



# A model for spills of SO<sub>3</sub> and oleum Part II. Results, conclusions and discussion

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## Abstract

Part I of this paper gives details of the model for pool behaviour [T. Kapias, R.F. Griffiths, A model for spills of SO<sub>3</sub> and oleum, Part I: Model description, J. Haz. Mater.]. The model has been run for a large number of release scenarios, and it is found that the behaviour of the pool is governed principally by the amount of water available for reaction. The friction velocity of the airflow also has a relatively strong effect on the results. The rest of the input parameters have less influence on the pool behaviour. The model is well behaved, and a number of useful conclusions and observations on the pool behaviour can be made. The sensitivity of the model to the three water sources (free water lying on the ground, atmospheric water and concrete water) is examined. It is shown that in most cases the model results are not sensitive to the assumptions concerning the height of the atmospheric layer from which moisture is absorbed into the pool, or the total water content of the concrete. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* SO<sub>3</sub>; Oleum; Model

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## 1. Introduction

SO<sub>3</sub> or oleums are usually stored and transported in their liquid form. Therefore, almost all of the accidents that have occurred in the past involved the generation of a liquid pool (with the exception of the Richmond accident [2]). Although there are numerous pool evaporation models in the literature, almost all of them deal with non-reactive liquids that have relatively low vapour pressures at ambient temperatures.

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The new model (apart from describing spills of  $\text{SO}_3$  and oleum) can be used (with slight modifications) for the description of other reactive chemicals. Its major advantages are:

- it describes the pool behaviour in a realistic way, taking into account all the relevant properties of the liquids,
- although the pool behaviour is very complicated, running times are very satisfactory (less than half hour on a Pentium 150),
- the same model can be used for spills of different strengths of oleum, either continuous (varying or steady) or instantaneous, and
- it can be used for other reactive liquids.

The model results show that the pool behaviour is governed by the amount of water available for reaction. This parameter influences the evolution rate and thus the initial dispersion behaviour of the cloud. This cloud can either behave as a dense-gas cloud or as a passive one depending on a number of conditions and mainly on the atmospheric water content and the vapour evolution rate [3,4].

## 2. Results

The results of a large number of different release scenarios were examined. The ones presented in the following section were judged to be the most representative and appropriate for each case. In the following pages, the values of the release scenarios input parameters are shown in Table 1.

### 2.1. Water supply to the pool

There are three sources of water supply to the pool: free water lying on the ground, atmospheric water and substrate water [1]. In Fig. 1, it is shown that the main water source is the free water lying on the ground. Atmospheric water is also a significant water source and it becomes the dominant source when the availability of water on the

Table 1

Values of the release scenarios input parameters

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Spill rate and duration = $16 \text{ kg s}^{-1}$ for 600 s
Type of spill: continuous spill of $\text{SO}_3$ , 65, 30 and 20% oleum
Maximum duration of the release to the atmosphere = 1800 s
Maximum radius of the pool = 50 m
Free water film thickness on the ground, $w_g = 0.00005, 0.0001, 0.0005, 0.001, 0.0015, 0.002, 0.0025 \text{ m}$
Air temperature = 288 K
Location: North England, UK (latitude = $54^\circ$ , longitude $2^\circ$ , time zone = 0)
Time and day: 0900 and 298 (25th of October)
Friction velocity of the airflow, $u^* = 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.5 \text{ m s}^{-1}$
Atmospheric radiation factor and cloud cover factors = 0.84 and 7, respectively
Type of surface and roughness length: concrete, 0.1 m
Time step used in the calculations: 0.01 s
Mass mixing ratio of the air = 0.007 ( $\approx 70\%$ relative humidity)

