

A model for spills of SO₃ and oleum Part I. Model description

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Received 5 March 1998; revised 3 June 1998; accepted 8 July 1998

Abstract

A new theoretical model describing spills of SO₃ and oleum and subsequent releases to the atmosphere of SO₃ and H₂SO₄ has been developed. SO₃ and oleum are aggressive materials which are used widely in the process industries, notably in the production of detergents, plastics and dyestuffs. On escape to the atmosphere, they create a H₂SO₄ mist which may cause serious damage to people and to the environment. Any humans or animals in contact with the mist suffer effects ranging from irritation of the airways to death, depending on the exposure. When spilled onto the ground, these substances create pools that can evaporate or boil or even solidify, depending on the conditions. The main feature of the pool behaviour is the violent exothermic reaction between SO₃ and water. In Part I, a description is given of the behaviour of the liquids in the pool, together with the associated modelling approaches. The model is based mainly on theoretical considerations, because although there are about two reported accidents per year in the USA and the UK taken together, there are almost no experimental data relevant to this modelling requirement. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: SO₃; Oleum; Spills

1. Introduction

SO₃ and oleum are aggressive materials whose major hazard potential comes from the clouds of H₂SO₄ mist produced when they escape from containment and are exposed to moisture. The potential to cause harm to people is recognised in the UK by

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the inclusion of SO_3 in the Notification of Installations Handling Hazardous Substances Regulations [1] and in the list of substances covered by the Control of Industrial Major Accident Hazards Regulations [2]. A recent report of the International Agency for Research on Cancer concludes that long-term occupational exposure to strong inorganic acid mists containing H_2SO_4 is carcinogenic to humans [3].

The only published attempts to model the overall behaviour of spills of SO_3 and oleum were conducted by Grint and Purdy [4], Singh et al. [5] and Kapias [6]. The earlier works [4,5], although they were satisfactory first steps, contained a number of gaps and were based on many simplifying assumptions. Kapias [6] introduced a number of improvements, but identified the need for further developments. The need for development of a new model was recognised in a recent monograph [7].

The majority of the experiments that have been conducted with sulphur trioxide or oleum have been designed to test the effectiveness of substances that are used to control such spillages. In 1978 and 1980, the Mond Division of ICI in collaboration with several other companies carried out a series of spillage trials at Porton Down in Wiltshire, UK [4,8]. The Du Pont Specialty Chemicals carried out field tests on mitigation methods for small spills of chlorosulphonic acid and oleum at the Liquefied Gaseous Fuels Spill Test Facility in NV, USA [9].

Accidental releases that have occurred also give an indication of the behaviour of spillages of SO_3 and oleum. A detailed description of them can be found elsewhere [4,6]. The level of detail in these reports is highly variable, limiting the usefulness of information as shown in the following case. One of the most serious accidents that has occurred was in Richmond, CA, USA, in July 1993. A leak of 97.5 tonnes over 90 min of 35% oleum occurred from a road tanker. The dispersion modelling report that has been prepared has revised the source estimate to 8 tonnes of SO_3 over 225 min [10]. The number of people who sought hospital treatment was variously reported to be between 2000 and 22 000 [7,10].

When SO_3 or oleum is spilled onto the ground, a highly exothermic and violent reaction between SO_3 and water takes place. The products of the reaction are H_2SO_4 and SO_3 . The volume of SO_3 that reacts per unit volume of water depends on the percentage free SO_3 in the pool [11]. The energy produced by the reaction increases the temperature of the pool and thus increases its evaporation rate. Depending on the pool temperature and composition (expressed as % free SO_3 in the pool) the liquid may boil (usually when there is high availability of water), and under different conditions (usually when there is low availability of water) it may solidify. The composition and the temperature of the liquid in the pool are not constant; they change continuously and so do all its properties such as the boiling and the freezing points. When the pool is created on a concrete surface, another exothermic reaction between H_2SO_4 and calcium hydroxide occurs [12]. The pool contains SO_3 , H_2SO_4 and water (when there is an excess of water). SO_3 and possibly H_2SO_4 vapour will evolve from the pool, the amount of which depends on the composition, the temperature and other characteristics of the liquid.

The most important parameter that governs the behaviour of the pool is the amount of water available for reaction. There are three sources of water: water present on the ground, water in the substrate (including that which is chemically bound in materials

such as concrete) and water coming from the atmosphere (SO_3 has such an affinity for water that it is able to take water from the atmosphere). Apart from SO_3 , which has a high vapour pressure, H_2SO_4 may also evolve under certain conditions (pool composition $< 35\%$ free SO_3 and pool temperature > 333 K) [13,14]. Two types of releases are modelled here: continuous (steady or varying) and instantaneous.

SO_3 vapour reacts with atmospheric moisture producing H_2SO_4 which further reacts with water in the atmosphere yielding H_2SO_4 aerosol. The dispersion behaviour of such a cloud is complicated by the fact that it is possible for the initial cloud to be denser than air [7].

2. Description of the models of phenomena that occur in the pool

2.1. Pool spreading

2.1.1. Instantaneous releases

For an instantaneous release, the liquid is considered as a cylinder that collapses. The principle of energy conservation gives [15]:

$$\frac{dR}{dt} = \sqrt{1.08 g (h_0 - h)} \quad (1)$$

where $R = R_0$ at $t = t_{\text{sp}}$ which is the time taken for the liquid to be spilled, and the pool depths h and h_0 are:

$$h = \frac{V}{\pi R^2} \quad (2)$$

$$h_0 = \frac{V_0}{\pi R_0^2} \quad (3)$$

The pool spreads until it reaches a minimum layer thickness (h_{min}) depending on the roughness of the substrate; the pool then shrinks as the volume decreases due to evaporation and the depth will remain constant at h_{min} . Shrinking of the area may also occur when the amount released is small and the time considered is large [15,16].

2.1.2. Continuous releases

For a continuous release, the liquid spread is given by [15,16]:

$$\frac{dR}{dt} = \sqrt{2 g (h - h_{\text{min}})} \quad (4)$$

The pool depth (or height) will be:

$$h = \frac{V}{\pi R^2} \quad (5)$$

where V (m^3) is the pool volume:

$$V = \frac{M_p}{\rho} \quad (6)$$

where M_p (kg) is the total mass of the pool and ρ (kg m^{-3}) is its density. The total mass of the pool at any time step is:

$$M_p = M't - S_1 \quad (7)$$

where M' (kg s^{-1}) is the spill rate of SO_3 , t (s) is the time since the spill started and S_1 (kg) is the cumulative quantity of SO_3 evolved since the start of the spill. The final spreading equation is:

$$\frac{dR}{dt} = \sqrt{2g \left(\frac{M't - S_1}{\rho\pi R^2} - h_{\min} \right)} \quad (8)$$

When $h = h_{\min}$ the spreading ceases unless the mass spill rate is greater than the mass evaporation rate, in which case spreading continues with $h = h_{\min}$. The shrinking pool case is described as for the case of an instantaneous release (Section 2.1.1)

It should be noted that the above spreading model is a simple theoretical model that does not incorporate effects of slopes, kerbs, drains, bunds or walls. The effect of bunds and walls as limits on pool size is incorporated into the model by introducing a maximum pool radius which accounts for these effects.

2.2. Water availability

There are three sources of water: water present on the ground, water coming from the atmosphere and water coming from the substrate.

2.2.1. Water present on the ground, M_{gw} (kg)

The mass of water available in each time step from that present on the ground is [4,7]:

$$M_{gw} = (\pi w_g 1000 (r^2 - r_1^2)) \quad (9)$$

where r (m) is the radius of the pool at the beginning of the time step t_n , r_1 (m) is the radius of the pool at the beginning of the time step t_{n-1} and w_g (m) is the thickness of the water film on the ground.

