume decreases due to vaporisation.

The above spreading model is quite widely adopted, but is not in accord with a correct understanding of the forces acting on the pool (see [12], [13] and most recently [14]).

A correlation relating h_{min} to the aerodynamic roughness length z_0 of the surface is given in equation (12) of [1]. The basis of this correlation is unclear, other than the statement in [1] that for very smooth surfaces a value of 5mm is suggested and for rougher surfaces the value can be a few centimetres. At $z_0 = 0.1\text{m}$ the correlation gives $h_{min} = 1\text{cm}$; at $z_0 = 1\text{m}$ the correlation gives $h_{min} = 2\text{cm}$.

2.5 PERMEATION THROUGH SUBSTRATE

The permeability, k_{subst} , of the water reactive substance in the substrate is estimated from the permeability of water, $k_{subst,w}$ in the substrate according to:

$$k_{subst} = k_{subst,w} \frac{\nu_w}{\nu}$$

where ν denotes the kinematic viscosity of the water reactive substance (subscript w refers to water values). For concrete, $k_{subst,w}$ is given in equation (2.2.3.6) of [6], as a function of time in hours from initial contact. This equation is a fit to behaviour over a period of many thousand of hours exposure. For vaporisation from accidental spillages, much shorter times are usually of interest (typically less than or of the order of 1 hour). In these cases, the variation with time implied by equation (2.2.3.6) in [6] is insignificant. A justifiable simplification in this case would be to use a fixed value corresponding to the short time behaviour ($k_{subst,w}(\text{concrete}) = 7.8 \times 10^{-7} \text{ m/s}$).

The permeability of other substrates is not given in the REACTPOOL references.

REACTPOOL assumes that penetration of the substrate occurs within a cone beneath the pool with the highest penetration being at the centre. This is shown schematically in Figure 2.

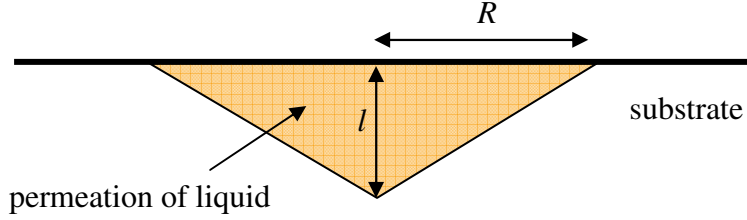


Figure 2 Schematic Diagram of Substrate Penetration in the REACTPOOL Model

The penetration depth , l , is given by

$$\frac{dl}{dt} = k_{subst}$$

Actually in [6], this is written in terms of the fixed timestep used by REACTPOOL for solving the ordinary differential equations (ODEs). The penetration volume $\frac{1}{3}\pi lR^2$ is used to determine the mass of reactive component and the mass of water encountered within the substrate.

The assumption of a conical penetration volume is an approximation, since assuming one-dimensional downwards permeation, the shape will depend upon the time dependent spreading behaviour. We believe that it is unnecessary to assume this, since it is just as easy to track the penetration volume, $V_{substrate}$, into the substrate using a single differential equation (replacing the one for penetration depth in REACTPOOL):

$$\frac{dV_{substrate}}{dt} = k_{subst} \pi R^2$$

In the model specification given in Section 3, only the rate of substrate penetration is in fact needed.

2.6 AVAILABILITY OF WATER

The availability of water is modelled according to section 2.2 in [6]. The different sources of water are outlined below.

2.6.1 Water present on the ground

The free surface water on the ground is modelled by specifying a free ground water thickness (equivalent to a volume per unit area), which is an input to the model. The free surface water volume encountered is calculated from this depth and the area of the pool.

Results using REACTPOOL indicate that the free surface water is usually the dominant water source for the pool.

2.6.2 Water from substrate

[6] discusses the division of water content in concrete, indicating that this can be described mainly in terms of free water, capillary water, gel water and water combined in hydrated cement compounds. In [6] the free water content of cement is said to vary between 130 kg m^{-3} and 230 kg m^{-3} and the three non-free forms of water are assumed to total to 0.2 kg water / kg cement.

The water content of other substrates is not given in the REACTPOOL references.

2.6.3 Atmospheric water

The flux of atmospheric moisture entering the pool is modelled by assuming that all the moisture content of the air from a height equal to the roughness length up to a height H' above the roughness length enters the pool. It is assumed in the model that

$$H' = \frac{R}{30} \frac{M_{AX}}{M_p}$$

where M_{AX} is the mass of water reactive substance in the pool of total mass M_p . This is a modification of a similar expression used in [8] for SO_3 . This implies that H' has a maximum value of $R/30$. Although it does seem reasonable that a greater depth of air to be affected for larger and more concentrated pools, the basis of the above expression is uncertain. It may be possible to improve on the REACTPOOL approach by using solutions of the diffusion equation over the pool and accounting for the variation in relative humidity with height. However, it is noted that the REACTPOOL model results generally show little sensitivity to the atmospheric moisture.

Although [1] indicates that REACTPOOL does not necessarily consider that a water reactive chemical will absorb atmospheric water, it appears that reaction with atmospheric water is assumed for the water reactive substances considered, namely:

- Sulphur trioxide (SO_3) and oleum (SO_3 in H_2SO_4)
- Phosphorus trichloride (PCl_3)
- Phosphorus oxychloride (POCl_3)
- Silicon tetrachloride (SiCl_4)
- Chlorosulphonic acid (HSO_3Cl)
- Acetyl chloride (CH_3COCl)

2.7 ENERGY BALANCE

The energy balance in REACTPOOL incorporates the following (see Section 2.5 of [8]):

- heat of addition of spill
- heat of reaction with water or substrate
- heats of vaporisation, fusion and sublimation
- net thermal radiation
- conduction from ground or frozen pool
- convective heat transfer from atmosphere

These terms are discussed further below.

2.7.1 Heat of addition of spill

This represents the addition of material to the pool due to the spill, which may be at a different temperature from that of the pool.

2.7.2 Heat of reaction

This represents the heat of reaction with water, plus any heat added due to reaction with substrate. All the heat generated is assumed to go directly into the liquid pool.

2.7.3 Heats of vaporisation, fusion and sublimation

These represent the enthalpy change due to vaporisation, freezing of the liquid pool, sublimation, or melting of the frozen pool. The heating rates are calculated directly from the calculated vaporisation or sublimation rates, or in the case of heat of fusion from the quantity that freezes or thaws. In REACTPOOL, freezing and thawing is assumed to be instantaneous – see Section 2.10.