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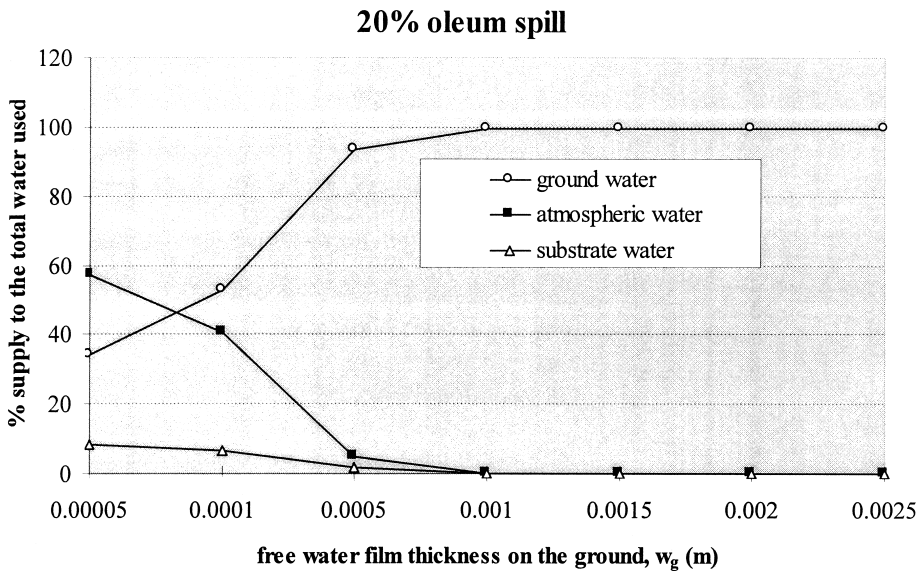
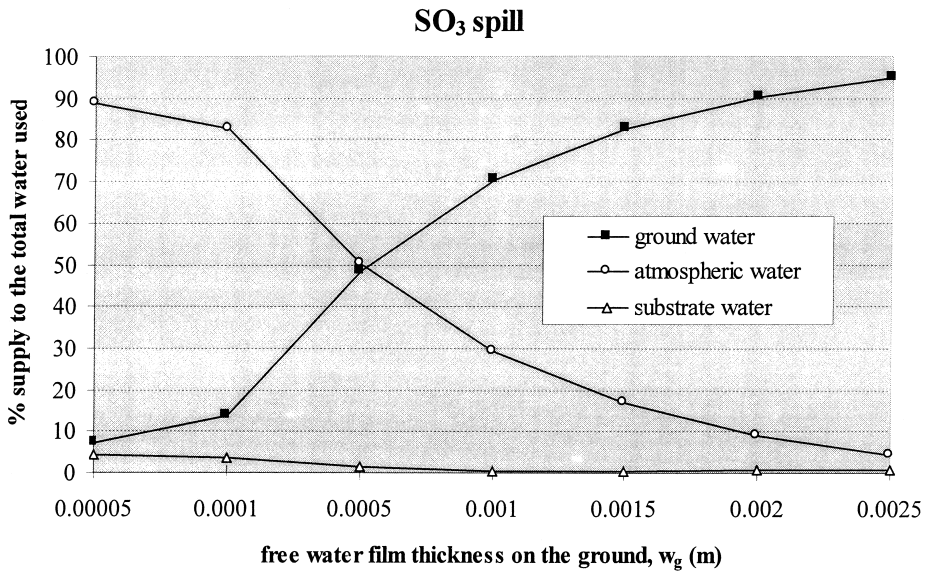


Fig. 1. Percentage supply of the three water sources to the total amount of water provided for reaction with SO<sub>3</sub> for spills of 16 kg s<sup>-1</sup> for 600 s (release duration = 1800 s) of SO<sub>3</sub> and 20% oleum ( $u^* = 0.2$  m s<sup>-1</sup>).

ground is very low. It is more significant for SO<sub>3</sub> spills than for spills of lower strength (the atmospheric water being absorbed is proportional to the percentage free SO<sub>3</sub> of the liquid in the pool [1]). Concrete water is the least important source and it is usually higher when the amount of ground water is low.

