



REACTPOOL: a code implementing a new multi-compound pool model that accounts for chemical reactions and changing composition for spills of water reactive chemicals

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Abstract

All chemicals that react violently with water or in contact with water liberate toxic gas are included in the list of substances covered by the majority of the international legislation on major hazards. This category includes a large number of chemicals that are used widely in the process industries. A survey of accidents that occurred in the last 10 years in the USA shows numerous major incidents that involved spillages of these substances. Even so, there are almost no experimental data on the behaviour of these chemicals on release. Furthermore, there are very few published studies on modelling the behaviour of such spillages, except in the case of hydrogen fluoride. In previous work we reported a new theoretical model [J. Haz. Mat. 62 (1998) 101–129, J. Haz. Mat. 62 (1998) 131–142, J. Haz. Mat. A67 (1999) 9–40], that describes accidental spills of SO₃ and oleum, which are substances with very complex behaviour that belong to this category. It describes both the pool [J. Haz. Mat. 62 (1998) 101–129, J. Haz. Mat. 62 (1998) 131–142] and the cloud behaviour [J. Haz. Mat. A67 (1999) 9–40]. In the work reported here the pool model was modified in a generic form in order to include other water reactive chemicals. REACTPOOL is a new code that can be used for both instantaneous and continuous liquid releases under a wide range of input parameters (steady or varying). It can be used for all liquids irrespective of their volatility and reactivity, and it describes pools consisting of more than one liquid that can have changing composition and properties. The purpose of this paper is to present the general procedure followed in REACTPOOL and to show how the new model has been modified and implemented for substances other than SO₃ and oleum. The modelling procedure has been implemented in a computer code written in Visual Basic, and results of the model have been generated using this code. It should be noted that this model requires

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validation data, but that the availability of such data awaits the performance of suitable experimental investigations. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Most existing pool models deal with pools that either boil or evaporate and which consist of one component with constant composition and properties. Some models can deal with multi-component pools of constant composition. Although this description is adequate for many chemicals, it cannot satisfactorily describe aggressive and reactive chemicals, e.g. water reactive substances. Furthermore the possibility of solidification is widely ignored in most models. REACTPOOL is a new code that can describe all liquids and can be used for chemicals with extremely complicated behaviour, such as water reactive substances.

Water reactive chemicals are generally aggressive materials with complicated properties. The hazardous nature of these substances is recognised in various items of legislation relating to industrial safety. Under the new Seveso II EU Directive, all substances that attract the risk phrases R14 'reacts violently with water' (including R14/15) or R29 'in contact with water, liberates toxic gas' are described as major hazards and are included in the list of chemicals covered by this Directive [1], which was implemented in the UK as the COMAH Regulations in 1999 [2].

A survey of accidents that occurred in the USA between January 1990 and November 1999 was conducted and its results are summarised in Table 1. With the exception of aluminium chloride, the rest of the chemicals listed are in liquid form at ambient conditions.

Table 1
Accidents that involved spills of water reactive chemicals that occurred in the USA in the last 10 years [6–9]

Chemical	Number of incidents	Number of hazardous incidents	Number of injuries	Number of deaths
TiCl ₄	473	13	13	–
SO ₃	206	14	59	–
Oleums	70	4	4	–
AlCl ₃	23	1	1	–
PCl ₃	18	3	8	–
BCl ₃	16	2	–	–
CH ₃ Cl ₃ Si	16	2	6	–
POCl ₃	14	5	144	–
SOCl ₂	12	2	17	–
HSO ₃ Cl	11	–	–	2
SiCl ₄	8	4	7	–
S ₂ Cl ₂	7	–	–	–
SCL ₂	5	–	–	–
SiHCl ₃	4	3	158	–
BBr ₃	4	–	–	–
CH ₃ COCl	2	1	–	–
Total	889	54	417	2

It should be noted that the third column in Table 1 corresponds to accidents where injuries or evacuations or deaths were reported and are described here as ‘hazardous incidents’.

In some accident reports, data on number of people evacuated, number of injuries, etc., were not known. Thus, it is probable that the number of incidents that involve evacuations or injuries is higher than indicated in Table 1. The table shows that there were more than 85 accidents per year in the USA alone involving spillages of these substances, and more than five of them involve evacuation and/or injuries. Two deaths were reported in a silicon tetrachloride accident that occurred in 1998 [3]. Titanium tetrachloride [4] and phosphorus oxychloride [5] were also reported to have caused fatal accidents (in Europe).

The toxicity and the effects of water reactive materials on humans and on the environment are highly variable, depending not only on their properties, but also on the properties of their products on reaction with water or the atmosphere or the substrate.