2.2.2. Atmospheric water, M_{aw} (kg)

SO_3 (or oleum) has such an affinity for water that it can even take water from the atmosphere [6]. In the absence of experimental data, a simple approximation for this flux is adopted. The moisture that enters the pool is calculated by integrating the atmospheric moisture content over the height range z_3 to H' . Considering the logarithmic windspeed profile:

$$u(z) = \frac{u_*}{\kappa} \ln \left(\frac{z}{z_0} \right) \quad (10)$$

and by taking an element of height increment dz , for a ‘tube’ of wind of width dy , the volumetric flow rate of the air, ΔV_a , through the element is:

$$\Delta V_a = u(z) dz dy \quad (11)$$

There is no y direction variation, so consider: $dy = 1$ m. By integrating over the height range z_3 to H' , and by using the standard result given by handbooks [17]:

$$\int (x^n \log(ax) dx) = \frac{x^{n+1}}{n+1} \log(ax) - \frac{x^{n+1}}{(n+1)^2} \quad (12)$$

where $n = 0$, $a = 1/z_0$ and $x = z$. So,

$$V_a = \frac{u_*}{\kappa} \int \ln\left(\frac{z}{z_0}\right) dz = \frac{u_*}{\kappa} \left[z \ln\left(\frac{z}{z_0}\right) - z \right]_{z_3}^H \quad (13)$$

Taking 10 m as the windspeed reference height:

$$u(10) = \frac{u_*}{\kappa} \ln\left(\frac{10}{z_0}\right) \quad (14)$$

$$\frac{u_*}{\kappa} = \frac{u(10)}{\ln\left(\frac{10}{z_0}\right)} \quad (15)$$

and by taking $z_3 = z_0$, the volumetric airflow rate per unit width between the heights z_0 and H' will be:

$$V_a = \frac{u(10)}{\ln\left(\frac{10}{z_0}\right)} \left(H' \left[\ln\left(\frac{H'}{z_0}\right) - 1 \right] + z_0 \right) \quad (16)$$

The main difficulty in modelling the atmospheric flux of moisture to the pool comes from the fact that there are two fluxes occurring simultaneously in the region above the pool, and both of them involve the atmospheric moisture. The first is the flux of moisture entering the pool, and the second is the flux of SO_3 vapour which reacts with any moisture present in the atmosphere yielding H_2SO_4 mist. The most appropriate way is to model these two fluxes simultaneously by looking at all the phenomena that occur in both the liquid and the vapour phase. In the absence of any relevant data, the flux of moisture entering the pool is modelled in a simple way by assuming that all the moisture content of the air from a height equal to the roughness length, z_0 , up to a height $H'(m)$ above the roughness length of the surface enters the pool. It is expected that the value of the height H' will be dependent on the pool size (a bigger pool size will correspond to larger value of H') and on the percentage free SO_3 of the liquid in the pool, p , (oleum of higher strengths will absorb more atmospheric water). It is assumed that:

$$H' = \frac{R}{30} \frac{p}{100} \quad (17)$$

It should be noted that although the above assumption is very simple, it describes the atmospheric water flux entering the pool as a function of the pool radius R and the percentage free SO_3 of the liquid in the pool.

Assuming $u(10) = 5 \text{ m s}^{-1}$, and an air density of 1.2 kg m^{-3} , the volumetric flow rate per unit width and the mass of moisture entering the pool in each time step, M_{aw} (kg s^{-1}), is:

$$V_a = \frac{5}{\ln\left(\frac{10}{z_0}\right)} \left(H' \left[\ln\left(\frac{H'}{z_0}\right) - 1 \right] + z_0 \right) \quad (18)$$

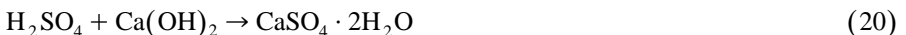
$$M_{\text{aw}} = V_a 1.2 f_w \delta t 2 R \quad (19)$$

where f_w (kg of water/kg of total air) is the mass mixing ratio of the water vapour in the air and δt (s) is the time step used in the calculations.

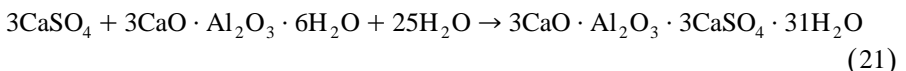
2.2.3. Water from concrete—reaction between H_2SO_4 and calcium hydroxide

In many cases, accidental releases of oleum or SO_3 occur in handling facilities, during loading or unloading of tanks or during transport. As a result, it is most probable that a spill of these substances will occur on a concrete (concrete oleum bunds are often coated to reduce any problems) or asphalt surface, or in unusual cases on stainless steel which is a material that does not react with oleum or SO_3 , and is sometimes used as protection around storage tanks. Generally there is limited information on the action of SO_3 or oleum on concrete. From the spillage trials that were conducted at Porton Down in Wiltshire, UK, in 1978 and 1980, it was observed that erosion of the concrete and asphalt trays had occurred [8].

Generally, acidic solutions are among the most aggressive to concrete. Reactions between attacking solutions and cement compounds (acid attacks the cement only) result in the formation of secondary compounds which are either leached from the concrete, or remain in a non-binding form, causing gradual loss of strength. All the Portland cement compounds are susceptible to acid attack, but the free lime is attacked most readily, which is why pozzolanic and slag cements, which have low free lime content, offer greater resistance to mild acid attack [12]. H_2SO_4 reacts with the calcium hydroxide in cement to produce calcium sulphate, which is deposited as gypsum:



As acid attack proceeds, all the cement compounds are eventually broken down and leached away, together with any carbonate aggregate material [12]. With H_2SO_4 attack, calcium sulphate formed by the initial reaction can proceed to react with the calcium aluminate phase in cement to form calcium sulpho-aluminate (ettringite), which on crystallisation can cause expansive disruption of the concrete:



The action of concentrated acids has not been investigated experimentally. With concentrated acids, saturated reaction of H_2SO_4 with cement would be expected to take

place. A mass of ~ 1.3 kg of H_2SO_4 (0.72 l) is required for saturated reaction with 1 kg of cement [18]. The permeation of oleum or SO_3 into concrete depends heavily on the porosity and the type of concrete and its components (aggregates, cement). In the early stages (first few hours), the rate of permeation is high and it decreases fairly rapidly until a steady state value is reached [8]. When modelling accidental spills the early stages are of great interest because the spill would be expected to be brought under control before the steady state value is reached. There are no data available on the rate of absorption and permeability curve of SO_3 or oleums. A typical curve of this type for water is shown in Fig. 1 [19] (it should be noted that the values of the y-axis should be multiplied by 10^{-8}).

The equation that best fits this curve is:

$$k_{H_2O} = (55.627\exp(-0.001852t) + 20.6315\exp(-0.0002375t) + 1.3821)10^{-8} \tag{22}$$

where k_{H_2O} ($m\ s^{-1}$) is the permeability of water in concrete and the time t is in hours. An empirical equation that gives the permeability of various fluids in different substrates is Ergun’s equation:

$$k = \frac{1}{\alpha \frac{(1 - \epsilon)^2}{d^2 \epsilon^3} + \beta \frac{(1 - \epsilon) \rho u}{\epsilon^3 d \mu}} \tag{23}$$

where k ($m\ s^{-1}$) is the permeability, ϵ is the porosity of concrete (2–7%, [20]), d (m) is the diameter of particles of concrete (an average value is 2 mm), ρ ($kg\ m^{-3}$) is the fluid density, μ ($kg\ m^{-1}\ s^{-1}$) is the fluid absolute viscosity, α is a constant ($= 150$), β is a constant ($= 1.75$) and u ($m\ s^{-1}$) is the superficial flow velocity.

It is obvious from the above equation that for the same substrate the permeability is directly proportional to the fluid’s kinematic viscosity ν ($m^2\ s^{-1}$), where:

$$\nu = \frac{\mu}{\rho} \tag{24}$$

An equation that calculates the kinematic viscosity of water has been developed [18],

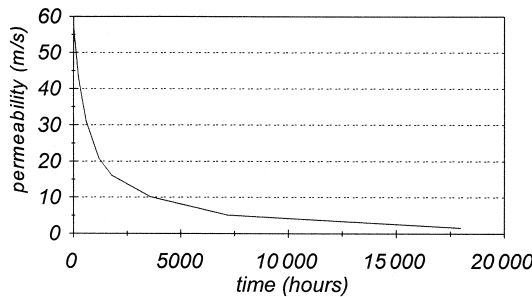


Fig. 1. Permeability curve of water in concrete (the values of the y-axis should be multiplied by 10^{-8}).

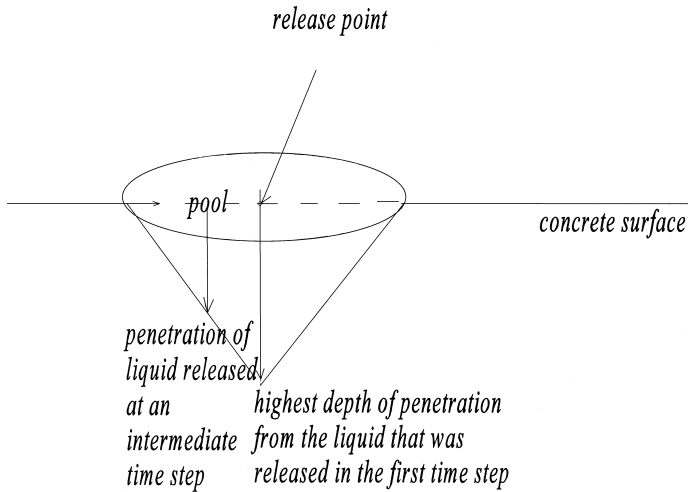


Fig. 2. Penetration of SO₃ or oleum in concrete.

which we use here. Combining Eqs. (22)–(24) produces the following estimation of the permeability of SO₃ or oleum:

$$k_{\text{SO}_3} = (55.627\exp(-0.001852t) + 20.6315\exp(-0.0002375t) + 1.3821)10^{-8} \frac{\nu_{\text{H}_2\text{O}}}{\nu_{\text{oleum}}} \tag{25}$$

It should be noted that it is more appropriate to use the above equation rather than Ergun’s equation because the latter refers to the steady state permeability value.