2.7.4 Radiation

The net radiation to the pool is calculated using the model adopted by Kawamura and MacKay in [15]. The model includes net solar (short-wave) radiation and long-wave radiation to and from the pool. The calculations take as input the longitude, latitude, cloud cover and atmospheric radiation factor (Figure 2 in [15]).

2.7.5 Conduction

The heat conduction between the liquid pool and the ground is calculated using the one-dimensional conduction model adopted in [15] with a constant ground temperature (which in REACTPOOL is set equal to the air temperature). The conduction model incorporates thermal resistance of the liquid pool using the average depth of the pool over the entire course of evaporation (assumed equal to half the initial pool depth) and an empirical resistance function which depends solely on the substance boiling point. This does not account for any effect due to pool temperature and ignores the important role of convective heat transfer in the pool.

For the frozen pool, heat conduction from the ground to the pool is calculated using the ground heat transfer coefficient. Heat transfer between the frozen pool and overlying liquid pool (if present) is calculated based on conduction only using a two layer model.

2.7.6 Convection from the atmosphere

The sensible heat flux, $\dot{H}_{p,conv}$ convected to the pool from the atmosphere is calculated from the mass transfer coefficient, k_m calculated using the Brighton vaporisation model [16] according to:

$$\begin{aligned}\dot{H}_{p,conv} &= k_h (T_a - T_p) A_p \\ k_h &= k_m \rho_a C_{pa} (Sc / Pr)^{0.67}\end{aligned}$$

where

$$\begin{aligned}\rho_a &\text{ is the air density} \\ C_{pa} &\text{ is the air specific heat capacity}\end{aligned}$$

T_a	is the air temperature
T_p	is the pool temperature
A_p	is the pool surface area
Sc	is the Schmidt number and
Pr	is the Prandtl number

[8] states that this is based on heat and mass transfer analogy. However, [17] is based on the same mass transfer model and uses a different, arguably more consistent, form involving replacement of Sc by Pr in the mass transfer model.

2.8 EVAPORATION MODEL

The evaporation model is based on that of Brighton [16] generalised to multi-components. As described in [6], [8] and [10], this generalisation is incorrect, except when a single volatile species dominates. There should be a coupling between vaporisation of the different components which arises from consideration of the “film theory” correction to the diffusive fluxes. The theory including these corrections is given in Section 3.9.2. It may be that inclusion of the corrections in the model always lead to a reduction in vaporisation rate. If this could be proved then the REACTPOOL approach, which neglects these corrections, would be conservative.

2.9 BOILING

In REACTPOOL when the pool temperature is predicted to rise above the boiling point, the rate of vaporisation (boiling) is determined from a heat balance on the pool, limiting the temperature by the boiling temperature.

The boiling point is determined accounting for the elevation due to the solute (hydrolysis product C), if present. The boiling point elevation, apart from for SO₃ and oleum, is determined based on ideal solution theory [1]. For SO₃ and oleum the boiling point is given by a correlation in terms of the free SO₃ mass fraction, p in the pool.

The REACTPOOL transition from evaporation to boiling is expected to fail if the evaporation model is being solved with step size error control. This is due to the behaviour of the vaporisation model as the boiling point is approached. The fixed step size solution method in REACTPOOL, which does not adjust to rapid changes, is likely to step past the boiling point, whereas a method with step size error control is likely to reduce its step size to maintain solution accuracy near the boiling point transition. The computer model GASP [17] overcomes the numerical difficulties in this region by introducing a “cut-off” which smoothes the transition and changing variable so that the temperature remains bounded by the boiling point. This allows GASP to treat evaporation and boiling in a unified way. Extension of this approach to the multi-component case may require further detailed consideration.

2.10 SOLIDIFICATION

When the pool temperature is predicted to fall below the freezing temperature of the pool then the pool is assumed to instantly solidify (freeze).

The depression of the freezing point due to the solute is calculated based on ideal solution theory [1].

The model considers two cases depending on whether the pool solidifies before or after the spill ceases.

2.10.1 Solidification before the spill ceases

In this case, the newly spilled liquid flows over the frozen pool and is assumed to only contact free surface and ground water when its radius exceeds that of the frozen pool.

The exposed area of the frozen pool is assumed to sublime, with the sublimation rate calculated using the Brighton evaporation model [16]. This implicitly assumes that vaporisation is limited by atmospheric diffusion above the pool. In reality, we would expect the diffusion in the solid phase to be the limiting factor. REACTPOOL's approach is therefore expected to be (possibly very) conservative.

The liquid and solid pools are modelled independently – the only interaction between them is considered to be heat exchange calculated assuming one-dimensional heat conduction through two uniform layers.

If the temperature (and concentration) of the pool change such that the freezing point is exceeded, then the frozen pool is assumed to melt instantaneously, mixing with the overlying liquid.

The instantaneous freezing and thawing of the pool is clearly an idealisation. An alternative, possibly preferable, approach for thawing of the pool would be to maintain the frozen pool at the freezing point and to use the heat balance to determine the quantity thawing.

The substance property correlations given in [1] for thermal conductivity do not state whether they apply to only the liquid phase, or whether they apply also to the solid phase.

2.10.2 Solidification after the spill ceases

In this case the pool sublimates and may thaw due to compositional change.

2.11 REACTION PRODUCTS

2.11.1 Liquid product

When at least one liquid is produced in the hydrolysis reaction, the pool will contain at least two liquids – one liquid reactant and one liquid product. The liquid composition will change continuously as the reaction proceeds. The liquid physical properties (density, vapour pressure, specific heat, viscosity etc) in REACTPOOL are calculated assuming an *ideal mixture*, e.g.

Density

$$\rho_{L,mix} = \sum_i x_i \rho_{iL}$$

where

x_i is the mole fraction of liquid component i .

Vapour pressure

$$P_{vi} = x_i P_{vi}^0$$

i.e. obeys Raoult's Law.

This treatment (and also the adopted heats of reaction) precludes REACTPOOL being used for cases dominated by production of a non-ideal aqueous solution, e.g. spillage of HF in pure or concentrated acid form.

2.11.2 Soluble product

When a soluble solid, C, is produced in the hydrolysis reaction, REACTPOOL determines the boiling point elevation and freezing point depression from ebullioscopic and cryoscopic constants assuming an ideal solution. The vapour pressure reduction is also determined based on an ideal solution:

$$\Delta P_{vi} = x_2 P_{vi}^0$$

where

x_2 is the mole fraction of solute.

2.11.3 Insoluble product

The model assumes that insoluble particles are either:

- suspended and homogeneously mixed in the liquid, or
- form a film layer at the bottom of the pool.

From the description in the REACTPOOL reports, it seems that for some reactions it is always assumed that a film layer forms. For the other reactions, it seems that a film layer is assumed only if the pool is not boiling.