In cases where these substances are stored, transported or used in their liquid form, spillage will create a liquid pool, usually on land (in most cases they are transported by road or rail tankers). The spreading liquid will react with any free water lying on the ground and will also extract any water present in the substrate. Depending on its properties it may absorb atmospheric moisture. It may also react with compounds present in the substrate. The reaction with water is usually highly exothermic, providing the pool with energy, raising the liquid temperature and its vapour pressure and thus increasing the vapour evolution rate. Depending on the pool temperature and the boiling and freezing points of the liquid, the pool may boil or evaporate or even solidify. The products of the reaction may be directly evolved (in cases where a product is generated in its gas phase) or be present in the pool in liquid form and thence evaporate. Hydrolysis products formed in the pool may be soluble or insoluble in the liquid pool. If insoluble they can either be suspended in the liquid or settle onto the bottom of the pool forming a film.

The core of REACTPOOL is based on the model developed for accidental releases of SO_3 and oleum ([10]; see also [11–15]). These substances have very complicated behaviour, since they usually create a liquid pool with changing composition and properties and may boil or evaporate or even solidify depending on the conditions. Water is supplied to the pool from three sources: free liquid on the ground, the atmosphere and the substrate. They also react with some substrate compounds. The pool behaviour is governed mainly by the amount of water available for reaction.

REACTPOOL consists of the core code, which is identical for all substances and describes general features of the pool behaviour (spreading, evaporation or boiling or solidification, energy and mass balances). The core is a generalised version of that used for SO_3 and oleum spills, modified to account for substances that react with water in a different way than SO_3 and oleum. For each of the incorporated substances an individual module has been developed that describes the properties of the substance and its products on reaction with water, and other individual features.

It should be noted that REACTPOOL can be used for any chemical irrespective of its affinity for water.

A particular difficulty is that data on properties of many water reactive chemicals and their reaction with water are not well established. Furthermore, there are almost no experimental data on their source behaviour.

2. Water reactive chemicals

2.1. Identification

An extensive literature review has been conducted in order to identify water reactive chemicals of significance in major hazards. The main ones have been categorised as follows [16–20]:

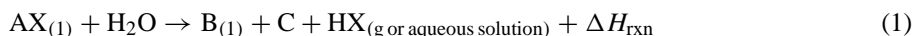
- inorganic acid halides, such as POX_3 , SOX_2 , SO_2X_2 ;
- organic halides, such as CH_3COX , CH_2COX ;
- sulphonic acids, such as HSO_3X ;
- halides of non-metals (mainly phosphorus-halogen, silicon-halogen and boron-halogen compounds), such as PX_3 , SX_2 , PX_5 , SiX_4 ;
- a number of silanes, such as HX_3Si , $\text{CH}_3\text{X}_3\text{Si}$;
- non-metal oxides, such SO_3 and oleum (mainly sulphur and phosphorus oxides);
- anhydrous metal halides, such as AlX_3 , TiX_4 , ZrX_4 , SnX_4 ;
- radioactive materials, such as UF_6 .

Most of the identified substances contain a halogen bond in their structure. The majority of water reactive chemicals are in the liquid phase at ambient conditions (AlX_3 , PX_5 and UF_6 are solids and fluorosilanes are vapours).

The Major Accident Hazards Bureau (MAHB) of the European Commission Joint Research Centre has published guidance documents for implementing Seveso II [21]. It should be noted that highly dangerous water reactive substances like PCl_3 , POCl_3 and AlCl_3 are not included in these guidance notes.

2.2. Reaction with water

The reactions of these chemicals with water are highly variable. The reaction products strongly affect the behaviour of the pool. The variety of products is shown by the following general reaction:



where AX is the water reactive chemical that contains a halogen X bond, B a possible liquid product, C a possible product (soluble or insoluble that may appear as a solid), HX the acid generated and ΔH_{rxn} the heat of hydrolysis.

In cases where at least one of the hydrolysis products is liquid (e.g. B), the pool will contain at least two liquids AX and B. The pool composition and properties will not be constant as AX continuously reacts with water producing B.

When a product C is formed, it could either be soluble or insoluble in the liquid. In the latter case, the solid particles may either settle or be suspended in the pool depending on the pool features and the characteristics of the solids, such as their size distribution and density. In cases of a soluble hydrolysis product and if the pool is not saturated all the pool characteristics change continuously. A new procedure has been developed to account for these changes as the SO_3 /oleum model did not account for such phenomena since no C hydrolysis products were involved.

In all cases, when the water reactive chemical contains a halogen bond, acid HX will be formed. The phase of this acid is strongly determined by the amount of water available for reaction. If water is in excess a liquid aqueous solution of this acid is usually generated. If water reactive chemical AX is in excess, HX will be directly evolved to the atmosphere as a gaseous product. Details of various hydrolysis reactions are to be found in a number of references [22–26]. Of particular interest here are the ones used in the companion papers covering the use of REACTPOOL for chlorosulphonic acid [27], silicon tetrachloride [28], phosphorus trichloride and oxychloride [29]. Details are given in these papers. Most of these reactions are rapid, complete and exothermic.