For continuous releases, penetration will not be uniform for the whole area of the pool. At the release point the penetration will be the highest and at the edges of the pool the lowest. The volume of the substrate that has been permeated by the liquid will have the form of a cone as depicted in Fig. 2. It should be noted that the depth is exaggerated in comparison to the diameter.

The cement content of concrete depends on the type of concrete and can vary widely. In most cases its value is in the range 200–600 (kg cement)/(m³ concrete). At every time step the liquid will meet the following mass of cement (kg).

$$M_{\text{cemr}} = \left(\left(\frac{1}{3} \pi R^2 l \right)_{\text{tn}} - \left(\frac{1}{3} \pi R^2 l \right)_{\text{tn}-1} \right) c \tag{26}$$

where $(1/3 \pi R^2 l)_{\text{tn}}$ is the volume of the cone at one time step and $(1/3 \pi R^2 l)_{\text{tn}-1}$ the volume of the cone at the previous time step, with R (m) the pool radius (base of the cone), l (m) is its depth (maximum penetration) and c (kg m⁻³) is the cement content of the concrete. Assuming saturated reaction between sulphuric acid and cement, the amount of sulphuric acid that reacts is:

$$M_{\text{acidr}} = 1.3 M_{\text{cemr}} \tag{27}$$

Table 1
Heats of formation [17]

Substance	Heat of formation (kcal mol ⁻¹)
H ₂ SO ₄	-193.31
Ca(OH) ₂	-235.8
CaSO ₄ ·2H ₂ O	-483.06

The maximum penetration at every time step will be the cumulative penetration up to that time step plus the permeability multiplied by the time step.

$$l_{n+1} = l_n + k \delta t \quad (28)$$

Assuming that the main reaction between cement and sulphuric acid is the one producing gypsum (Eq. (20)), the heat of reaction is calculated from the heats of formation of reactants and products as shown in Table 1. The heat of reaction under normal conditions is: $Q_{r2} = -53.35 \text{ kcal mol}^{-1}$. The reaction between H₂SO₄ and calcium hydroxide is exothermic and provides the pool with energy. The energy provided to the pool in each time step will be:

$$Q_{r2} = 2278 M_{\text{acidr}} \quad (29)$$

where Q_{r2} (kJ) is the heat of reaction.

As oleum permeates the concrete, apart from participating in the reaction between H₂SO₄ and calcium hydroxide, it will meet water that is present in concrete and the reaction between SO₃ and water will occur. This reaction is described in the Section 2.3. There are many different categories of the water content of concrete, but mainly there is free water, capillary water, gel water and water combined in hydrated cement compounds [19]. Another classification of the water in cement is into evaporable and non-evaporable. Water is bound to varying degrees. At one extreme there is free water; at the other, chemically combined water forming a part of the hydrated compounds. Between these two categories there is gel water held in a variety of ways [21].

The amount of water in concrete depends heavily on the type of concrete, its compounds (cement and aggregates), the environment it is exposed to etc. The amount of free water (W_{cem}) usually varies from 130 kg m⁻³ to 230 kg m⁻³ [21,22]. The amount of chemically combined water, gel water and capillary water is difficult to determine and depends on the type of cement, the hydration process that took place in the formation of the concrete etc. The amount of combined water usually varies from 0.04 to 0.14 kg/kg dry cement [19]. The amount of gel and capillary water takes a great variety of values. In order to determine the amounts of combined, capillary and gel water, laboratory analysis is required. It is assumed that these three forms of water have a total value of 0.2 kg/kg cement. The total mass of water M_{cw} (kg), that the liquid encounters in each time step from concrete is:

$$M_{\text{cw}} = \left(\left(\left(\frac{1}{3} \pi R^2 l \right)_{\text{tn}} - \left(\frac{1}{3} \pi R^2 l \right)_{\text{tn}-1} \right) W_{\text{cem}} \right) + 0.2 M_{\text{cemr}} \quad (30)$$

2.3. Description of the SO₃/water reaction

The previous models assumed that the reaction that takes place between SO₃ and water occurs on 1 mol to 1 mol basis and that the liquid phase consists only of SO₃ [4,7]. Hermann has found that the reaction that takes place is [11]:



The factor x depends on the percentage free SO₃ [11]. No experimental data are available for pure SO₃. An equation has been developed that parameterises the factor x as a function of p , the percentage free SO₃, and this suggests that for pure SO₃ this factor is equal to about 21.5 (see Appendix A). It is obvious that the liquid phase does not consist only of SO₃. If for example SO₃ is continuously spilled, it will react with water, and oleum is produced. At the beginning (first time step), 1 mol of water will react with 21.5 mol of SO₃ yielding 1 mol of H₂SO₄ and 20.5 mol of free SO₃. Because the properties of the pool change continuously, all the properties have been parameterised as functions of the pool temperature and composition (see Appendix A).

2.4. Mass balances

2.4.1. Sulphur trioxide

The mass of free SO₃ in the pool at each time step will be:

$$\begin{aligned} \text{free SO}_3 = & (\text{free SO}_3)_{\text{spilled}} - (\text{free SO}_3)_{\text{reacted}} + (\text{free SO}_3)_{\text{in oleum that is generated}} \\ & - (\text{free SO}_3)_{\text{evolved}} \end{aligned}$$

2.4.2. Sulphuric acid

H₂SO₄ is produced in every time step and is present in the released liquid in cases of oleum spills. Depending on the conditions (pool temperature and composition), H₂SO₄ vapour may evolve from the pool. At every time step the quantity of H₂SO₄ in the pool is obtained from the following balance:

$$\text{H}_2\text{SO}_4 = (\text{H}_2\text{SO}_4)_{\text{spilled}} - (\text{H}_2\text{SO}_4)_{\text{evolved}} + (\text{H}_2\text{SO}_4)_{\text{generated}}$$

2.4.3. Water

When there is a high availability of water, there may be an excess of water that will be present in the pool. In other cases unreacted water is not present in the pool because the whole quantity encountered in the time step reacts with SO₃.

2.5. Energy balance

Possible energy sources are shown in Fig. 3: where: (1) Q_{sol} , net solar radiation energy (shortwave); (2) Q_{atm} , atmospheric radiation energy (longwave); (3) Q_{sen} , sensible heat energy; (4) Q_{sur} , emitted radiation energy (longwave); (5) Q_{ev} , evaporation energy; (6) Q_{reac} , energy given to the pool by the reaction with water; (7) Q_{grd} , ground

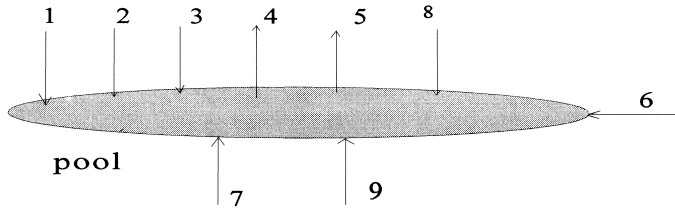


Fig. 3. Energy balance of the pool.

conduction energy; (8) Q_{add} , energy of addition of sulphur trioxide into oleum; (9) Q_{r2} , energy of reaction between sulphuric acid and calcium hydroxide.

For continuous releases an energy balance is conducted in each time step and the temperature of the pool is calculated for every time step:

$$Q_{sol} + Q_{atm} - Q_{sur} - Q_{ev} + Q_{sen} + Q_{grd} + Q_{reac} + Q_{r2} + Q_{add} = Q_t \quad (32)$$

2.5.1. Q_{sol} : net solar radiation (corrected for the amount reflected from the surface) (kJ)

The net solar radiation in each time step is estimated from Raphael’s solar insolation curves which are plots of the net solar radiation on a water surface as a function of cloud cover and solar altitude [23]:

$$Q_{sol} = 4000(1 - 0.0071C^2)(\sin SA - 0.1) \frac{\delta t}{3600} A \quad (33)$$

where C is the cloud cover factor in tenths (0 for clear day, 10 for complete cloud cover) and SA is the solar altitude in degrees which is calculated from the following expression:

$$\sin SA = \sin(LA)\sin(D) + \cos(LA)\cos(D)\cos(H) \quad (34)$$

where LA is the latitude in degrees and D is the declination of the sun given from [24]:

$$D = 23.45\sin(0.97(N - 80)) \quad (35)$$

where N is the day number of the year and H is the hour angle in degrees given from [24]:

$$H = 15(12 - (LCT + TZ - (LG/15))) \quad (36)$$

where LCT is the local standard time in hours, TZ is the time zone factor and LG is the longitude in degrees following the formulation of Kawamura and MacKay [25]. Eq. (33) is valid only for $\sin SA > 0.1$. For values between 0 and 0.1, solar insolation is very small and can be considered to be negligible.