2.2. Free water film thickness on the ground  $w_g$  (m)

As shown in Section 2.1, the main water source into the pool is the free water lying on the ground. Therefore, the input parameter that mostly affects the results is the free water film thickness on the ground. The effect of the water film thickness on the total

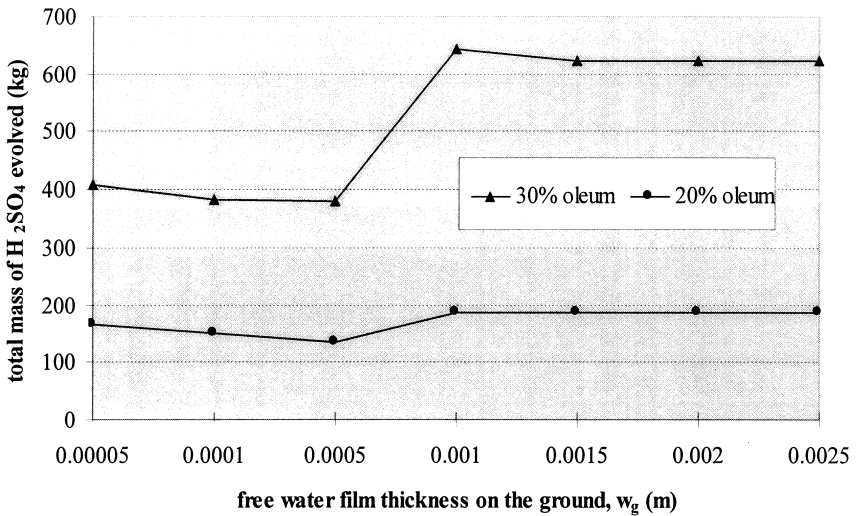
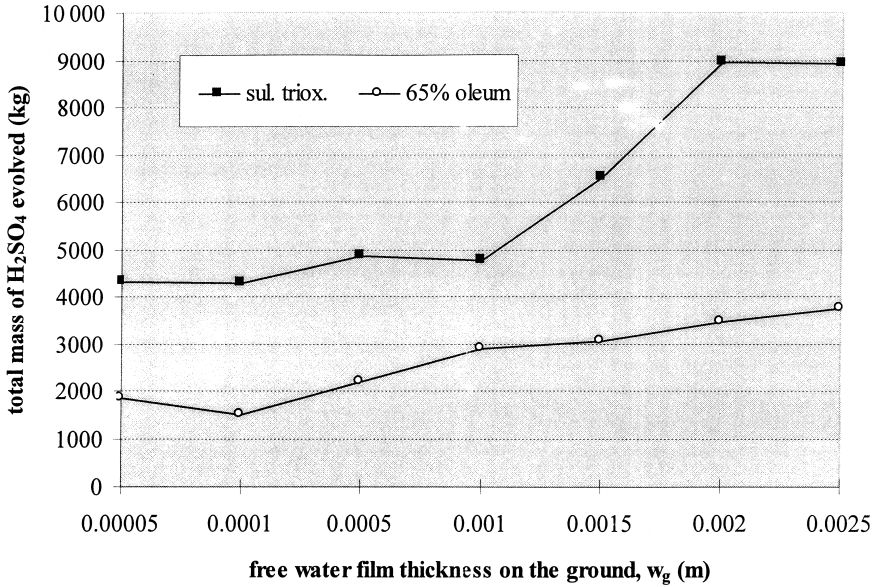


Fig. 2. Effect of free water film thickness effect on the total amount of H<sub>2</sub>SO<sub>4</sub> evolved to the atmosphere for spills of 16 kg s<sup>-1</sup> for 600 s (release duration = 1800 s) of SO<sub>3</sub>, 65, 30 and 20% oleum ( $u^* = 0.2$  m s<sup>-1</sup>).

amount of  $H_2SO_4$  evolved is shown in Fig. 2. The total amount of  $H_2SO_4$  evolved to the atmosphere is calculated by the following equation:

$$(\text{total } H_2SO_4 \text{ evolved}) = (\text{total } H_2SO_4 \text{ evolved}) + (98/80) * (\text{total } SO_3 \text{ evolved})$$

In other words, although  $SO_3$  vapour will be evolved from the pool, this will react with any atmospheric moisture yielding  $H_2SO_4$  vapour.