3. REACTPOOL model description

Phenomena taken into account are depicted in Fig. 1.

3.1. Core of the modelling procedure

The core of the model is identical for all substances and describes phenomena, such as pool spreading, vapour evolution, mass and energy balances, reaction with water, etc. It consists of different sub-models that describe different features of the behaviour of the liquids.

3.1.1. Pool spreading

The spreading behaviour of the pool is described by differential equations that are based on the principles of mass, momentum and energy conservation [30,31]. In cases of instantaneous spills, spreading Eqs. (1)–(3) in reference [10] are used to calculate the pool radius. For continuous spills Eqs. (4)–(8) in reference [10] are used. In both cases, the pool spreads until it reaches a minimum layer thickness (h_{\min}); it then shrinks as the volume decreases due to evaporation and the pool depth remains constant at h_{\min} [10].

Many of the available pool models that describe the spreading behaviour by algorithms that make use of the minimum layer thickness on a surface, disregard the significance of variations of this parameter, setting it at a constant value for any type of surface.

Overall, the minimum layer thickness has a very strong effect on the pool radius. When the pool depth h , reaches the value of the minimum layer thickness (h_{\min}), spreading ceases,

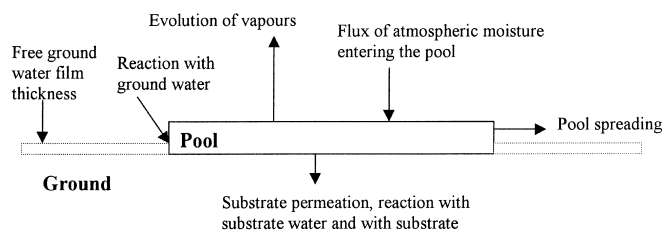


Fig. 1. Phenomena taken into account in the model (some dimensions are exaggerated).

unless the rate of mass entering the pool is higher than the mass efflux, in which case spreading continues at $h = h_{\min}$. The mass entry rate is the sum of the spill rate plus the mass rate of addition from other sources (e.g. addition of water). The mass efflux rate is the mass evolution rate plus the mass rate of any other loss (e.g. production of solids that are insoluble in the liquid medium) (see also Appendix A).

The value of h_{\min} is determined by the physical surface roughness (this term is used to distinguish it from the aerodynamic roughness length, z_0). It is suggested in other work that a minimum value of 5 mm should be applied in cases of extremely smooth surfaces. For rougher surfaces, the value can be as large as a few centimetres [30]. Unfortunately, there is no experimentally based correlation that relates the value of the minimum layer thickness with the physical surface roughness. In the absence of better information, the recommendations of the previous work [30] are adopted here, and h_{\min} is taken to be within the range 5 mm–5 cm. The value used in REACTPOOL is selected by the user.

3.1.2. Availability of water

The amount of water available for reaction is determined by estimating the amount available from each source. In all cases, water reactive chemicals will encounter free ground water and will extract substrate water. Most will also absorb atmospheric moisture. All these sources are modelled according to Section 2 in reference [10] (see also [13,32,33]).

3.1.3. Reaction with the substrate

Water reactive materials are usually highly aggressive and can react with some of the components of any type of substrate (e.g. in the case of a concrete surface on which SO_3 /oleum or chlorosulphonic acid is spilled H_2SO_4 reacts exothermically with calcium hydroxide [34]). These possible reactions are modelled according to Section 2.2.3 in reference [10].

3.1.4. Energy balance

An energy balance that takes into account all the significant energy sources is implemented to calculate the pool temperature in each time step. This energy balance expands some ideas previously reported [35] by incorporating energy sources that are significant for water reactive chemicals. The following sources are taken into account in cases of evaporation (see Section 2.5 in reference [10]):

- energy of reaction with water;
- evaporation energy;
- energy of addition (to allow for the difference in temperature between the spill liquid and that already in the pool);
- net solar radiation;
- long-wave radiation from the atmosphere;
- long-wave radiation emitted by the pool;
- sensible heat transfer between the ground and the pool;
- conduction of heat from the ground;
- heat of reaction between chemical and substrate.

The energy balance is modified for boiling or solidification as shown in Sections 2.7 and 2.8 in reference [10].

3.1.5. Evaporation model

In cases where the pool temperature is within the range set by the boiling and freezing points, the pool evaporation rate is calculated by Brighton's model [36]. This analytic model takes into account effects of surface roughness, friction velocity of the airflow and high vapour pressure on the mass transfer process (for details see Section 2.6 in reference [10]).

3.1.6. Boiling

In cases where the heat balance is such that the pool boils, its temperature is set equal to the boiling point and any excess heat is used in the vaporisation process. The possible boiling point difference between successive time steps is taken into account in a modified energy balance (compared to the one shown in Section 3.1.4) (for details see Section 2.6 in reference [10]).