2.5.2. Q_{atm} : long-wave radiation from the atmosphere absorbed by the surface (kJ)

From the Stefan–Boltzmann radiation law [25]:

$$Q_{atm} = (1 - r') B\sigma T_a^4 \frac{\delta t}{3600} A \quad (37)$$

where σ is the Stefan–Boltzmann constant ($= 2.04 \times 10^{-7} \text{ kJ m}^{-2} \text{ h}^{-1} \text{ K}^{-4}$), r' is the reflectivity of the surface with respect to long-wave radiation, T_a (K) is the absolute temperature of the air, B is the atmospheric cloud factor which is a function of cloud cover and vapour pressure of water in air [23].

2.5.3. Q_{sur} : long-wave radiation emitted by the pool (kJ)

This is given from the following relationship [25]:

$$Q_{sur} = e\sigma T_s^4 \frac{\delta t}{3600} A \quad (38)$$

where e is the emissivity of the surface and T_s (K) is the absolute temperature of the pool.

2.5.4. Q_{ev} : evaporation energy (kJ)

The evaporation rate, M'_e (kg s^{-1}), is calculated according to the model of Brighton, the theory of which is summarised in Section 2.6. The evaporation energy, Q_{ev} , is [26]:

$$Q_{ev} = M'_e H_v \frac{\delta t}{3600} \quad (39)$$

where H_v (kJ kg^{-1}) is the heat of vaporisation.

2.5.5. Q_{sen} : sensible heat transfer between the air and the pool (kJ)

This occurs as a result of a temperature difference between the two phases [25]:

$$Q_{sen} = U_{liq}(T_a - T_s) \frac{\delta t}{3600} A \quad (40)$$

where U_{liq} ($\text{kJ m}^{-2} \text{ h}^{-1} \text{ K}^{-1}$) is the heat transfer coefficient, which can be estimated from the heat and mass transfer analogy:

$$U_{liq} = k\rho_a C_{pa} (\text{Sc}/\text{Pr})^{0.67} \quad (41)$$

where ρ_a (mol m^{-3}) is the molar density of air, C_{pa} ($\text{kJ mol}^{-1} \text{ K}^{-1}$) is the heat capacity of air, Sc is the Schmidt number and Pr is the Prandtl number.

2.5.6. Q_{grd} : conduction of heat from the ground (kJ)

$$Q_{grd} = U_{grd}(T_{grd} - T_s) \frac{\delta t}{3600} A \quad (42)$$

where U_{grd} ($\text{kJ m}^{-2} \text{ h}^{-1} \text{ K}^{-1}$) is the overall heat transfer coefficient given by [25]:

$$U_{grd} = 1 / \left[(1/h_{grd}) + (1/h_{liq}) \right] \quad (43)$$

where h_{liq} ($\text{kJ m}^{-2} \text{ h}^{-1} \text{ K}^{-1}$) is the heat transfer coefficient that accounts for the

thermal resistance from the surface of the ground to the lower surface of the pool and h_{grd} ($\text{kJ m}^{-2} \text{ h}^{-1} \text{ K}^{-1}$) is the heat transfer coefficient of the ground [25]:

$$h_{\text{liq}} = \frac{k_{\text{liq}}}{\phi d_1} \quad (44)$$

where k_{liq} ($\text{kJ m}^{-1} \text{ h}^{-1} \text{ K}^{-1}$) is the thermal conductivity of SO_3 or oleum, d_1 (m) is the average depth of the pool over the entire course of evaporation and ϕ is a liquid resistance factor:

$$\phi = 1 / [1 + \exp(-0.06(T_{\text{bp}} - 70))] \quad (45)$$

where T_{bp} ($^{\circ}\text{C}$) is the normal boiling point of the liquid. In the absence of any data on the scale of the temperature gradient region, the average depth of the pool over the entire course of evaporation d_1 , is assumed to be equal to the initial half depth [25]. For the current modelling purposes, we follow the practice of other authors in setting the ground temperature in Eq. (42) equal to the air temperature in Eq. (40) because it is desirable to use the same driving forces in the two equations.

2.5.7. Q_{reac} : Heat generated by the reaction between SO_3 and water (kJ)

The heat generated due to reaction H_r (kJ per kg of water reacted), will be [7]:

$$H_r = (a + bp + cp^2 + dp^3 + ep^4)10^3 \quad (46)$$

where: $a = 4.9218$, $b = 1.4225 \times 10^{-2}$, $c = 1.95 \times 10^{-4}$, $d = -3.99 \times 10^{-6}$ and $e = 3.4 \times 10^{-8}$ Therefore:

$$Q_{\text{reac}} = (a + bp + cp^2 + dp^3 + ep^4)10^3 M_w \quad (47)$$

Eqs. (46) and (47) are only valid for $p > 0$. When $p = 0$ (pure H_2SO_4 in the pool), $Q_{\text{reac}} = 0$.

2.5.8. Q_{add} : Heat of addition of SO_3 and oleum (kJ)

SO_3 is usually stored at a temperature of around 35°C (10°C below its boiling point, 18°C above its freezing point) [13]. Because of the complex freezing and boiling curves of oleums, their storage temperature depends on the percentage free SO_3 and it is usually chosen to be around 15°C above their freezing points.

In case of a spillage, the temperature of the pool will be different to that of the liquid spilled because, depending on the percentage free SO_3 of the liquid spilled and the temperature of the pool, the heat of addition can either be an energy input or output. The heat of addition is given by the following equation:

$$Q_{\text{add}} = M' C_p \delta t (T_1 - T_s) \quad (48)$$

where C_p ($\text{kJ kg}^{-1} \text{ K}^{-1}$) is the specific heat of the liquid spilled and T_1 (K) is the released liquid temperature. It should be noted that for continuous releases the heat of addition is zero after the spill ceases. For instantaneous releases this term will only be different to zero for the time taken for the liquid to be spilled (usually some seconds).

2.5.9. Q_{r2} : Heat of reaction between H_2SO_4 and calcium hydroxide (kJ)

When the spill occurs on a concrete surface, H_2SO_4 reacts with calcium hydroxide to form gypsum, as already discussed in Section 2.2.3. The energy provided to the pool in each time step is given from Eq. (29).

The final form of the energy balance is ($Q_t = 0$):

$$\begin{aligned} Q_{sol} + Q_{atm} + Q_{reac} + Q_{r2} + T_a(U_{liq} + U_{grd}) \frac{\delta t}{3600} A + Q_{add} + Q_{fus} \\ = T_s(U_{liq} + U_{grd}) \frac{\delta t}{3600} A + Q_{ev} + Q_{sur} \end{aligned} \quad (49)$$

The above equation is solved for every time step and the mean temperature of the pool is calculated. The term Q_{fus} represents the heat of fusion liberated when the pool solidifies. It should be noted that this term is zero except for the time step in which solidification occurs (see Section 2.8).

2.6. Evaporation model

The evaporation model developed by Brighton [26] has been incorporated into the model. The evaporation model of MacKay and Matsugu [27], that was used by Grint and Purdy, uses formulae for mean evaporation rates with power-law dependencies on windspeed and pool size, and does not incorporate knowledge of turbulent diffusion gained recently. Parameters such as the friction velocity of the airflow and the roughness length of the surface are not taken into account [4,27]. Brighton's model takes into account the turbulent characteristics of the airflow, and the effect of high vapour pressure on the mass transfer process [26].