In the case of a layer forming, REACTPOOL includes extra thermal resistance due to conduction. In the case of suspended particles, the liquid properties are modified as described in Section 3.3 of [1].

2.11.4 Gaseous product

In reactions where the product HX is in the vapour phase, then this is assumed to be evolved directly into the atmosphere. REACTPOOL assumes this is always the case, even when the water reactive chemical is in excess.

2.12 CALCULATIONAL PROCEDURE

Section 4 of [1] outlines the calculational procedure adopted by REACTPOOL. The model calculations are performed for small fixed time increments (0.01 s), with each step split into three sub-steps:

- Spill
- Reaction
- Evolution

These are described further below:

2.12.1 Spill

The mass of the pool components at the current time step is determined from the mass at the previous time step plus the mass added due to the spill. The physical properties (density, boiling point, etc) are determined for this new composition. The new pool radius is

determined using a 4th order Runge-Kutta step based on the pool spreading equations given in Section 2.4. The new pool area and depth are hence determined.

2.12.2 Reaction

The calculations undertaken depend upon whether:

- the water reactive chemical absorbs water vapour from the air
- any of the liquids react with substrate compounds
- any solid particles are produced.

The amount of water available for reaction is calculated. If water is in excess, the mass of water that reacts is equal to that required to consume all the water reactive chemical. The heat of reaction is then determined. If the composition of the pool has changed due to the reaction, the new pool properties are calculated. The pool temperature is calculated from the energy balance by an unspecified trial and error method.

The REACTPOOL documentation does not say that the spill step is recalculated here, despite the pool properties having possibly been changed.

2.12.3 Evolution

If the pool temperature is below the boiling point and above the freezing point, then vaporisation is calculated as described in Section 2.8. If the pool boils, then the amount evolved is calculated as described in Section 2.9. Otherwise the pool is assumed to freeze as described in Section 2.10. At the end of the time step the composition has changed due to evolution of vapour. The new composition is calculated and the pool properties recalculated.

The REACTPOOL documentation does not say that the prior sub-steps are recalculated due to the change in pool properties.

The time variable is incremented by the fixed time step and the above calculational sub-steps are repeated in REACTPOOL until all the water reactive has evolved, or the user specified release duration has been exceeded.

2.12.4 Problems with the REACTPOOL calculational procedure

The calculational procedure as described above is likely to suffer from numerical problems due to a lack of error control on the step size and model inconsistencies introduced by splitting of the sub-steps.

A preferred approach would be to write the model directly as a coupled set of ordinary differential equations (ODE's) of the form:

$$\frac{dY_i}{dt} = F_i(Y_1, Y_2, \dots, Y_N)$$

and to use a ODE solver employing a standard algorithm with step size error control suitable for this type of model (e.g. variable step, variable order Gears method for stiff problems). The calculational approach would then be to initialise the Y_i from the input data, to provide a function which calculates the gradients F_i from a set of new variables $\{Y_1, Y_2, \dots, Y_N\}$ chosen

by the solver. Where there is a discontinuous change in F_i (e.g. when the pool freezes) then the solver may have to be stopped and restarted with the new equation set.

2.13 SUBSTRATE PROPERTIES

According to [1], REACTPOOL incorporates five types of substrate. These are listed in Table 1. [1] indicates that the characteristics and properties (thermal conductivity, porosity, density etc) of these substrates are stored by REACTPOOL. Unfortunately, apart from concrete, which is largely specified in [6], the values assumed for these standard substrate types are not given in the REACTPOOL reports.

Table 1 Substrates incorporated into REACTPOOL

<i>Substrate</i>
Concrete
Asphalt
Soil (sandy,dry)
Soil (moist, 8% water, sandy)
Soil (average)

2.14 SUBSTANCE PROPERTIES

The properties of water reactive chemicals and their hydrolysis products are given in Appendix B of [1] and for SO_3 and oleum in Appendix A of [8], noting the corrections given in [10].

Omissions include the properties for TiCl_4 and its reaction products and the properties for H_2SO_4 . Also there is no information given in the REACTPOOL reports on the partial pressure of HCl over aqueous solutions that could be formed in excess water cases.

2.15 REVIEW CONCLUSIONS

The novel aspect of REACTPOOL is its inclusion of chemical reaction with water of spilled substances. We are not aware of other spill models including as wide a range of water reactive chemicals. The reactions included within REACTPOOL are based on a review of the literature by acknowledged experts in the field and have not been checked under this study.

Our review indicates a number of areas that might be dealt with differently in a new model. In particular, we have noted the following:

- The calculational procedure lacks adequate error control and the sub-splitting of the time step introduces possible inconsistencies.
- The pool spreading model is of a form that has previously been criticised as being inappropriate for a pool spreading on land.
- Given the other approximations in the model, some of the sub-models appear to be over-elaborate or of dubious applicability. An example of this is the model for thermal resistance of the liquid layer.
- The evaporation model of Brighton has been applied to multi-component vaporisation without consideration of the effect of the other components on the “film theory” factor (see Section 3.9.2).
- There are some gaps in the substance property values assumed for substrates (e.g. the cement content assumed for concrete, the permeability assumed for other substrates) and for some of the reaction products (e.g. for TiO_2 to characterise the solid complex formed produced from the reaction of TiCl_4 with water).

- For cases where there is excess water, the calculation of heat of reaction accounting for the degree of solvation of the product HX and its vapour evolution is unclear. The REACTPOOL reports emphasise that for accidental spills on land the water reactive chemical is most likely to be in excess. All the example calculations in the REACTPOOL reports are for excess water reactive chemical.
- The REACTPOOL model assumes complete reaction of the spilled substance with water, with the reaction products forming an ideal solution. The model would require non-ideal mixtures, such as might be formed by mixing anhydrous HF with water, to be treated as a special case.

3 MODEL SPECIFICATION

3.1 INTRODUCTION

In this section we give the specification of a model of a pool formed from the spillage of a water reactive chemical on land. This is based upon REACTPOOL model, but has been modified to address some of the issues highlighted in review in Section 2.

The specified model uses the following from:

- The same chemical reaction models
- Where available, the same substance property correlations (smoothed to make them continuous where necessary)

Changes of particular note are:

- The model is restructured to be directly of the form

$$\frac{dY_i}{dt} = F_i(Y_1, Y_2, \dots, Y_N)$$

where the pool properties and rates of change are written as functions of the $\{Y_1, Y_2, \dots, Y_N\}$.