3.1.7. Solidification

In cases where the heat balance is such that the pool temperature falls to the freezing point, the pool solidifies. Depending on whether spreading has ceased two cases are encountered; solidification before and after spreading ceases. The former case is the most complicated one as there would be a newly spilled liquid pool on top of a solid phase and between these two layers there would be a temperature difference. The free solid area will sublime (see Section 2.8 in reference [10]).

Detailed descriptions of the above sub-models can be found elsewhere ([10]; see also [11–15]). In this paper the main modifications and additions to the SO₃/oleum model are described in detail. Some modifications are listed in Appendix A. Reaction of the chemical with water has been incorporated into the core model in a general form, that accounts for all possible scenarios as described in Sections 3.2–3.4. Three different cases are encountered depending on whether liquid or solid or gas products are formed.

3.2. Liquid hydrolysis product

When at least one liquid is formed from the hydrolysis reaction, the liquid pool will contain at least two liquids; water reactive chemical AX and liquid product B. As the reaction of the chemical with water proceeds, chemical AX will continuously yield B. Therefore, the liquid composition and properties will change. All the pool properties are assumed to be dependent on the mole fractions of the liquids present [37,38]. For example density will be given from the following:

$$\rho_1 = X_{AX}\rho_{AX} + X_B\rho_B \quad (2)$$

where ρ_1 (kg m⁻³) is the density of the mixture of liquids in the pool, ρ_{AX} (kg m⁻³) the density of water reactive chemical AX and ρ_B (kg m⁻³) the density of product B. X_{AX} and X_B are the mole fractions of components AX and B, respectively.

Apart from AX (which is usually volatile), liquid B may also evolve from the pool depending on its volatility and the pool temperature. Given that the heat of reaction is generated mainly at the advancing edge of the spreading pool, it is to be expected that the pool will be warmer in this region than in its centre. Accordingly, the vapour pressure

of the reaction product-components would be higher towards the pool edge. The cooler region near the centre of the pool is rich in the water reactive component, which is usually more volatile than the products. Thus, there is some compensation between these effects, as discussed in an earlier paper (Section 4 of [11]). Information on the details of this complex relationship are not available for the situations modelled here. In the absence of a more realistic description the simple assumption adopted here is that Raoult's law applies. Thus, the vapour pressure of product B, P_B (atm) will be:

$$P_B = X_B P_B^0 \quad (3)$$

where P_B^0 (atm) is the vapour pressure of the pure component B.

The rest of the pool properties are calculated according to Eq. (2). If more than one liquid product is present, the pool will contain more than two components and its properties are then calculated according to the above scheme.

3.3. C hydrolysis product

Two different cases are encountered depending on whether the solid product of the hydrolysis reaction is soluble or insoluble in the pool liquid.

3.3.1. Soluble hydrolysis product

When the C product of the hydrolysis reaction (Eq. (1)) is soluble in the spilled liquid the following phenomena take place:

- boiling point elevation;
- freezing point depression;
- vapour pressure reduction.

In addition, if the pool is not saturated its density, viscosity, specific heat and thermal conductivity change continuously as long as the concentration of the soluble product C changes. These changes depend on the quantity of product C present in the liquid medium. They are calculated as functions of the molar fractions of the liquid and product C according to Eq. (2). As the pool spreads the quantity of product C increases. Depending on the amount present in the pool and other characteristics, the pool may reach its saturation point. From this point and onwards any excess will be precipitated. This scenario is investigated in Section 3.4.

The boiling point of a dilute solution of a non-volatile, non-dissociating solute is elevated compared to that of the pure solvent. For an ideal solution (a solution that follows Raoult's Law), the boiling point elevation ΔT_b is given by the following relationship [39]:

$$\Delta T_b = E_b m \quad (4)$$

where m is the molality and E_b the ebullioscopic constant, a characteristic property of the solvent which can be calculated from the following equation [39]:

$$E_b = \frac{RT_b^2 M}{\Delta H_{\text{vap}}} \quad (5)$$

where R is the molar gas constant, M the molar mass of the solvent and ΔH_{vap} the molar enthalpy of vaporisation of the solvent.

The freezing point of a dilute solution of a non-volatile, non-dissociating solute is depressed compared to that of the pure solvent. If the solution is ideal, the absolute freezing point depression is expressed as [37]:

$$\Delta T_f = E_f m \quad (6)$$

where E_f is the cryoscopic constant given from [39]:

$$E_f = \frac{RT_f^2 M}{\Delta H_{fus}} \quad (7)$$

where ΔH_{fus} is the molar enthalpy of fusion of the solvent.

The vapour pressure reduction ΔP for an ideal solution of a non-volatile solute is given by the following equation [37,38]:

$$\Delta P = P_1^0 x_2 \quad (8)$$

where P_1^0 is the vapour pressure of the solvent and x_2 is the molar fraction of the solute.