The reference height, z_1 (m), for calculating the windspeed should be related to the depth of the vapour layer at some intermediate point along the diameter of the pool, x_2 (m), and is given from the equation:

$$z_1 = \frac{c' z_2 x_2}{e} \quad (50)$$

$$c' = e^{-\gamma} \quad (51)$$

where $\gamma = 0.5772$ is Euler's constant, so $c' = 0.5615$ (the constant c' was evaluated by Chatwin as given in Eq. (51) [28]). The intermediate point is usually set equal to the radius of the pool, $x_2 = R$ and z_2 (m) is the height of centroid of a puff of contaminant:

$$z_2 = 0.013953 \ln(231.8436 x_2) + 0.086665 x_2^2 \quad (52)$$

The above equation has been derived from:

$$x_2 = \frac{\sigma'}{\kappa^2} z_2 \left(\ln \left(\frac{c z_2}{z_0} \right) - 1 \right) \quad (53)$$

where σ' is the turbulent Schmidt number of the air (equal to 0.85) and κ is Von Karman's constant (equal to 0.40). The reference height is given finally from:

$$z_1 = z_0 + \frac{c z_2 x_2}{e} \quad (54)$$

Brighton does not incorporate the term z_0 in his model, but it was judged that its addition was necessary, because the reference height should always take higher values than the roughness length z_0 . The windspeed is calculated using the logarithmic equation:

$$u = \left(\frac{u_*}{\kappa} \right) \ln \left(\frac{z_1}{z_0} \right) \tag{55}$$

The wind driven evaporation rate, M'_e (kg s^{-1}), is:

$$M'_e = C_s j_1 u_* \pi R^2 \tag{56}$$

where C_s (kg m^{-3}) is the vapour concentration which is determined by the condition that at the liquid surface it takes the value for saturated vapour. Assuming that the perfect gas law holds,

$$C_s = \frac{M_p P_v}{R_g T_s} \tag{57}$$

where P_v is given in atm. In Eqs. (55) and (56) u_* (m s^{-1}) is the friction velocity of the airflow and j_1 is the dimensionless local evaporation rate, which takes into account the effect of high vapour pressure:

$$j_1 = -j \left(\frac{1}{P_v} \right) \ln(1 - P_v) \tag{58}$$

The dimensionless local evaporation rate is given from the following equation:

$$j = \left(\frac{k}{\sigma} \right) (1 + n) Q' \tag{59}$$

where n is the power-law exponent of the wind profile:

$$n = \frac{1}{\ln \frac{z_1}{z_0}} \tag{60}$$

and Q' is a function of two parameters, l'_1 and X_1 :

$$Q' = f(e^{l'_1} X_1) \tag{61}$$

$$l'_1 = n^{-1} + 1 + 2 \ln(1 + n) - 2\gamma + \left(\frac{k}{\sigma'} \right) (1 + n) B \tag{62}$$

where the parameter B' for rough surfaces is given from:

$$B'_{\text{rough}} = (7.3 \text{Re}^{0.25} \text{Sc}^{0.5}) - 5\sigma' \tag{63}$$

Sc is the Schmidt number (equal to 1.1 for SO_3 [7]), $\text{Re} = u_1 z_0 / \nu$, where ν is the kinematic viscosity of the air (equal to about $0.000015 \text{ m}^2 \text{ s}^{-1}$). For smooth surfaces:

$$B'_{\text{smooth}} = (3.85 \text{Sc}^{1/3} - 1.3)^2 + \left(\frac{\sigma'}{\kappa} \right) \ln(\text{Sc}) + \left(\frac{\sigma'}{\kappa} \right) \ln(0.13) \tag{64}$$

X_1 is the dimensionless value of x at the downwind edge of the pool, which Brighton has found is equal to $2e/c' = 9.681$ [26]. Letting $el'_1 X_1 = W$, then:

$$Q' = 0.5 - \left(\frac{1}{\pi} \right) \tan^{-1} \frac{\ln W}{\pi} + \frac{0.4228}{\ln^2 W + \pi^2} + \frac{2.824 \ln W}{(\ln^2 W + \pi^2)^2} + \frac{1.025 \left(\ln^2 W - \frac{\pi^2}{3} \right)}{(\ln^2 W + \pi^2)^3} \quad (65)$$

Apart from SO_3 and depending on the composition and temperature of the pool, H_2SO_4 may evaporate as well. For concentrations below 35% free SO_3 and temperatures above 333 K (both conditions are required), the vapour evaporated from the pool is a mixture of SO_3 , H_2SO_4 and H_2O [10]. The quantities of water vapour are insignificant. Thus there are two dimensionless evaporation rates, one for SO_3 and one for H_2SO_4 , and they are calculated using the same Eqs. (50)–(65). There is a criterion for the validity of Brighton's model, namely that $n < 0.25$, where n is the power-law exponent for the wind profile.

2.7. Boiling of the pool

During the spill stages (before spreading has ceased) it is possible that the pool boils. Whether the pool will be boiling, evaporating or sublimating depends on a number of parameters such as the availability of water, the composition of the pool, and the area of the pool. If the pool boils, the temperature of the pool is limited to the boiling point and any extra energy is used up in the evolution of SO_3 and H_2SO_4 . The energy balance will be different to that in cases of evaporation only. The evaporation energy term will be replaced by another term, Q_b , which represents two energy terms, one due to the boiling point difference between successive time steps, and one due to the evolution of SO_3 and H_2SO_4 (the amount of water evolved even at very high temperatures is negligible).

$$Q_b = M_p C_p \Delta T + M_e H_v \quad (66)$$

where M_p (kg) is the total mass in the pool at each time step, ΔT (K) = $T_n - T_{n-1}$ is the temperature difference between two successive time steps and M_e (kg) is the mass evolved from the pool to the atmosphere at each time step (either SO_3 or H_2SO_4). The energy balance is then:

$$Q_{\text{sol}} + Q_{\text{atm}} - Q_{\text{sur}} - Q_b + Q_{\text{sen}} + Q_{\text{grd}} + Q_{\text{reac}} + Q_{r2} + Q_{\text{add}} = Q_t \quad (67)$$

Because the composition of the pool changes continuously, so does the boiling point. Thus, between successive time steps, the temperature difference ΔT is the difference in the boiling points. The energy balance is rearranged, so that the mass evolved from the pool, M_e , is calculated:

$$M_e = \left(Q_{\text{sol}} + Q_{\text{reac}} + Q_{r2} + Q_{\text{atm}} + Q_{\text{grd}} + Q_{\text{sen}} - Q_{\text{sur}} + Q_{\text{add}} \right) - \frac{\left(M_p C_p (\text{bp}_0 - \text{bp}_1) \right)}{H_v} \quad (68)$$

where bp_0 (K) is the boiling point of the pool at the beginning of the time step and bp_1 (K) is the boiling point at the end of the time step. The mass evolved will be a mixture of SO_3 , H_2SO_4 and H_2O depending on the partial pressures of these substances at the boiling point.

2.8. Solidification of the pool

Because of the complex freezing curve of oleums, and depending on the composition of the pool and its temperature, solidification of the pool may occur. There are two cases depending on whether the pool solidifies before or after the spill ceases. There are no data on the heat of fusion of oleums. Even for SO_3 , there are inconsistencies in the literature [13]. Generally there are three forms of solid SO_3 , alpha, beta and gamma. The one most often encountered is γ - SO_3 . The latent heat of fusion of this form is reported to be equal to 94.07 kJ kg^{-1} by Duecker and West [29], and equal to 24.05 kJ kg^{-1} by Brasted [30]. Du Pont Chemicals [14] uses the value reported by Duecker and West. The latent heat of fusion of H_2SO_4 is equal to 109.3 kJ kg^{-1} [29]. In the present study a value of $H_f = 100 \text{ kJ kg}^{-1}$ is adopted (around midway between the two reported values for pure SO_3 and H_2SO_4 [29]) for any liquid encountered (SO_3 and different strengths of oleums). This aspect has been incorporated in both cases of solidification.

2.8.1. Solidification occurs before the spill ceases

For continuous releases, the pool may solidify before the release ceases and for these cases SO_3 or oleum will then be spilled onto a solid surface of oleum. The newly spilled liquid will not meet the water on the ground until its radius exceeds the radius of the solid phase. There will be a temperature and a concentration gradient between the solid and the liquid phase and at the same time the free solid phase (the area that is not covered from the liquid phase) will sublime. This situation is depicted in Fig. 4.