- The liquid pool spreading model is replaced by the spreading model given in [17].
- A unified approach to vapourisation and boiling, based on a multi-component generalisation of [16].
- Simplification of the thermal modelling by
 - making the net solar radiative flux a user supplied input,
 - ignoring long wave heating and cooling
 - neglecting thermal resistance of the liquid pool (assumption that the pool is efficiently mixed by convection currents)
- Species balance represented by component moles rather masses.

3.2 DIFFERENTIAL EQUATIONS

The differential equations governing the evolution of the pool with time are:

For the liquid pool:

Species: $\frac{dN_{i,p}}{dt} = \dot{N}_{i,p}$

Enthalpy: $\frac{dH_p}{dt} = \dot{H}_p$

Radius: $\frac{dR_p}{dt} = \dot{R}_p$

Radial velocity: $\frac{dU_p}{dt} = \dot{U}_p$

For the film layer formed by settled solid C:

$$\frac{dN_{C,layer}}{dt} = \dot{N}_{C,layer}$$

For the frozen pool (if present)

Species: $\frac{dN_{i,f}}{dt} = \dot{N}_{i,f}$

Enthalpy: $\frac{dH_f}{dt} = \dot{H}_f$

Radius: $\frac{dR_f}{dt} = U_f$

The right hand sides of the above equations will be specified as functions of the primary variables $\{N_{i,p}, H_p, R_p, U_p, N_{C,layer}, N_{i,f}, H_f \text{ and } R_f\}$. Generally, subscript p refers to the liquid pool, subscript f to the frozen pool and subscript i to a molar component. For a more complete definition of the variables above, and throughout Section 3, please refer to Section 5.

3.3 RATES OF CHANGE

The rates of change are broken down into the following contributions

Species in liquid pool:

$$\dot{N}_{AX,p} = \dot{N}_{AX,spill} - \dot{N}_{AX,evap} - \dot{N}_{AX,react}$$

$$\dot{N}_{w,p} = \dot{N}_{w,avail} - \dot{N}_{w,evap} - \dot{N}_{w,react}$$

$$\dot{N}_{HX,p} = \dot{N}_{HX,prod} - \dot{N}_{HX,evap}$$

$$\dot{N}_{B,p} = \dot{N}_{B,prod} - \dot{N}_{B,evap} - \dot{N}_{B,react}$$

$$\dot{N}_{C,p} = \dot{N}_{C,prod} - \dot{N}_{C,layer}$$

Enthalpy of liquid pool:

$$\dot{H}_p = \dot{H}_{p,add} + \dot{H}_{p,react} - \dot{H}_{p,evol} + \dot{H}_{p,cond} + \dot{H}_{p,rad} + \dot{H}_{p,conv}$$

Species in the solid pool:

$$\dot{N}_{i,f} = -N_{i,sub\ lim e}$$

Enthalpy of the solid pool

$$\dot{H}_f = \dot{H}_{f,cond} - \dot{H}_{f,evol} + \dot{H}_{f,rad} + \dot{H}_{f,conv}$$

The calculation of the terms on the right hand sides of the above is specified in the following sections.

3.4 UPDATE FROM PRIMARY VARIABLES

3.4.1 Area

Liquid pool surface area:

$$A_p = \pi R_p^2$$

Frozen pool surface area:

$$A_f = \pi R_f^2$$

Liquid pool surface area exposed to ground:

$$A_{p,ground} = \max(A_p - A_f, 0)$$

Frozen pool surface area exposed to air:

$$A_{f,air} = \max(A_f - A_p, 0)$$

3.4.2 Mass

Mass of each species: $M_{i,p} = N_{i,p} M_{m,i}$

Pool mass: $M_p = \sum_i M_{i,p}$

Similarly for the frozen pool.

3.4.3 Temperature

The temperature of the pool is obtained by solving the enthalpy equation for temperature (for the given pool composition):

$$H_p = H_{pool}(T_p)$$

Similarly for the frozen pool.

3.4.4 Volume

Pool volume: $V_p = \sum_i N_{i,p} V_{m,iv}(T_p)$

3.4.5 Density

Pool density: $\rho_p = M_p / V_p$

3.4.6 Depth

Pool depth: $h_p = V_p / A_p$

Effective depth (accounting for puddles): $h_e = h_p - h_{puddle}$

3.5 AVAILABLE WATER

The rate of addition of water is considered as a sum from the separate sources:

$$\dot{N}_{w,avail} = \dot{N}_{w,subst} + \dot{N}_{w,atmos} + \dot{N}_{w,surface}$$

3.5.1 Free-surface water

Free surface water is encountered at a rate given by the radial spreading velocity and the free-surface water depth. In terms of a molar rate:

$$\dot{N}_{w,surface} = \dot{R}_p h_{w,surface} / V_{m,wL}$$

where $V_{m,wL}$ is the molar volume of liquid water.

The above holds for spreading over land.

For spreading over a frozen pool:

$$\dot{N}_{w,surface} = 0$$

3.5.2 Atmospheric water

If the water reactive substance is specified as reacting with water vapour, the rate of addition of water from the moist air is calculated from the moisture flux over the pool up to a specified height H' given by:

$$H' = \frac{R_p}{30} \frac{M_{AX,p}}{M_p}$$

$$\dot{N}_{w,atmos} = \sqrt{A_p} \dot{V}_a(H') / V_{m,wv}(T_a)$$

where $V_{m,wv}(T_a)$ is the molar volume of water vapour at temperature T_a .

3.5.3 Substrate water

The rate of encountering water in the substrate (both free and bound water) is dependent upon the permeability, k_{subst} of the pool liquid through the substrate and $n_{w,subst}$, the water moles available per unit volume of the substrate:

$$\dot{N}_{w,subst} = k_{subst} A_p n_{w,subst}$$

3.6 REACTION WITH WATER

3.6.1 Excess water reactive chemical

For excess water reactive chemical ($N_{AX,p} > 0$), the reaction rate is determined by the rate, $\dot{N}_{w,avail}$ of encountering water. The rates of consumption of reactants and formation of reaction products is then determined from $\dot{N}_{w,avail}$ and the reaction stoichiometry. The rate of addition of reaction heat is given by $\dot{N}_{w,avail}$ and the heat of reaction per mole of water reacted.

3.6.2 Excess water

For excess water ($N_{w,p} > 0$), the reaction rate is determined by the rate, $\dot{N}_{AX,spill}$ of water reactive chemical addition. The rates of consumption of reactants and formation of reaction products is then determined from $\dot{N}_{AX,spill}$ and the reaction stoichiometry. The rate of addition of reaction heat is given by $\dot{N}_{w,spill}$ and the heat of reaction per mole of water reactive chemical reacted.