3.3.2. Insoluble hydrolysis product

Depending on the turbulence and thus the mixing in the pool and on the particle size distribution and density of the solid, the insoluble particles could either settle on the bottom of the pool or be suspended in the liquid pool.

In cases where there is a lack of turbulence in the pool, the solid particles may settle on the bottom forming a film. The solid film that is formed may change the rate of heat conduction from the ground. In these cases the equation that gives the overall heat transfer coefficient U_{grd} ($\text{kJ m}^{-2} \text{h}^{-1} \text{K}^{-1}$) (Eq. (43) in reference [10]) should be modified to include the resistance of heat transfer due to the presence of the solid film:

$$U_{grd} = \frac{1}{(1/h_{grd}) + (1/h_{liq}) + (1/h_{solids})} \quad (9)$$

where h_{liq} ($\text{kJ m}^{-2} \text{h}^{-1} \text{K}^{-1}$) is the heat transfer coefficient that accounts for the thermal resistance between the ground surface and the lower pool surface, h_{grd} ($\text{kJ m}^{-2} \text{h}^{-1} \text{K}^{-1}$) the heat transfer coefficient of the ground and h_{solids} ($\text{kJ m}^{-2} \text{h}^{-1} \text{K}^{-1}$) the heat transfer coefficient of the solid film, given from the following equation:

$$h_{solids} = \frac{k_{solids}}{d_f} \quad (10)$$

where k_{solids} ($\text{kJ m}^{-2} \text{h}^{-1} \text{K}^{-1}$) is the thermal conductivity of the solid particles and d_f (m) the depth of the film. Assuming uniform distribution of the solid particles on the bottom of the pool:

$$d_f = \frac{V_{solids}}{A} = \frac{M_{solids}}{\rho_{solids} \pi A} \quad (11)$$

where M_{solids} (kg) is the mass of the solid particles, ρ_{solids} (kg m^{-3}) the density of the solid and A (m^2) is the pool area.

If the particles are settled, the liquid pool properties will not be affected by their presence.

If the pool is turbulent the particles will be mixed throughout the liquid. Boiling will usually ensure that particles are suspended, affecting the liquid properties. All the pool properties change continuously as more particles are generated, until the liquid becomes saturated. The pool density ρ (kg m^{-3}) will be given from the following relationship:

$$\rho = \frac{M_p}{V_p} = \frac{M_1 + M_{\text{solids}}}{(M_1/\rho_1) + (M_{\text{solids}}/\rho_{\text{solids}})} \quad (12)$$

where M_p (kg) and V_p (m^3) are the mass and volume of the pool and M_1 (kg) and ρ_1 (kg m^{-3}) the mass and density of the liquid phase in the pool.

The specific heat C_p ($\text{kJ kg}^{-1} \text{K}^{-1}$) of the pool will be:

$$C_p = \frac{M_{\text{solids}}}{M_p} C_{ps} + \frac{M_1}{M_p} C_{pl} \quad (13)$$

For spherical particles at low concentrations, the relative viscosity μ_p/μ_1 (where μ_p ($\text{kg m}^{-1} \text{s}^{-1}$) is the viscosity of the pool and μ_1 ($\text{kg m}^{-1} \text{s}^{-1}$) is the viscosity of the liquid component) is related to the volume fraction φ of the particles according to the following equation [40]:

$$\frac{\mu_p}{\mu_1} = 1 + 2.5\varphi \quad (14)$$

The volume fraction of the solid particles in a liquid pool is calculated as follows [40]:

$$\varphi = \frac{(M_{\text{solids}}/\rho_{\text{solids}})}{(M_{\text{solids}}/\rho_{\text{solids}}) + (M_1/\rho_1)} \quad (15)$$

This description is strictly valid under conditions of infinite dilution where only single particle/medium interactions are important.

All the rest of the pool properties are calculated according to Eq. (2).

3.4. Gas or vapour hydrolysis product

In cases where product HX of reaction (1) is in its gas (or vapour) phase, it will evolve directly to the atmosphere. Depending on halogen X, toxic gases like HCl and HF may be produced. HX is produced in its gas phase usually when there is an excess of water reactive chemical AX. When water is in excess an aqueous solution of liquid HX is formed and is part of the liquid pool (see Section 3.2). The model encompasses both these regimes.

4. Calculation procedure-inputs and outputs

A simplified algorithm of the modelling procedure is depicted in Fig. 2. Modelling calculations are performed at small time increments. The user first selects which water reactive chemical is spilled. The code responds by loading its characteristics from the individual module. Every time step, δt (s), is split into three steps: the spill, the reaction and the evolution steps.