The temperatures of the two layers (T_1 and T_2) (solid and liquid) are assumed to be uniform and so are the thermal conductivities (k_1 and k_2). The layer depths are Y_1 and Y_2 for the liquid and the solid pool, respectively. At steady state, the heat flux through

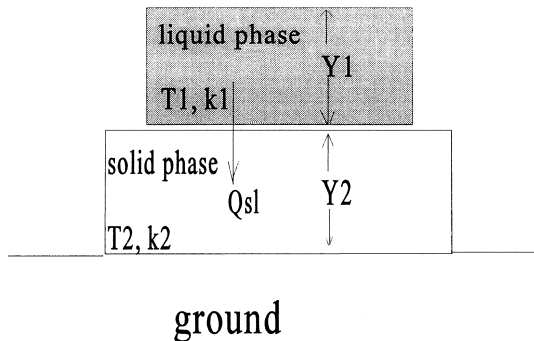


Fig. 4. Temperature gradient between solid and liquid phase.

the two layers will be constant. According to Themelis, the heat exchange that takes place in each time step will be [31]:

$$Q_{sl} = \frac{T_1 - T_2}{\frac{Y_1}{k_1} + \frac{Y_2}{k_2}} \frac{\delta t}{3600} A \quad (69)$$

where T_1 and T_2 (K) are the temperatures of the two phases, Y_1 and Y_2 (m) are the pool depths and k_1 and k_2 ($\text{kJ m}^{-1} \text{h}^{-1} \text{K}^{-1}$) are the thermal conductivities of the substances in the pools.

It should be noted that there are no data on mass diffusivity between solid and liquid SO_3 and oleum. Because of that, the molar flux can not be modelled satisfactory. So, it is assumed that if the pool temperature drops to the freezing point solidification of the liquid occurs. For continuous releases, and if spreading has not ceased, liquid SO_3 or oleum will then be spilled onto the solid phase.

The two pools are considered to be independent. The only interaction between them will be the energy exchange, which is expressed by the term Q_{sl} . The liquid phase will only meet water on the ground when its radius exceeds the radius of the solid phase, which remains constant. The free area of the solid phase will sublime until it is entirely covered by the liquid phase. The radius of the liquid pool is calculated as described above. The energy balance for the liquid phase will be:

$$Q_{sol} + Q_{atm} - Q_{sur} - Q_{ev} + Q_{sen} + Q_{grd} + Q_{fus} + Q_{reac} + Q_{r2} + Q_{add} - Q_{sl} = Q_t \quad (70)$$

Unless the liquid phase encounters the ground, the term due to conduction of heat from the ground, Q_{grd} , will be equal to zero. When the liquid pool becomes bigger than the solid one, only the area of the liquid pool that is in contact with the ground will exchange heat with it. The energy balance for the solid phase will then be:

$$Q_{sol} + Q_{atm} - Q_{sur} - Q_{subl} - Q_{fus} + Q_{sen} + Q_{grd} + Q_{sl} = Q_t \quad (71)$$

where Q_{subl} (kJ) is the sublimation energy:

$$Q_{subl} = M'_s H_s \delta t \quad (72)$$

where M'_s (kg s^{-1}) is the sublimation rate and H_s (kJ kg^{-1}) is the heat of sublimation. The heat of fusion Q_{fus} in Eq. (71) will be equal to zero except for the time step in which melting of the solid layer occurs.

The energy balances are solved at every time step for steady-state conditions ($Q_t = 0$) and the temperature of each layer is calculated. It should be noted that only the free area of the solid pool will be subliming (not the one in contact with the liquid phase). The terms Q_{sol} , Q_{atm} and Q_{sen} also refer to the free area. After the solid phase is entirely covered all the above terms (Q_{subl} , Q_{sol} , Q_{atm} , Q_{sur}) will be equal to zero (Q_{sol} is equal to zero because the liquid layer is considered opaque). The term Q_{add} is also equal to zero.

There is a possibility of melting of the solid pool due to the heat exchange and due to the fact that the solid phase sublimates only SO_3 . As a result, its temperature and

Sublimation of the free solid phase occurs. The exposed area is the area of the solid pool minus the area of the liquid pool. Sublimation will stop when the whole solid phase is covered by the liquid one.

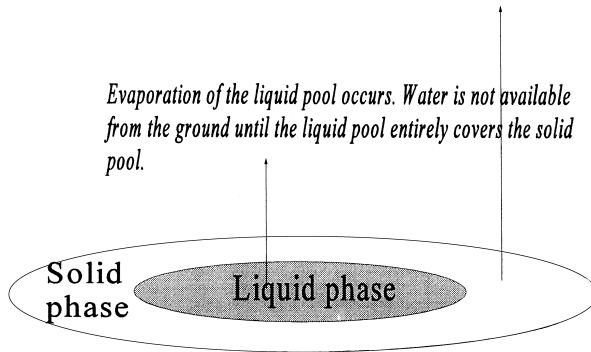


Fig. 5. Description of the behaviour when the pool solidifies.

composition will change and so it is possible that the solid phase will melt. In this case, the two pools are considered to mix instantaneously and a new liquid pool is formed. The total amount evolved will be the amount evaporated from the liquid pool (see Section 2.6) plus the amount that sublimates if the solid pool is not entirely covered. The sublimation model is identical to that for evaporation (see Section 2.6).

The solidification behaviour before the spill ceases is depicted in Fig. 5.

2.8.2. Solidification occurs after the spill ceases

There will be only a solid pool that will be subliming SO_3 and it is possible that it will melt due to the composition change occurring because of the sublimation of SO_3 .

The energy balance will be:

$$Q_{\text{sol}} + Q_{\text{atm}} - Q_{\text{sur}} - Q_{\text{subl}} - Q_{\text{fus}} + Q_{\text{sen}} + Q_{\text{grd}} + Q_{\text{reac}} = Q_{\text{t}} \quad (73)$$

The energy balance is solved at every time step for steady state conditions ($Q_{\text{t}} = 0$) and the temperature of the pool is calculated. The amount of SO_3 evolved is found using Brighton's model (see Section 2.6).

3. Inputs to the model

The inputs of the model are the release rate (M') (or the quantity released (M)), the time step (δt), the spill duration (t_{s1}), the type of release (SO_3 or different strengths of oleum), the maximum duration of the release to the atmosphere (t_{s2}), the maximum radius of the pool (r_{max}), the free water film thickness on the ground (w_g), the air temperature (T_a), the location defined by the longitude (LG) and the latitude (LA), the time and day (τ and d), the friction velocity of the airflow (u_*), the type of surface (s),

the roughness length of the surface (z_0), the atmospheric radiation and cloud cover factors (B and C) and the mass mixing ratio of the air (f_1). The model has been implemented as a programme in Microsoft Visual Basic Professional 5.0.

4. Calculations performed by the model

Every time step, δt , can be split into three steps: the spill, the reaction and the evolution steps.

4.1. Spill

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

$$M_p = M_p + \delta t M' \quad (74)$$

The total quantity of SO_3 in the pool at this stage is:

$$M_s = M_s + \delta t \frac{p'}{100} M' \quad (75)$$

where p' is the percentage free SO_3 of the liquid spilled. The percentage free SO_3 of the liquid in the pool (p) is calculated from the following equation:

$$p = \frac{M_s}{M_p} 100 \quad (76)$$

All the properties of the liquid (density, freezing point, boiling point, heat capacity, factor x etc.) are calculated (see Appendix A for the parameterisation equations of these properties). The volume of the pool is:

$$V = \frac{M_p}{\rho} \quad (77)$$

The pool radius is calculated by solving the spreading equations. For an instantaneous release, Eq. (77) is solved and for a continuous release, Eq. (79). The method followed in order to solve these equations is the fourth-order Runge–Kutta method at a time increment of 0.01 s. After calculating the pool radius, the pool depth, h (m), is calculated:

$$h = \frac{V}{A} \quad (78)$$

The surface area of the pool, A (m^2), is equal to:

$$A = \pi R^2 \quad (79)$$

The pool depth is assumed to remain constant throughout the time step.

4.2. Reaction

The total mass of water available for reaction is calculated (Eqs. (9), (18) and (30)). If water is in excess, the mass of water that reacts will be equal to the amount required

to consume all the spilled SO_3 . The heat of reaction is then calculated (Eq. (47)). At this stage the composition of the pool changes again, as SO_3 has reacted with water to produce SO_3 and H_2SO_4 . The mass of SO_3 in the pool is:

$$M_s = M_s - (80/18) M_w \quad (80)$$

where M_w (kg) is the mass of water that reacts at each time step. The mass of H_2SO_4 is:

$$M_{\text{acid}} = M_{\text{acid}} + (98/18) M_w \quad (81)$$

where M_{acid} (kg) is the mass of H_2SO_4 in the pool. The total mass in the pool when there is no excess of water is:

$$M_p = M_s + M_{\text{acid}} \quad (82)$$

The total mass in the pool when there is excess of water is:

$$M_p = M_s + M_{\text{acid}} + M_{w2} \quad (83)$$

where M_{w2} (kg) is the excess of water. As a result of the composition changes, the percentage free SO_3 in the pool and the rest of the properties of the liquid will have changed and they are recalculated. The values of all the energy terms are found from the relevant equation (see Section 2.5). 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 (Eq. (49)).