3.7 REACTION WITH SUBSTRATE

For water reacting chemical which reacts with compounds (other than water) in the substrate, the rate of reaction is assumed to depend on the rate at which the substrate compounds are encountered by the permeating liquid. This is modelled simply as

$$\dot{N}_{subst,react} = k_{subst} A_p n_{c,subst}$$

where k_{subst} is the permeability of the pool liquid through the substrate and $n_{c,subst}$ is the moles of the compound per unit volume of the substrate.

The rate of consumption of the liquid reactant is obtained from the stoichiometry of its reaction with the substrate compound. The rate of addition of reaction heat, which is assumed to go directly into the pool, is given by $\dot{N}_{subst,react}$ and the heat of reaction per mole of the substrate compound reacted.

3.8 SPREADING OF THE POOL

3.8.1 Liquid Pool

The spreading of the liquid pool over land is modelled according to the pool spread model in [17]. This model includes a gravity driving term and frictional resistance term. The model is for liquid spreading on horizontal smooth or rough land. For rough land, the pool spreading is limited by the input puddle depth h_{puddle} .

The pool spreading is dependent on a shape parameter, s , which is determined as follows:

For smooth land ($h_{puddle}=0$):

$$\begin{aligned} \text{Surface tension minimum depth} \quad \lambda_{st} &= \sqrt{\frac{\sigma_p}{g\rho_p}} \\ \text{Viscosity minimum depth} \quad \lambda_v &= \left(\frac{6\nu_p \dot{V}_{p,spill}}{\pi g} \right)^{1/4} \\ \text{Shape parameter} \quad s &= \max(\lambda_{st}, \lambda_v) \end{aligned}$$

Rough land ($h_{puddle}>0$):

$$\text{Shape parameter} \quad s = \frac{\Phi_1(\varepsilon)h_{puddle}}{2h_e}$$

where

$$\varepsilon = \frac{8U_p^2}{gh_{puddle}}$$

$$\Phi_1(\varepsilon) = (1 + \varepsilon)^{1/2} - 1$$

ν_p is the viscosity of the liquid in the pool and σ_p is the surface tension.

For spreading over rough land:

$$\dot{R}_p = \Phi_2(\varepsilon)U_p$$

with

$$\Phi_2(\varepsilon) = 1 - \frac{2}{\varepsilon}\Phi_1(\varepsilon)$$

For spreading over smooth land:

$$\dot{R}_p = U_p$$

The balance of forces on the pool is expressed as:

$$\dot{U}_p = \gamma(s) \frac{4g'h_e}{R_p} - F$$

where

$$g' = g \quad \text{for a pool spreading on land}$$

$$\begin{aligned} \gamma(s) &= 1 - s & s < 2 \\ &= -s^2 / 4 & \text{otherwise} \end{aligned}$$

In the model, only the part of the pool above the puddle depth contributes to the outward spreading.

The friction is given by the maximum of the turbulent and laminar friction terms:

$$F = \text{sign}(U_p) \cdot \max(|F_T|, |F_L|)$$

Laminar friction

$$F_L = \beta(s) \frac{c v_p U_p}{h_e^2}$$

$$\beta(s) = 2.53 j(s)^2$$

$$c = 3.0 \quad \text{for spreading on land.}$$

Turbulent friction

$$F_T = \alpha(s) \frac{C U_p |U_p|}{h_e}$$

$$\alpha(s) = 4.49 j(s)$$

with

$$j(s) = 1 \quad s < 2$$

$$= 2/s \quad \textit{otherwise}$$

and a friction (drag) coefficient $C = 1.5 \times 10^{-3}$.

3.8.2 Frozen (solid) pool

The frozen pool is assumed to have a constant radius, i.e.

$$U_f = 0$$

3.9 VAPOUR EVOLUTION FROM THE POOL

Vapour is evolved from the pool by the following means:

- directly as a reaction product
- vaporisation of volatile liquid components
- sublimation of volatile components from the frozen pool

3.9.1 Directly evolved vapour

In this case, the rate of production of vapour moles is calculated directly from the reaction rate and the reaction stoichiometry.

3.9.2 Vaporisation of a volatile liquid component

In this case the vaporisation rate is calculated using Brighton's model generalised to multi-components.

The molar flux per unit area, j_{iv} of species i is given by [18]:

$$j_{iv} = k_m \frac{P}{R_m T_p} \varphi_i \ln \left(\frac{y_{ia} - \varphi_i}{y_i - \varphi_i} \right) \quad (1)$$

where

- k_m is a molar transport coefficient, calculated here using Brighton's theory (without film theory correction) – see below
- y_i is the vapour phase mole fraction of i immediately above the pool surface
- φ_i is the molar flux of vapour component i as a fraction of the total vapour molar flux leaving the pool (including the directly evolved vapour), i.e.
 $\varphi_i = j_{iv} / j_{iv}$
- y_{ia} is the vapour phase mole fraction of component i in ambient air.

For volatile liquid components, vapour-liquid equilibrium above the pool implies:

$$y_i = x_i \gamma_i P_{iv}^0(T_p) / P$$

where

- x_i is the liquid phase mole fraction of component i
- $P_{iv}^0(T_p)$ is the pure component vapour pressure at the pool temperature
- P is the ambient pressure
- γ_i is an activity coefficient for the component in the liquid mixture

Apart from SO_3 in oleum, REACTPOOL assumes an ideal liquid solution (i.e. $\gamma_i = 1$).

For N_{volatile} liquid components, equation (1) represents N_{volatile} equations in N_{volatile} unknowns (the j_{iv} for the volatile liquid components) and hence may be solved using a suitable numerical algorithm. The solution is expected to require special care due to the logarithmic singularity as $y_i \rightarrow \varphi_i$ (also $y_{ia} \rightarrow \varphi_i$).

The molar transport coefficient, k_m is given by Brighton's model. The specification below follows that in [17]:

$$k_m = u_* [\kappa / \sigma] [1 + n_{\text{wind}}] G(e^\lambda)$$

with

$$\lambda = n_{\text{wind}}^{-1} + 2 + \ln [2(1 + n_{\text{wind}})^2] - \gamma + [\kappa / \sigma] [1 + n_{\text{wind}}] \beta(\text{Sc})$$

$$\beta(\text{Sc}) = 7.3 \text{Re}_0^{1/4} \text{Sc}^{1/2} - 5\sigma \quad \text{smooth pool surface}$$

$$\beta(\text{Sc}) = (3.85 \text{Sc}^{1/3} - 1.3)^2 + [\sigma / \kappa] \ln(0.13 \text{Sc}) \quad \text{rough pool surface}$$

and

$$G(e^\lambda) = \frac{1}{2} - [g_0/\pi] \arctan(\lambda/\pi) + g_1/(\lambda^2 + \pi^2) + g_2\lambda/(\lambda^2 + \pi^2)^2 + g_3(\lambda^2 - \pi^2/3)/(\lambda^2 + \pi^2)^3$$

with

$$\begin{aligned} g_0 &= 1 \\ g_1 &= 1 - \gamma \\ g_2 &= 1 + (1 - \gamma)^2 + \pi^2/6 \\ g_3 &= (1 - \gamma)^3 + (3 + \pi^2/2)(1 - \gamma) - 2\zeta(3) \end{aligned}$$

ζ is the Riemann zeta function and γ is Euler's constant.