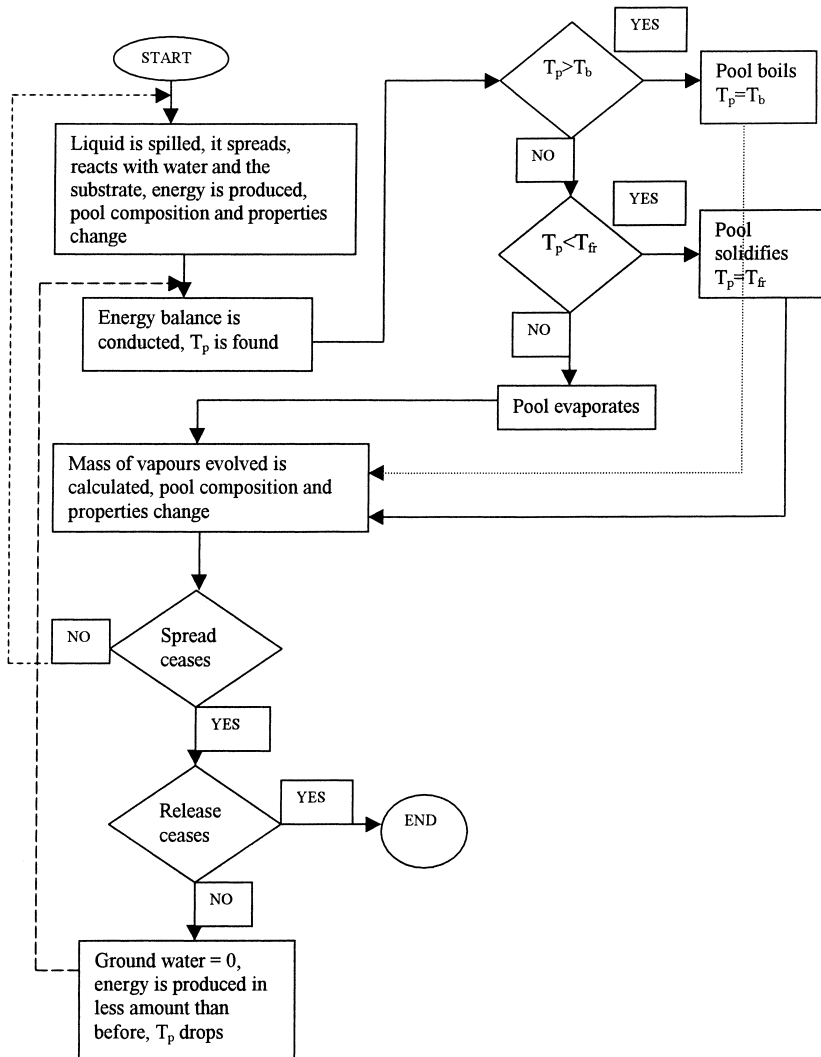


Fig. 2. Logical representation of the algorithm of the modelling procedure.

4.1. Spill

At the beginning of the time step the total quantity of liquid in the pool will be:

$$M_p = M_p + \delta t M' \quad (16)$$

The pool may consist of one or more liquid phases and it also may contain soluble solids or insoluble suspended particles. All the properties of the liquid (density, freezing point, boiling point, heat capacity, etc.) are calculated. The pool radius R (m) is calculated by

solving the spreading equations. For an instantaneous release, Eq. (1) of reference [10] is solved and for a continuous release, Eq. (8). The method followed to solve these equations is the fourth-order Runge–Kutta method, using a time increment of 0.01 s. After calculating the pool radius, the depth, h (m), and the surface area of the pool, A (m²), are calculated.

4.2. Reaction

Descriptions of this step requires the following questions to be answered for each water reactive chemical:

- Does the water reactive chemical absorb atmospheric moisture?
- Do any of the liquids react with components of substrates like concrete, asphalt or soil?
- Are solid particles produced?

If the answer to any of the above is positive, descriptions of the phenomena have to be provided. In view of the lack of any relevant data, it is assumed that if the pool absorbs atmospheric moisture, then the amount absorbed can be estimated in a way similar to that used to describe SO₃ and oleum pools (see Appendix A) [10]. In all cases, the pool will encounter free ground water while spreading and it will also extract substrate water, so that there will be at least two sources of water available for reaction.

The total mass of water available for reaction is calculated (Eqs. (9), (19) and (30) in reference [10]). If water is in excess, the mass of water that reacts will be equal to the amount required to consume all the available water reactive chemical. The heat of reaction is then calculated. At this stage the composition of the pool may change again (in cases where liquid, or soluble solid or insoluble suspended solid is generated). As a result of the composition changes the properties of the pool will change and they are recalculated. The values of all energy terms are found from the relevant equation (see Section 2.5 in reference [10]). The temperature of the pool is calculated by the trial and error method because there are several interrelated parameters that are dependent on the pool temperature.