4.3. Evolution

If the temperature is below the boiling point and above the freezing point the pool will evaporate and all the calculation steps given in Section 2.6 are followed in order to find the amount of SO_3 and H_2SO_4 evaporated. If the temperature found is above the boiling point of the pool, the pool will be boiling and its temperature will be equal to its boiling point. The amount of SO_3 and H_2SO_4 evolved is calculated using Eq. (68). If the temperature found is below the freezing point, solidification occurs. Depending on whether solidification occurs before or after the spill ceases, the equations given in Sections 2.8.1 and 2.8.2, respectively, are solved so that the quantity of SO_3 evolved is found. At the end of the time step, the composition of the pool changes again:

$$M_s = M_s - M_{\text{se}} \quad (84)$$

$$M_p = M_p - M_{\text{se}} - M_{\text{ae}} \quad (85)$$

$$M_a = M_a - M_{\text{ae}} \quad (86)$$

where M_{se} and M_{ae} (kg) are, respectively, the masses of SO_3 and H_2SO_4 evolved. The amount of water evolved can be ignored because even at the highest allowable boiling point that can be observed ≈ 548 K (boiling point of pure H_2SO_4), its partial pressure is negligible compared to the ones of SO_3 and H_2SO_4 [13]. The percentage free SO_3 in the pool 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 and from the ground. Some of the

energy terms will be equal to zero as already discussed (e.g. Q_{add}). These calculations steps are repeated until either the whole amount of SO_3 has evolved, or even if all the amount of SO_3 has evolved and both the percentage free SO_3 in the pool is $p < 35\%$ and its temperature $T_s > 333 \text{ K}$ all the quantity of H_2SO_4 has evolved or emergency intervention has taken place. The same model can be used for releases of oleum or SO_3 for instantaneous or continuous releases. Results of the model are presented in part II of this paper [32].

5. Nomenclature

A	Pool area (m^2)
bp_0	Boiling point of the liquid in the pool at a time step t_n (K)
bp_1	Boiling point of the liquid in the pool at a time step t_{n-1} (K)
B	Atmospheric cloud factor used in Eq. (37)
c	Cement content of concrete (kg cement/ m^3 concrete)
C	Cloud factor (tenths)
C_p	Specific heat of the liquid ($\text{kJ kg}^{-1} \text{ K}^{-1}$)
C_{pa}	Heat capacity of air ($\text{kJ mol}^{-1} \text{ K}^{-1}$)
C_s	Sulphur trioxide concentration (kg m^{-3})
C_v	Vapour concentration (kg m^{-3})
d_1	Average depth of the pool over the entire course of evolution (m)
d_2	Diameter of concrete particles (m)
D	Declination angle of sun ($^\circ$)
D_{ls}	Mass diffusivity between liquid and solid phase ($\text{m}^2 \text{ s}^{-1}$)
e	Emissivity of the surface
f_w	Mass mixing ratio of the water vapour in the air (kg of water vapour/kg of air)
g	Gravitational acceleration (m s^{-2})
h	Pool depth (m)
h_0	Pool depth at time $t = 0$ (m)
h_{grd}	Heat transfer coefficient of the ground (kJ h^{-1})
h_{liq}	Heat transfer coefficient that accounts for the thermal resistance from the ground to the pool (kJ h^{-1})
h_{min}	Minimum pool depth (m)
H	Hour angle of sun ($^\circ$)
H'	Upper height up to which the atmospheric water enters into the pool (m)
H_f	Heat of fusion (kJ kg^{-1})
H_r	Heat of reaction with water (kJ kg^{-1})
H_s	Heat of sublimation (kJ kg^{-1})
H_v	Heat of vaporisation (kJ kg^{-1})
j	Dimensionless local evaporation rate
j_1	Dimensionless local evaporation rate, which takes into account the effect of high vapour pressure
J_{sx}	Molar flux of SO_3 in the x-direction in cases of solidification (kg s^{-1})
k	The mass transfer coefficient (m h^{-1})

k_1	Thermal conductivity of the liquid phase in cases of solidification ($\text{kJ m}^{-1} \text{h}^{-1} \text{K}^{-1}$)
k_2	Thermal conductivity of the solid phase in cases of solidification ($\text{kJ m}^{-1} \text{h}^{-1} \text{K}^{-1}$)
$k_{\text{H}_2\text{O}}$	Permeability of water in concrete (m s^{-1})
k_{liq}	Thermal conductivity of SO_3 or oleum ($\text{kJ m}^{-1} \text{h}^{-1} \text{K}^{-1}$)
k_{SO_3}	Permeability of SO_3 or oleum in concrete (m s^{-1})
l	Depth of penetration of concrete from the pool liquid (m)
l'_1	Parameter used in Eqs. (61) and (62)
LA	Latitude ($^\circ$)
LCT	Local standard time (h)
LG	Longitude ($^\circ$)
M	Quantity of SO_3 or oleum spilled instantaneously (kg)
M_{acid}	Mass of H_2SO_4 in the pool (kg)
M_{acidr}	Mass of H_2SO_4 that reacts with calcium hydroxide in concrete (kg)
M_{ae}	Mass of H_2SO_4 evolved during a time step (kg)
M_{aw}	Mass of atmospheric water (kg)
M_{cemr}	Mass of cement that the pool liquid meets at every time step (kg)
M_{cw}	Concrete water (kg)
M_{e}	Mass evolved during a time step (kg)
M_{gw}	Mass of water present on the ground available in each time step (kg)
M_{p}	Total mass of the liquid in the pool (kg)
M_{s}	Mass of SO_3 in the pool (kg)
M_{se}	Mass of SO_3 evolved during a time step (kg)
M_{w}	Mass of water that reacts in each time step (kg)
M_{w2}	Mass of water in excess (kg)
MW	Molecular weight of the liquid in the pool
M'	Spill rate of SO_3 or oleum (kg s^{-1})
M'_e	Evolution rate (kg s^{-1})
M'_s	Sublimation rate (kg s^{-1})
n	Power-law exponent of wind profile
N	Day number of the year
p	Percentage free SO_3 in the pool
p'	Percentage free SO_3 of the liquid spilled
Pr	Prandtl number
P_v	Vapour pressure (atm)
Q'	Parameter used in Eqs. (59) and (61)
Q_{add}	Energy of addition of sulphur trioxide into oleum in each time step (kJ)
Q_{atm}	Atmospheric radiation (longwave) in each time step (kJ)
Q_{ev}	Evaporation energy in each time step (kJ)
Q_{grd}	Ground conduction in each time step (kJ)
Q_{r2}	Energy of reaction between sulphuric acid and calcium hydroxide in each time step (kJ)
Q_{reac}	Energy given to the pool by the reaction with water in each time step (kJ)
Q_{sen}	Sensible heat in each time step (kJ)

Q_{sol}	Net solar radiation (shortwave) in each time step (kJ)
Q_{sur}	Emitted radiation (longwave) in each time step (kJ)
r	Radius of the pool at the beginning of the time step t_n used in Eq. (10) (m)
r_1	Radius of the pool at the beginning of the time step t_{n-1} used in Eq. (10) (m)
r'	Reflectivity of surface with respect to long-wave radiation
r_{max}	Maximum radius of pool (m)
R	Pool radius (m)
R_0	Pool radius at time $t = 0$ (m)
Re	Reynold's number
SA	Solar altitude ($^\circ$)
Sc	Schmidt number
t	Time since the spill started (s)
t_{s1}	Spill duration (s)
t_{s2}	Release duration (s)
T_1	Temperature of the liquid phase in cases of solidification (K)
T_2	Temperature of the solid phase in cases of solidification (K)
T_a	Air temperature (K)
T_{grd}	Ground temperature (K)
T_1	Released liquid temperature or storage temperature (K)
T_s	Pool temperature (K)
TZ	Time zone factor
u_*	Friction velocity of the airflow (m s^{-1})
$u(z)$	Windspeed at a height z (m s^{-1})
U_{grd}	Overall heat transfer coefficient from the ground ($\text{kJ m}^{-2} \text{h}^{-1} \text{K}^{-1}$)
U_{liq}	Heat transfer coefficient ($\text{kJ m}^{-2} \text{h}^{-1} \text{K}^{-1}$)
V	Pool volume (m^3)
w_g	Water film thickness on the ground (m)
W	Parameter used in Eq. (65)
W_{cem}	Free water in concrete (kg m^{-3})
x	Factor used in Eq. (31)
X_1	Dimensionless parameter used in Eq. (61)
z_0	Roughness length of the substrate (m)
z_1	Reference height (m)
z_2	Height of centroid of a puff of contaminant (m)
z_3	Lower height over which the atmospheric water enters into the pool (m)