The index n_{wind} which best approximates a logarithmic profile over the pool is given by

$$1/n_{wind} = N\left(\left[A_L^{1/2}/z_0 \left[\kappa^2/\sigma\right] e^{-(1+\gamma)}\right]\right)$$

where $N(X)$ is a function given implicitly by

$$N.e^N = X.$$

3.9.3 Sublimation of volatile components from the pool

Sublimation of volatile components from the frozen pool is calculated as for vaporisation from the liquid pool. Only the free surface (not covered by overlying liquid) is assumed to sublime.

This approach will overestimate the sustainable vapour evolution since it assumes that vaporisation is limited by transport away from the pool surface by atmospheric diffusion, rather than being limited by diffusion in the frozen solid, as is more likely to be the case.

3.10 HEATING OF THE LIQUID POOL

Rate of change of enthalpy of liquid pool:

$$\dot{H}_p = \dot{H}_{p,add} + \dot{H}_{p,react} - \dot{H}_{p,evol} + \dot{H}_{p,cond} + \dot{H}_{p,rad} + \dot{H}_{p,conv}$$

The change in enthalpy due to freezing of the pool is not included in the above. This is because when the pool temperature reaches the freezing point the liquid pool is assumed to instantaneously freeze. This will require the ODE solver to be stopped at this point and restarted, with the initialisation of the frozen pool accounting for the enthalpy change on freezing.

Each of the remaining terms is specified below:

3.10.1 Added material

Enthalpy change due to material added

$$\dot{H}_{p,add} = \dot{N}_{AX,p} h_{m,AXL}(T_{spill}) + (\dot{N}_{w,surface} + \dot{N}_{w,subst}) h_{m,wL}(T_{ground}) + \dot{N}_{w,atmos} h_{m,wv}(T_a)$$

where

$h_{m,iL}(T)$ is the molar specific enthalpy of component i in the liquid phase at temperature T

$h_{m,iv}(T)$ is the molar specific enthalpy of component i in the vapour phase at temperature T

Note, implicitly all enthalpies are relative to the enthalpy at a reference temperature T_{ref} .

3.10.2 Reaction

The rate of heat addition due to the reaction with water and substrate compounds is calculated as described in Sections 3.6 and 3.7 respectively. All the heat of reaction is assumed to go directly into the liquid pool.

3.10.3 Vapour Evolution

The enthalpy change due to vapour evolution from the liquid pool is written as

$$\dot{H}_{p,evol} = \dot{H}_{p,evap} + \dot{H}_{p,gas}$$

The enthalpy of vaporisation of volatile liquid components is given by

$$\dot{H}_{p,evap} = \sum_i \dot{N}_{i,evap} \Delta H_{m,i,evap}(T_p)$$

with

$\dot{N}_{i,evap}$ the rate of vaporisation of component i , calculated according to Section 3.9.2

$\Delta H_{m,i,evap}(T_p)$ the molar enthalpy of vaporisation of component i at temperature T_p

and the enthalpy of gas directly evolved (as a result of chemical reaction) is given by

$$\dot{H}_{p,gas} = \dot{N}_{i,gas} h_{m,gas}(T_p)$$

with

$\dot{N}_{i,gas}$ the molar production rate of gaseous reaction product calculated according to Section 3.6.

$h_{m,gas}(T_p)$ the molar specific enthalpy of the gas at the pool temperature T_p .

3.10.4 Conduction

The heat conduction from the ground to the pool is calculated based on one-dimensional conduction, assuming a fixed ground temperature:

$$\dot{H}_{p,cond} = k_{ground} (T_{ground} - T_p) A_{p,ground}$$

Note, this is a simplification of the REACTPOOL approach in that the thermal resistance of the pool is neglected. This is based upon the assumption that convection in the liquid is efficient at transferring heat through the pool. This is regarded as a reasonable approximation, especially in light of REACTPOOL sensitivity studies.

In the presence of a solid film layer, the heat transfer coefficient is modified as described in [1].

3.10.5 Convection

Heat convection to the pool from the atmosphere is calculated from the vaporisation model by heat and mass transfer analogy:

$$\dot{H}_{p,conv} = k_h (T_a - T_p) A_p$$

where

$$k_h = \rho_a C_{pa} u_* [\kappa / \sigma] [1 + n_{wind}] G(e^{\lambda'})$$

$$\lambda' = n_{wind}^{-1} + 2 + \ln[2(1 + n_{wind})^2] - \gamma + [\kappa / \sigma] [1 + n_{wind}] \beta(\text{Pr})$$

with Pr being the Prandtl number.

3.10.6 Radiation

The additional heat flux per unit area due to solar radiation is provided as a user input to the model. This is multiplied by the exposed pool area A_p to give the heat addition rate to the liquid pool.

3.11 HEATING OF THE FROZEN POOL

Rate of change of enthalpy of liquid pool:

$$\dot{H}_f = -\dot{H}_{f,evol} + \dot{H}_{f,cond} + \dot{H}_{f,rad} + \dot{H}_{f,conv}$$

The enthalpy change on melting is not included in the above since, as for freezing of the liquid pool, the melting of the frozen pool is assumed to occur instantaneously, with the initialisation of the melted pool accounting for the enthalpy change of fusion.

Each of the remaining terms is specified below:

3.11.1 Vapour Evolution

The enthalpy change due to vapour evolution from the solid pool is given by

$$\dot{H}_{f,evol} = \sum_i \dot{N}_{i,sublim e} \Delta H_{m,i,sublim e}(T_f)$$

with

$$\Delta H_{m,i,sublim e}(T_f) \text{ the molar enthalpy of sublimation of component } i \text{ at temperature } T_f$$

3.11.2 Conduction

The heat conduction from the ground to the frozen pool is calculated based on one-dimensional conduction, assuming a fixed ground temperature:

$$\dot{H}_{f,cond} = k_{ground} (T_{ground} - T_f) A_f$$

3.11.3 Convection

Heat convection to the frozen pool from the atmosphere is calculated from the vaporisation model by heat and mass transfer analogy:

$$\dot{H}_{f,conv} = k_h (T_a - T_f) A_{f,air}$$

where

$$k_h = \rho_a C_{pa} u_* [\kappa / \sigma] [1 + n_{wind}] G(e^{\lambda'})$$
$$\lambda' = n_{wind}^{-1} + 2 + \ln[2(1 + n_{wind})^2] - \gamma + [\kappa / \sigma] [1 + n_{wind}] \beta(\text{Pr})$$

with Pr being the Prandtl number.