The relationship between water availability and  $SO_3$  and  $H_2SO_4$  evolution rates is very complicated. It might be expected that when there is more water available, the

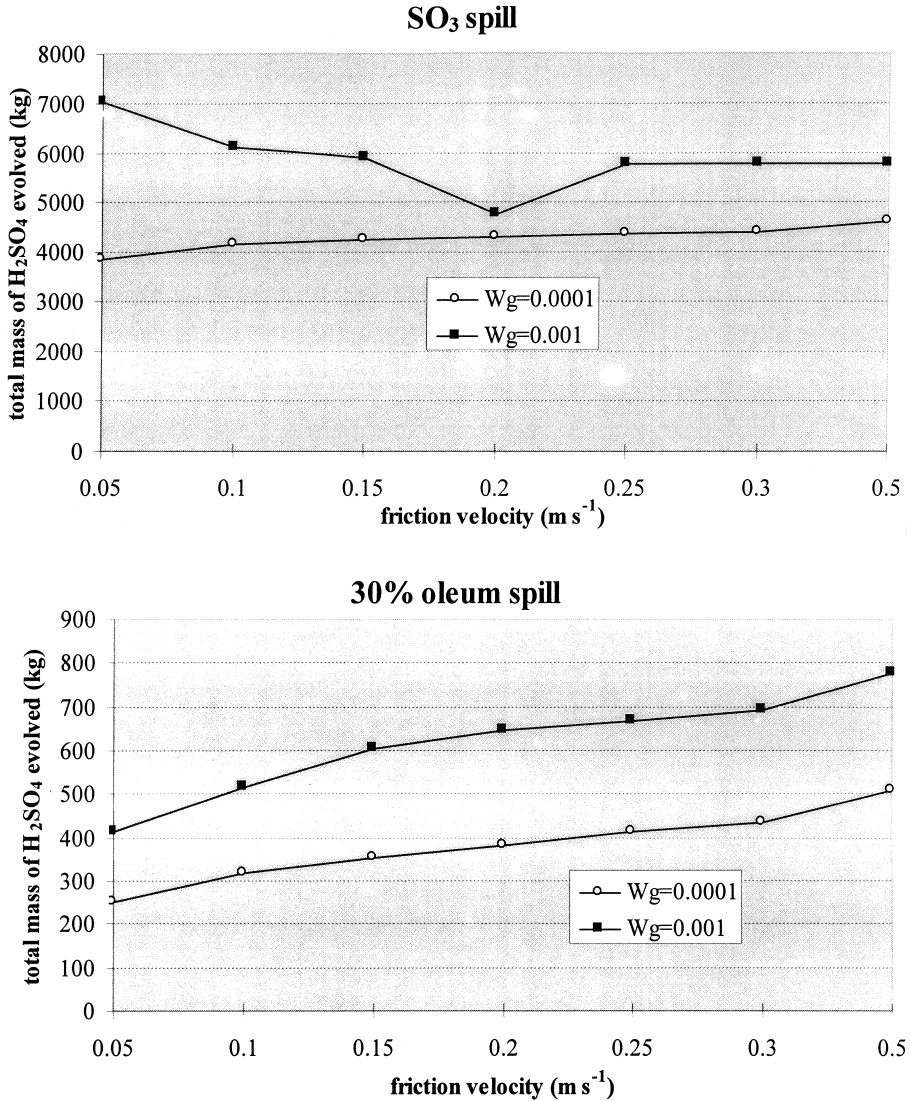


Fig. 3. Effect of friction velocity of the airflow on the total amount of  $H_2SO_4$  evolved for spills of  $16 \text{ kg s}^{-1}$  for 600 s (release duration = 1800 s) of  $SO_3$  and 30% oleum.