4.3. Evolution

If the temperature is below the boiling point and above the freezing point the pool will evaporate and the amount evolved is calculated using Brighton's model [36]. If the pool boils, the amount evolved is calculated using Eq. (68) of reference [10]. In both these cases and if the pool contains more than one liquid (e.g. water reactive chemical AX and product B), liquid B may also evolve depending on its volatility and the pool temperature. In the case of solidification of the pool the procedure depends on whether solidification occurs before or after the spill ceases. The equations given in Sections 2.8.1 and 2.8.2 of reference [10], respectively, are solved and the quantity of water reactive chemical sublimed, is calculated. At the end of the time step, the composition of the pool changes again and all the properties of the pool are recalculated. If solidification has occurred the possibility of melting is checked. When the spill ceases, the pool stops spreading, and water will only be available from the atmosphere (in cases where the substance absorbs atmospheric moisture) and from the substrate. These calculation steps are repeated until either the whole quantity of water reactive chemical has been evolved, or the episode is terminated by emergency action intervention.

4.4. Model inputs

REACTPOOL has been provided with a user-friendly interface and all the necessary help and information on the spill behaviour.

The model inputs are:

- Substance spilled: there is a list of chemicals that have been incorporated into the model. Modules for additional chemicals are readily added.
- Type of spill: the user should define whether it is a continuous or instantaneous spill.
- Amount spilled in cases of instantaneous release (kg).
- Spill rate in cases of continuous releases (kg s^{-1}).
- Type of surface: whether it is concrete, or asphalt or soil of different types (see Appendix A).
- Wind speed at a reference height of 10 m (m s^{-1}).
- Roughness length of the substrate (m): this parameter determines the value of the minimum layer thickness as shown in Eq. (12).
- Location of the accident: defined by the longitude and latitude (degrees).
- Time of the accident (hours) and day number of the year that the accident occurred.
- Free ground water film thickness (m): free ground water is assumed to be present as a film and the average value of the film depth is used to estimate the amount of free ground water available for reaction. For wet ground conditions the value of this parameter should be higher than 0.002 m [32].
- Atmospheric relative humidity (%).
- Spill duration (s): for continuous releases it is the time at which the spill terminates. For instantaneous releases the value of this parameter is set equal to 10 s.
- Release duration (s): this is the time at which the pool ceases to release material to the atmosphere.
- Minimum layer thickness (m) (see also Section 3.1.1.): it is taken to be within the range 5 mm (extremely smooth surfaces)–5 cm (extremely rough surfaces).
- Maximum pool radius (m): this parameter accounts for the presence of confinement, such as the walls of a bounded area [30].
- Air temperature (K) and release temperature (K): in many cases these two temperatures will be equal.
- Cloud cover factor (tenths): this parameter is equal to 10 for total cloud cover and 0 for a clear sunny day.

It should be noted that the input parameters can either be steady or varying. In cases of varying input parameters the user defines the time varying function.

4.5. Model outputs

The model outputs appear both as a result report and in the form of graphic displays. The result report shows the average values of the pool features in three regimes: in the spreading period, in the period after spreading ceases and for the total release duration. Graphs of the pool characteristics as function of time show the changing characteristics of the pool. The time dependent model outputs are:

- pool radius (m);
 - pool temperature (K);
 - pool composition (in cases where two or more liquids are present);
 - for each species released to the atmosphere, the amount of vapour evolved (kg) and the vapour evolution rate (kg s^{-1});
 - boiling and freezing points (K).
- Other outputs are:
- spreading duration (s);
 - total release duration (s).

5. Clouds generated from spills of water reactive chemicals

In many cases, clouds generated from accidental spills of water reactive chemicals will contain more than one species. The water reactive vapour usually interacts with the atmospheric moisture, yielding either secondary vapour or aerosols or both, which may further interact with moisture. It has become common practice to model the dispersion of these chemicals in a simplified way, ignoring these reactions, or assuming that they are effectively complete at the instant of release from the pool into the atmosphere. In some cases, it has been assumed that in spite of these reactions, the generated cloud will behave as passive from its outset. As has been shown in the case of SO_3 and oleum spills, there is not usually enough atmospheric moisture in the flow over the pool for complete and instantaneous reaction. The generated cloud is usually denser than air, with several chemical and physical interactions taking place ([41]; see also [42,43]).

It is expected that accidental spills of water reactive chemicals will result in the generation of a cloud with complex behaviour with several processes occurring in it. Whether it will initially be denser than air or passive is a function of many parameters, such as the vapour evolution rates from the pool, the wind speed, the atmospheric stability, etc. It can be expected that in many cases the cloud behaviour would be similar to that generated from spillage of SO_3 /oleum. It is clear that each of these chemicals should be treated individually in respect of its spillage and dispersion behaviour.