3.11.4 Radiation

The additional heat flux per unit area due to solar radiation is provided as a user input to the model. This is multiplied by the exposed frozen pool area $A_{f,air}$ (the liquid is assumed to be opaque in REACTPOOL) to give the heat addition rate to the frozen pool.

3.12 INITIALISATION

The initialisation of the model from the input conditions is described below.

3.12.1 Instantaneous Spill

An instantaneous spill is initialised from the following inputs

$$M_{AX,0} \quad \text{initial mass of water reactive chemical spilt}$$
$$R_0 \quad \text{initial radius of spill}$$
$$T_0 \quad \text{initial spill temperature}$$

In the case of an instantaneous spill, the initial radial velocity is assumed to be zero.

The instantaneous spill is assumed to react instantaneously with the free surface water within the initial pool radius. The resultant pool composition is determined, together with the heat of reaction. The pool temperature is determined from a heat balance on the pool accounting for the heat of reaction. If the predicted temperature exceeds the boiling point, then a (multi-component) flash calculation (enthalpy balance and vapour-liquid equilibrium) is required to determine the quantity of volatile liquid that is instantaneously vaporised together with the post flash pool composition and temperature.

3.12.2 Continuous Spill

Initialisation for a continuous spill is more straightforward. The continuous spill is initialised from the following inputs

- $\dot{m}_{AX,0}$ initial mass release rate of water reactive chemical spilt
- R_0 initial radius of spill
- T_0 initial spill temperature

The initial pool radial velocity is set equal to the liquid discharge velocity and the initial pool depth is set to half the initial pool radius.

3.13 MODEL INPUT AND OUTPUT

Table 2 summarises the typical user input data that would be required for the model.

Table 2 Input data defining the spill scenario

<i>Input</i>	<i>Units</i>	<i>Description</i>
Substance		Selection of the water reactive chemical to be modelled
Release type		Specification of whether the spill is instantaneous, steady continuous or time varying
Release mass	kg	Quantity of water reactive chemical released in instantaneous spill
Release rate	kg s ⁻¹	Rate of spillage for continuous spill
Initial pool radius	m	Initial radius of the pool
Release temperature	K	Temperature of the released substance
Substrate		Selection of the substrate on which the spill occurs
Free surface water depth	m	Free surface water volume per unit area
Puddle depth	m	Volume per unit area held up in puddles (to limit spreading)
Windspeed	m/s	Wind speed at reference height
Windspeed reference height	m	Reference height used for windspeed
Ambient temperature	K	Air (and initial ground) temperature
Relative humidity	%	Relative humidity of the ambient air
Roughness length	m	Aerodynamic roughness length characterising the wind speed profile
Additional heat flux	W m ⁻²	Additional heat flux into pool due to solar radiation
Maximum pool radius	m	Restriction on pool radius e.g. due to bunding
Maximum time	s	Maximum time (from release) over which to calculate the pool evolution

Typical output from the model (in tabular and graphical form) that may be required as a function of time is summarised in Table 3.

Table 3 Output data from modelling a spill scenario

<i>Output</i>	<i>Units</i>	<i>Description</i>
Liquid pool mass	kg	Mass of liquid pool
Liquid pool radius	m	Radius of liquid pool
Liquid pool depth	m	Average depth of liquid pool
Liquid pool composition		Composition (e.g. mol/mol) of liquid pool
Liquid pool temperature	K	Temperature of liquid pool
Liquid pool boiling temperature	K	Boiling temperature of the liquid pool
Liquid pool freezing temperature	K	Freezing temperature of the liquid pool
Vapour evolution rate	kg/s	Rate of evolution of vapour from liquid and solid (subliming) pool
Vapour composition		Composition of the evolved vapour
Frozen pool mass	kg	Mass of frozen pool
Frozen pool radius	m	Radius of frozen pool
Frozen pool depth	m	Depth of frozen pool
Frozen pool composition		Composition of frozen pool
Frozen pool temperature	K	Temperature of frozen pool

3.14 SUBSTRATE PROPERTIES

The REACTPOOL reports only give limited information on the standard substrates used by the model (substrate types listed in Table 1). It will therefore be necessary to review the literature to obtain estimates for the following properties:

- water content
- permeability
- density
- thermal conductivity
- calcium carbonate content.

3.15 SUBSTANCE PROPERTIES

As indicated in Section 2.14, there are omissions for some substance properties. It will therefore be necessary to review these and search the literature to obtain estimates. Also, it will be necessary to smooth out the discontinuities present in the SO₃/oleum property correlations and check for consistency between correlations for vapour pressure and correlations for boiling point.

Uncertainty regarding the heat of reaction with excess water may place restrictions on the use of the model. This should be reviewed.

4 CONCLUSIONS

The work presented in this report concerns reviewing the REACTPOOL reports and writing down a mathematical model as input to the specification for a new computational model.

During the course of reviewing the REACTPOOL reports a number of mainly minor omissions have been identified and noted. Areas where the modelling might be improved have also been suggested. Based upon the review findings, a new pool model has been specified. This new model is closely based upon REACTPOOL, but differs in several respects, including:

- improvement of the REACTPOOL computational approach,
- use of a better founded spreading model,
- simplification of the sub-models for heat transfer by conduction from the ground and by net radiation.