values of the evolution rates should be higher. However, when there is more water available there is more  $\text{H}_2\text{SO}_4$  being produced in the liquid phase and although the pool temperature is higher, the percentage free  $\text{SO}_3$  in the liquid is lower. The vapour pressure of the liquid in the pool is affected by both parameters. It increases with increasing temperature but it decreases with decreasing pool strength (expressed as percentage free  $\text{SO}_3$ ) [1,5,6]. Therefore, it depends on the degree of change of the values of these parameters as to whether the evolution rates will be higher or lower. In Fig. 2 (spills of 30 and 20% oleum), it is shown that above a certain value of free water film thickness, the amount of total  $\text{H}_2\text{SO}_4$  evolved remains almost stable. This occurs because above a certain value, all the  $\text{SO}_3$  will be reacted to  $\text{H}_2\text{SO}_4$  liquid. The higher availability of water will only affect the pool behaviour by the excess of water that will be present in the pool.

### 2.3. Friction velocity of the airflow

The friction velocity influences the value of the wind speed and thus the evolution rates of  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  from the pool. Fig. 3 depicts its effect on the total amount of

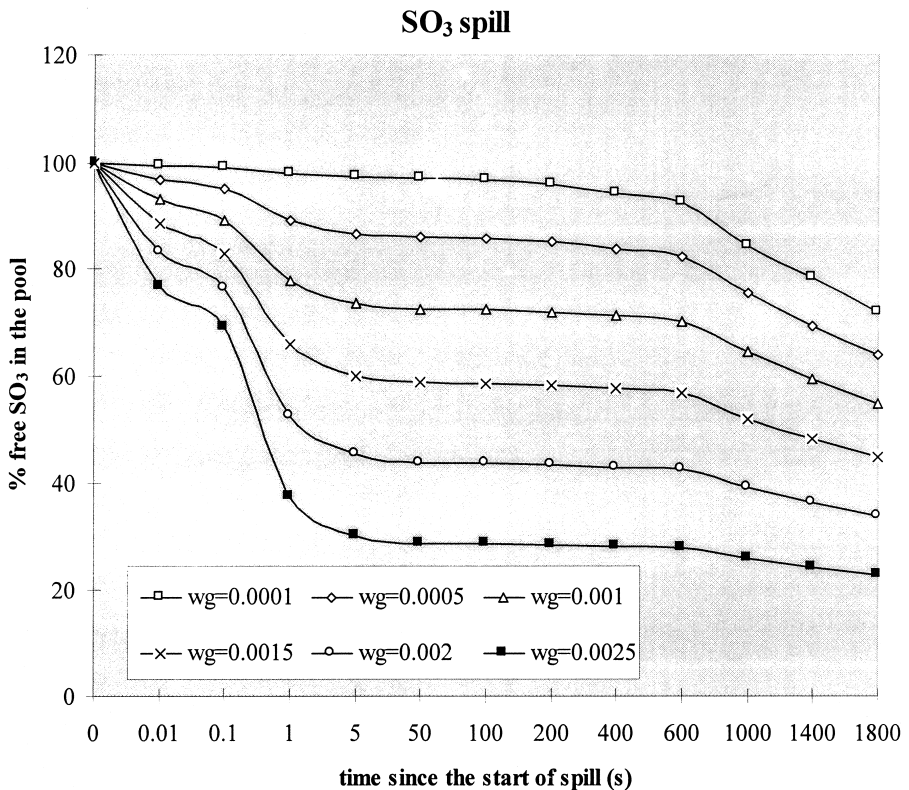


Fig. 4. Pool composition change during the release duration (= 1800 s) for spills of  $16 \text{ kg s}^{-1}$  for 600 s of  $\text{SO}_3$  at different  $w_g$  ( $u^* = 0.2 \text{ m s}^{-1}$ ).