Greek letters

α	Constant in the Ergun's equation (= 150)
β	Constant in the Ergun's equation (= 1.75)
γ	Euler's constant (= 0.5772)
δt	Time step (s)
ΔT	Temperature difference of the pool between two successive time steps (K)
ΔV_a	Air volumetric flow rate through and element of height increment dz (m^3)
ϵ	Porosity of concrete
κ	Von Karman's constant

μ	Absolute viscosity of the liquid in the pool (kg s m^{-1})
ν	Kinematic viscosity of the liquid in the pool ($\text{m}^2 \text{s}^{-1}$)
ρ	Density of the liquid in the pool (kg m^{-3})
ρ_a	Molar density of air (mol m^{-3})
σ	Stefan–Boltzmann constant ($= 2.04 \times 10^{-7} \text{ kJ m}^{-2} \text{ h}^{-1} \text{ K}^{-4}$)
σ'	Turbulent Schmidt number of the air ($= 0.85$)
τ	Time of the day when the spill occurs (h)
ϕ	Liquid resistance factor

Constants

a	Constant used in the calculation of the heat of reaction ($= 4.9218$)
b	Constant used in the calculation of the heat of reaction ($= 1.4225 \times 10^{-2}$)
c	Constant used in the calculation of the heat of reaction ($= 1.95 \times 10^{-4}$)
c'	Constant defined by Eq. (51)
d	Constant used in the calculation of the heat of reaction ($= -3.99 \times 10^{-6}$)
e	Constant used in the calculation of the heat of reaction ($= 3.4 \times 10^{-8}$)
R_g	Gas constant

Acknowledgements

The authors wish to thank the HSE (Health and Safety Executive) and especially Mr. David Carter of the Major Hazards Assessment Unit (MHAU), for their invaluable help and for sponsoring this project (project reference number: RSU 3582/R75.025).

Appendix A

All the properties of the liquids in the pool that are used by the model have been parameterised. The values of these properties were found in a number of different literature sources. The equations that have been developed represent values within an accuracy limit of $\pm 3\%$ in most cases. In all cases the error that occurs is less than 10%.

A.1. Density, ρ , (kg/m^3)

Depending on the percentage free sulphur trioxide (p) of the liquid in the pool, the density of the pool is given: For $p \geq 65$:

$$\rho = (1.83 + 0.0025p)1000$$

For $p < 65$:

$$\rho = (2.165 - 0.0025p)1000$$

A.2. Factor x (mol of SO_3 that react per mol water)

An equation has been developed that parameterises the factor x as a function of p , the percentage free SO_3 . This equation consists of two parts. For $x < 65\%$:

$$x = -0.292199\exp(-0.026793p) + 0.142492\exp(0.041691p) + 0.146366$$

For $x \geq 65\%$:

$$x = 0.021125\exp(0.069274p)$$

A.3. Boiling point, bp , (K)

The equation used to calculate the boiling point of the pool is:

$$bp = -30.0719\exp(0.008941p) + 188.2065\exp(-0.052122p) + 385.0089$$

A.4. Freezing point, fr , (K)

For $p \leq 18.5$:

$$fr = -8.1432\exp(-0.29042p) + 303.9425\exp(-0.006582p) - 12.7906$$

For $18.5 < p \leq 45$:

$$fr = -230.1817\exp(-0.048165p) + 315.9571\exp(-0.001328p) + 39.1946$$

For $45 < p \leq 64$:

$$fr = 430.7867\exp(-0.007073p)$$

For $64 < p \leq 86$:

$$fr = 220.2846\exp(0.003326p)$$

For $84 < p \leq 100$:

$$fr = 312.26\exp(0.000765p)$$

A.5. Vapour pressure of SO_3 , P_v , (atm), (T_s is the temperature of the pool in K)

It should be noted that this parameter is a function of two parameters (T_s and p). For $0 < p \leq 10$:

$$P_v = (2.759 + p0.48) * 10^{-8}\exp(0.036532T_s)$$

For $10 < p \leq 20$:

$$P_v = (3.558 + (p - 10)0.666) * 10^{-8}\exp(0.038747T_s)$$

For $20 < p \leq 30$:

$$P_v = (2.104 + (p - 20)0.274) * 10^{-8}\exp(0.043223T_s)$$

For $30 < p \leq 40$:

$$P_v = (1.55 + (p - 30)0.163) * 10^{-8}\exp(0.046453T_s)$$

For $40 < p \leq 50$:

$$P_v = (1.355 + (p - 40)0.168) * 10^{-8}\exp(0.048873T_s)$$

For $50 < p \leq 60$:

$$P_v = (0.99 + (p - 50)0.1152) * 10^{-8}\exp(0.05241T_s)$$

For $60 < p \leq 70$:

$$P_v = (1.5 + (p - 60)0.1143) * 10^{-8} \exp(0.053485T_s)$$

For $70 < p \leq 80$:

$$P_v = (0.547 + (p - 70)0.0086) * 10^{-8} \exp(0.058362T_s)$$

For $80 < p \leq 100$:

$$P_v = (0.672 + (p - 80)0.01015) * 10^{-8} \exp(0.058302T_s)$$

A.6. Vapour pressure of H_2SO_4 , P_{va} , (atm)

For $0 < p \leq 10$:

$$P_{va} = (1 - (p/0.04))2.42 * 10^{-8} \exp(0.053758T_s) / 101325$$

For $10 < p \leq 15$:

$$P_{va} = (1 - (p - 10)0.0522)3.94 * 10^{-11} \exp(0.070878T_s) / 101325$$

For $15 < p \leq 20$:

$$P_{va} = (1 - (p - 15)0.0585)3.08 * 10^{-12} \exp(0.077188T_s) / 101325$$

For $20 < p \leq 25$:

$$P_{va} = (1 - (p - 20)0.0683)8.22 * 10^{-13} \exp(0.079706T_s) / 101325$$

For $25 < p \leq 35$:

$$P_{va} = (1 + (p - 25)0.0874)1.43 * 10^{-11} \exp(0.071161T_s) / 101325$$

A.7. Partial pressure of SO_3 and H_2SO_4

The equations that best calculate the partial pressure of SO_3 , H_2SO_4 at the boiling point are: For $0 < p \leq 10$:

$$P_{vSO_3} = -0.242984 \exp(-0.2322143p) + 1.0949 \exp(-0.0002507p) - 0.087486$$

$$P_{vH_2SO_4} = 1 - P_{vSO_3}$$

For $p \leq 35$ and $p > 10$:

$$P_{vSO_3} = -0.242984 \exp(-0.2322143p) + 1.0949 \exp(-0.0002507p) - 0.087486$$

$$P_{vH_2SO_4} = 1 - P_{vSO_3}$$

A.8. Heat capacity, C_p , ($kJ kg^{-1} K^{-1}$)

For $0 < p \leq 20$:

$$C_p = 1.4$$

For $20 < p \leq 97$:

$$C_p = 1.0069 \exp(0.010268 p)$$

For $97 < p \leq 100$:

$$C_p = 2.75 - 0.0005 p$$

A.9. Thermal conductivity, K_{liq} , ($\text{kJ m}^{-1} \text{s}^{-1} \text{K}^{-1}$)

$$K_{liq} = (0.051755_s - 4.4237) \times 10^{-6}$$

A.10. Kinematic viscosity, ν , ($\text{m}^2 \text{s}^{-1}$)

This parameter is also a function of two parameters (T_s and p). For $0 < p \leq 20$:

$$\nu = (-0.002529 T_s^2 + 1.3025 T_s - 141.9836) / 1\,820\,000$$

For $20 < p \leq 30$:

$$\nu = (-0.009846 T_s^2 - 6.87485 T_s + 1207.3045) / 1\,875\,000$$

For $30 < p \leq 40$:

$$\nu = (-0.0109615 T_s^2 - 7.69745 T_s + 1359.2725) / 1\,910\,000$$

For $40 < p \leq 50$:

$$\text{For } T_s < 308 \quad \nu = 35.5 / 1\,930\,000$$

$$\text{For } T_s \geq 308 \quad \nu = (0.01359 T_s^2 - 9.50815 T_s + 1671.612) / 1\,930\,000$$

For $50 < p \leq 60$:

$$\nu = (0.0362075 T_s^2 - 23.7712 T_s + 3918.894) / 1\,945\,000$$

For $60 < p \leq 70$:

$$\nu = (0.0472855 T_s^2 - 30.543 T_s + 4946.7375) / 1\,925\,000$$

For $70 < p \leq 80$:

$$\nu = (0.0397145 T_s^2 - 25.47515 T_s + 4094.647) / 1\,885\,000$$

For $80 < p \leq 100$:

$$\nu = (0.02063315 T_s^2 - 13.147119 T_s + 2098.36635) / 1\,860\,000$$

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