5 NOMENCLATURE

<i>symbol</i>	<i>unit</i>	<i>description</i>
AX		water reactive chemical
A_p	m^2	top area of liquid pool surface
$A_{p,ground}$	m^2	area of liquid pool exposed to ground
A_f	m^2	top area of frozen pool surface
$A_{f,air}$	m^2	area of frozen pool exposed to air
B		possible liquid product of reaction
C		possible solid product (soluble or insoluble)
C_{pa}	$J\ kg^{-1}K^{-1}$	specific heat capacity of air
g	ms^{-2}	acceleration due to gravity
h_p	m	pool depth
h_e	m	pool depth above puddle depth
$h_{w,surface}$	m	depth of free surface water
h_{min}	m	minimum pool depth in REACTPOOL
h_{puddle}	m	puddle depth used to restrict spreading
$h_{m,iv}$	$Jmol^{-1}$	molar specific enthalpy of vapour component i
$h_{m,iL}$	$Jmol^{-1}$	molar specific enthalpy of liquid component i
HX		acid generated by reaction
H'	m	depth over which water vapour is extracted from air
H_p	J	total enthalpy of liquid pool
$H_{pool}(T)$	J	enthalpy of the pool as a function of temperature
H_f	J	total enthalpy of frozen pool
$\dot{H}_{p,add}$	W	rate of addition of heat to liquid pool due to spilled material
$\dot{H}_{p,react}$	W	rate of addition of heat to liquid pool due to chemical reaction
$\dot{H}_{p,evol}$	W	rate of loss from liquid pool due to vapour evolution
$\dot{H}_{p,cond}$	W	rate of addition of heat to liquid pool due to heat conduction (from ground or frozen pool)
$\dot{H}_{p,rad}$	W	rate of addition of heat to liquid pool due to thermal radiation
$\dot{H}_{p,conv}$	W	rate of addition of heat to liquid pool due to convection from the atmosphere
$\dot{H}_{f,evol}$	W	rate of loss from frozen pool due to vapour evolution (sublimation)
$\dot{H}_{f,cond}$	W	rate of addition of heat to frozen pool due to heat conduction (from ground or liquid pool)
$\dot{H}_{f,rad}$	W	rate of addition of heat to frozen pool due to thermal radiation
$\dot{H}_{f,conv}$	W	rate of addition of heat to frozen pool due to convection from the atmosphere
$j(s)$		function of shape parameter s , used in calculating pool spreading on land (Section 3.8.1)

symbol	unit	description
j_{iv}	$\text{mol}\cdot\text{m}^{-2}\text{ s}^{-1}$	molar flux of vapour component i from pool surface per unit area
j_{tv}	$\text{mol}\cdot\text{m}^{-2}\text{ s}^{-1}$	total molar flux of vapour from pool surface per unit area
k_m	ms^{-1}	molar transport coefficient
k_h	$\text{Wm}^{-2}\text{K}^{-1}$	heat transport coefficient
k_{subst}	ms^{-1}	permeability of liquid through substrate
$k_{subst,w}$	ms^{-1}	permeability of water through substrate
l	m	depth of penetration into substrate
M_p	kg	mass of liquid pool
M_{AX}	kg	mass of water reactive chemical
M_f	kg	mass of frozen pool
$M_{m,i}$	kg/mol	molar mass of component i
N	mol	number of moles
$\dot{N}_{i,spill}$	mol s^{-1}	spill rate of component i
$\dot{N}_{i,evap}$	mol s^{-1}	vaporisation rate of component i
$\dot{N}_{i,react}$	mol s^{-1}	reaction (removal) rate of component i
$\dot{N}_{i,prod}$	mol s^{-1}	production rate (due to chemical reaction) of component i
$\dot{N}_{i,layer}$	mol s^{-1}	deposition rate to layer of component i
$\dot{N}_{w,avail}$	mol s^{-1}	rate of addition of water from all sources
$\dot{N}_{w,atmos}$	mol s^{-1}	rate of addition of water from atmosphere
$\dot{N}_{w,surface}$	mol s^{-1}	rate of addition of free surface water
$N_{volatile}$	-	number of volatile liquid components
$n_{c,subst}$	mol m^{-3}	number of moles of reactive compound (e.g. calcium carbonate) per m^3 of substrate
$n_{w,subst}$	mol m^{-3}	number of moles of available water per m^3 of substrate
n_{wind}	-	wind profile index
p	-	percentage by mass of free SO_3 in the pool
P	Nm^{-2}	atmospheric pressure
P_{vi}^0	Nm^{-2}	pure substance vapour pressure for component i
P_{vi}	Nm^{-2}	substance vapour pressure for component i over the mixture
Pr	-	Prandtl number = kinematic viscosity / thermal diffusivity
R_p	m	liquid pool radius
R_f	m	frozen pool radius
R_m	$\text{Jmol}^{-1}\text{K}^{-1}$	universal molar gas constant
Re_0	-	roughness Reynolds number $Re_0 = u_* z_0 / \nu_a$
s	-	pool shape parameter (used in spreading model)
Sc	-	Schmidt number = kinematic viscosity / mass diffusion coefficient
t	s	time from start of spill
T_a	K	air temperature

<i>symbol</i>	<i>unit</i>	<i>description</i>
T_p	K	liquid pool temperature
T_{ground}	K	ground surface temperature
U_p	ms^{-1}	radial velocity at edge of liquid pool
U_f	ms^{-1}	radial velocity at edge of frozen pool (= 0)
u_*	ms^{-1}	atmospheric friction velocity above the pool
$V_{m,iL}$	$\text{m}^3 \text{mol}^{-1}$	liquid molar volume of component i
$V_{m,iv}$	$\text{m}^3 \text{mol}^{-1}$	vapour molar volume of component i
$\dot{V}_{p,spill}$	$\text{m}^3 \text{s}^{-1}$	volumetric rate of spillage
$V_{substrate}$	m^3	volume of substrate penetrated by liquid pool
$x(p)$		moles SO_3 reacted with one mole water (see Section 2.2.1)
x_i	mol/mol	mole fraction of component i in the liquid pool
y_i	mol/mol	mole fraction of vapour component i immediately above the pool surface
z_0	m	aerodynamic roughness length of the pool
<i>Greek</i>		
ΔH_{rxn}	various units (see text)	enthalpy of hydrolysis
\mathcal{E}		parameter relating to spreading over rough land (see Section 3.8.1)
γ	-	Euler's constant
κ	-	von Karman constant (= 0.4)
γ_i	-	activity coefficient for vapour pressure of component i above the liquid mixture
λ_{st}	m	surface tension minimum depth
λ_v	m	viscosity minimum depth
ϕ_i		= j_{iv} / j_{iv}
ν_a	$\text{m}^2 \text{s}^{-1}$	kinematic viscosity of air
ν_p	$\text{m}^2 \text{s}^{-1}$	kinematic viscosity of pool liquid
ν_w	$\text{m}^2 \text{s}^{-1}$	kinematic viscosity of water liquid
ρ	kg m^{-3}	Density
ρ_a	kg m^{-3}	density of air
$\rho_{L,mix}$	kg m^{-3}	density of the liquid mixture
σ		turbulent Schmidt number (taken to be 0.85)
σ_p		surface tension of the pool liquid
ζ		Riemann zeta function
<i>subscripts</i>		
0		initial condition
a		relating to air or ambient value
f		relating to frozen pool
i		relating to i^{th} component
L		relating to liquid phase

<i>symbol</i>	<i>unit</i>	<i>description</i>
p		relating to liquid pool
v		relating to vapour phase
<i>superscripts</i>		
0		pure substance property
.		differential with respect to time

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