$\text{H}_2\text{SO}_4$  evolved. For spills of oleum of low strength (30 and 20%), it is shown that the evolution rates increase with increasing friction velocity (due to the higher wind speed). The same behaviour is observed for spills of oleum of high strength ( $\text{SO}_3$  and 65%) at low values of free water film thickness on the ground (e.g.  $w_g = 0.0001$  m). However, for spills of oleum of high strength or  $\text{SO}_3$  spills, at higher values of  $w_g$  (e.g.  $w_g = 0.001$  m), the influence of the friction velocity becomes very complicated. The percentage free  $\text{SO}_3$  content of the liquid in the pool decreases with increasing free water film thickness. Additionally, if the friction velocity is high, the amount of  $\text{SO}_3$  evolved at the early stages of the spill would be higher resulting in an even lower pool strength. Accordingly, the vapour pressure would be lower and so both the vapour concentration and the dimensionless local evaporation rate would be lower (Eqs. (58) and (59) of part I [1]). The evaporation rate is directly proportional to the friction velocity, to the vapour concentration and to the local evaporation rate (Eq. 2.6.7 of part I [1]). Thus, it depends on the degree of change of these parameters as to whether the evolution rates will be lower or higher. Generally, it might be expected that the evolution rates will increase with increasing friction velocity in every case. However, at high  $w_g$  and high spill strengths, the influence of the friction velocity becomes very complicated. The effect of the friction velocity on the total amount of  $\text{H}_2\text{SO}_4$  evolved is less strong than the effect of the free ground water film thickness.

#### 2.4. Pool composition (percentage free $\text{SO}_3$ of the liquid in the pool)

The pool composition expressed as percentage free  $\text{SO}_3$  of the liquid in the pool is not constant; it changes continuously and so do all the pool properties [1]. In Fig. 4, it is

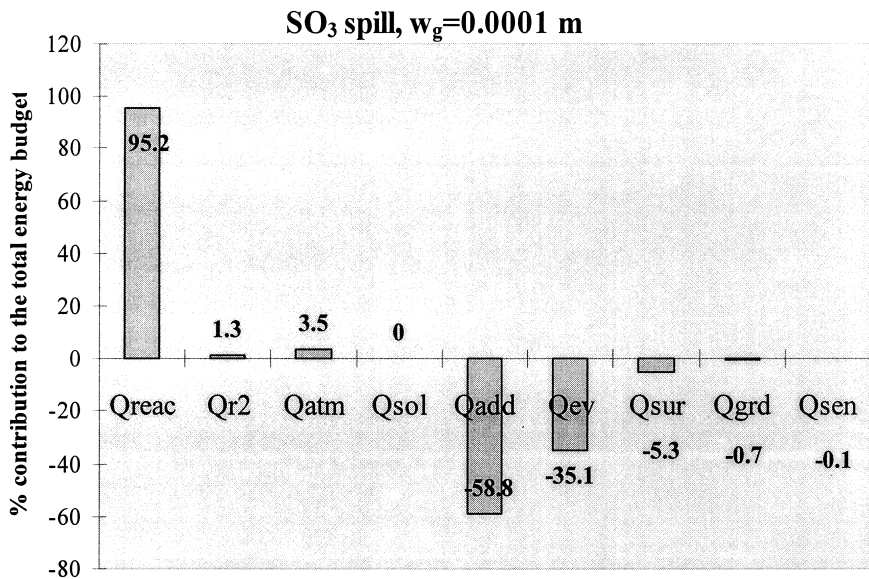


Fig. 5. Percentage contribution of all the energy terms to the total energy budget for a spill of  $16 \text{ kg s}^{-1}$  for 600 s of  $\text{SO}_3$  (release duration = 1800 s,  $w_g = 0.0001$  m,  $u^* = 0.2 \text{ m s}^{-1}$ ).

shown that even if  $\text{SO}_3$  is spilled, at the end of the release the pool will consist of oleum of a much lower strength. The percentage free  $\text{SO}_3$  content of the pool decreases with increasing free water film thickness on the ground ( $w_g$ ).