6. Discussion, conclusions, recommendations

Water reactive chemicals are important substances in the field of major hazards and are included in many relevant items of international legislation. A number of major accidents have occurred that involved spillages of these materials. Some of these incidents have caused fatalities and serious injuries. None of the existing source models was judged to be satisfactory in describing the pool behaviour of accidental spills of water reactive substances.

REACTPOOL is an implementation of a new model that describes the pool behaviour of water reactive chemicals in a realistic way. It can incorporate any water reactive chemical and it can also be used for spills of non-reactive substances. Substances that have already been incorporated into the software are: sulphur trioxide and oleums, phosphorus trichloride, phosphorus oxychloride, silicon tetrachloride, chlorosulphonic acid and acetyl chloride.

The code is designed to facilitate the addition of further substances. Overall, REACTPOOL is very well behaved and its main advantages are:

- It describes the pool behaviour of water reactive chemicals in a realistic way taking into account the significant processes and interactions that occur in the liquid phase.
- Although the pool behaviour can be very complicated, calculation times are very satisfactory (usually <10 min on a Pentium II).
- It can be used for either instantaneous or continuous liquid spills, under a wide range of input parameters (steady or varying).
- The code is very easy to use, having a user-friendly interface and providing all the necessary help and information on the release behaviour.
- It can also be used for any liquid irrespective of its reactivity and volatility.

Model results indicate that the pool behaviour is principally affected by the way that the reaction of the chemical with water occurs, and by the amount of water available for reaction. Surface roughness and wind speed also have significant effects. The pool behaviour for the spreading period is different to that after spreading. The pool temperature is higher for the spreading period, and so are the vapour evolution rates since during this period there is more water available for reaction (free ground water is only available during the spreading period). Results of modelling for spills of a number of water reactive chemicals are presented in the companion papers [27–29] and in the earlier work on SO₃ and oleums [10,11].

The main difficulty in the modelling procedure is that properties and reactions of water reactive chemicals are not very well defined in the literature. Furthermore, although there are numerous accidents occurring every year, there are no experimental data on their release behaviour. Further improvement and validation of the model depends on the availability of these data.

Running the programme for different substances revealed the significance of their individual properties and features. It is concluded that this model constitutes a substantial advance in the modelling of clouds generated from spills of water reactive chemicals, where (except for modelling of HF spills) much of the current practice has been based on excessive use of simplifying assumptions. Future investigation will be aimed at the development of a dispersion model for water reactive chemicals that will include a general thermodynamic description of possible interactions that occur in such clouds. It should be noted that the main focus of such a project should be the development of the thermodynamic model.

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Appendix A

The changes made to the core model of REACTPOOL compared to the SO₃/oleum model are listed here.

A.1. Mass balances

The mass of water reactive chemical M_{AX} (kg) in the pool at each time step is:

$$M_{AX} = (M_{AX})_{\text{spilled}} - (M_{AX})_{\text{reacted}} - (M_{AX})_{\text{evolved}}$$

The mass of liquid B, M_B (kg) possibly produced by reaction 1 is:

$$M_B = (M_B)_{\text{generated}} - (M_B)_{\text{evolved}}$$

At each time step there may be solid particles and excess water present in the liquid pool.

A.2. Spreading equations

In spreading Eq. (8) of reference [10], for continuous spills, term S_1 (kg) represents the total mass loss of the pool, and is given by the following equation:

$$S_1 = (M_w)_{\text{reacted}} - (M_{AX})_{\text{evolved}} - (B)_{\text{evolved}} - (HX_g)_{\text{evolved}} - (C_s)_{\text{settled}}$$

where $(M_w)_{\text{reacted}}$ (kg) is the cumulative mass of reacted water, $(HX_g)_{\text{evolved}}$ (kg) is the cumulative amount of gas or vapour HX evolved directly to the atmosphere and $(C_s)_{\text{settled}}$ (kg) is the cumulative amount of particles settled on the bottom of the pool.

A.3. Atmospheric water

The flux of moisture entering the pool is modelled in a simple way assuming that all moisture content of the air from a height equal to the roughness length, up to a height H' (m) above the roughness length of the surface enters the pool. In reference [10] it has been assumed that (Eq. (17)):

$$H' = \frac{R}{30} \frac{p}{100}$$

where p is the % free SO_3 in the liquid. In the current approach this equation has been modified:

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

The effect of this change is that if only water reactive chemical is present in the liquid, H' will be equal to $R/30$.

A.4. Different types of surface

The following surfaces have been incorporated into the code:

- concrete;
- asphalt;
- soil (sandy, dry);

- soil (moist, 8% water, sandy);
- soil (average).

The user can choose any of these five types of substrate and the characteristics and properties (thermal conductivity, porosity, density, etc.) of each type are automatically loaded in the code. For each water reactive chemical an investigation should be conducted for identifying and describing possible reactions with any components of these five types of substrate.

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