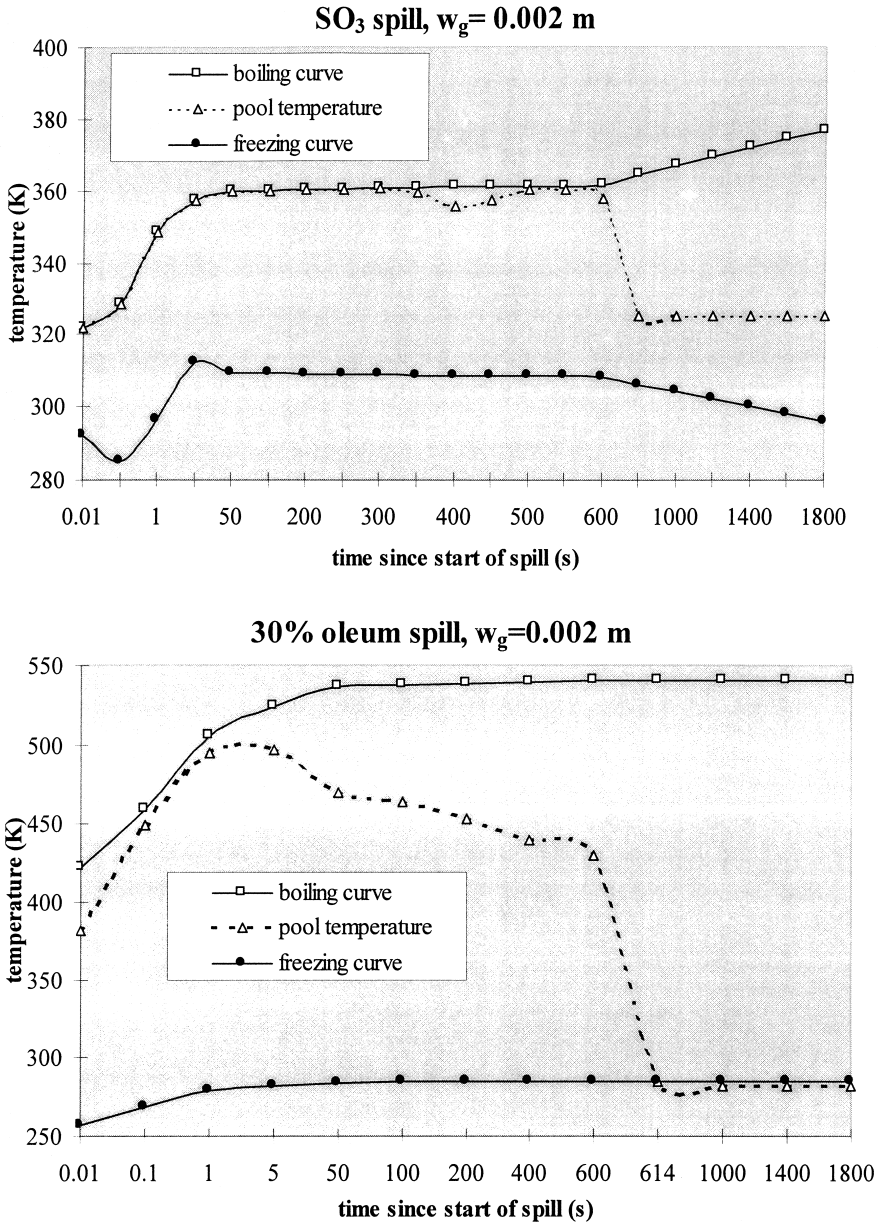


Fig. 6. Pool boiling and solidification for spills of  $16 \text{ kg s}^{-1}$  for 600 s (release duration = 1800 s) of  $\text{SO}_3$  and 30% oleum ( $u^* = 0.2 \text{ m s}^{-1}$ ).



### 2.5. Energy balance

The supply of each energy term in the final energy balance [1] has been examined. It has been found that the heat of reaction ( $Q_{\text{reac}}$ ) between water and  $\text{SO}_3$  is the main energy input to the pool ( $> 90\%$ ) even at low values of free water film thickness ( $w_g = 0.0001$  m). The main energy outputs are the energy of addition ( $Q_{\text{add}}$ ) ( $\approx 40\text{--}60\%$ ) and the evaporation energy ( $Q_{\text{ev}}$ ) ( $\approx 30\text{--}50\%$ ). It should be noted that the energy of addition is equal to zero after the spill ceases (in the investigated scenarios, between 600 and 1800 s). The rest of the energy inputs and outputs (all of them taken together) (see part I [1]) contribute less than 10% of the energy budget. The scenario depicted in Fig. 5 involves only pool evaporation. The energy balance is modified in cases of pool boiling or solidification [1].

### 2.6. Pool boiling and solidification

The pool usually boils at relatively high values of free water film thickness ( $w_g > 0.0005$  m). It usually boils in the early stages of the spill ( $< 200$  s since the spill started) as shown in Fig. 6. This occurs because at the early stages the pool area is still small and the main energy input per unit area, the heat of reaction between  $\text{SO}_3$  and water, is high. It should be noted that although the reaction of  $\text{SO}_3$  and ground  $\text{H}_2\text{O}$  (which usually is the dominant water source) occurs at the edges of the pool, it is assumed that this heat is mixed instantaneously and distributed equally to the whole area of the pool. Therefore, in the early stages it is distributed to a smaller area. In the later stages (time since the spill has started between 200 and 600 s), the pool area becomes bigger, the heat input per unit area becomes lower, and the percentage free  $\text{SO}_3$  drops, resulting in a higher boiling point. Thus, it is more unlikely that boiling will occur, unless the water availability is high.

Solidification of the pool occurs in most cases after the spill ceases (after the 600 s of the spill duration) as shown in Fig. 6. Generally, it is almost impossible to predict the possibility of solidification (after the spill ceases) of a known spill, because of the complexity of the oleum freezing curves [5,6] and furthermore solidification occurrence is a function of many parameters. The pool rarely solidifies before the spill has ceased. This can only happen when the water availability is extremely low.

## 3. Model sensitivity to the assumptions involving the atmospheric water and the total concrete water

### 3.1. Concrete water

The total concrete water is the sum of the free water in the void spaces (excluding the capillary voids), the chemically combined water, the gel water and the capillary water. The last three concrete water sources are assumed to be equal to 0.2 kg/kg of dry cement [7]. These concrete water sources are difficult to determine because they depend heavily on the concrete type, its compounds (cement and aggregates), the environment it is exposed to etc. [7,8]. In this section, 'concrete water' corresponds to these last three concrete water sources. The sensitivity of the model to this variable is examined for a

Table 2

Model sensitivity to the water concrete assumption

Scenario	Concrete water (kg/kg of dry cement)	Percentage change from the adopted value	Total amount of H <sub>2</sub> SO <sub>4</sub> evolved (kg)	Percentage change from scenario b
a	0.1	−50%	1822.35	−0.2%
b	0.2	0	1826.1	0
c	0.4	+100%	1834.44	+0.46%

fixed value of the free water in the void spaces (set at 180 kg m<sup>−3</sup> of concrete). In Section 2.1, it is shown that the concrete water is the least significant water source and it is more significant for low values of free ground water film thickness. Therefore, the model sensitivity has been examined for spills of 65% oleum for 600 s (release duration = 1800 s,  $u^* = 0.2 \text{ m s}^{-1}$ ) at a free water film thickness equal to 0.00005 m. The results of the runs for three different spill scenarios were examined as shown in Table 2. Scenario b corresponds to the value that was adopted in the model.

As shown in Table 2, the model results are not sensitive to the assumption about the water content of the concrete. Even for water concrete content changes of 100%, for spill scenarios in which the water concrete is of most importance, the results change less than 0.5%. Therefore, it concluded that the model is not sensitive to this assumption.

### 3.2. Atmospheric water

The atmospheric water content is described by assuming that all the atmospheric water content of up to a height  $H'$  above the surface roughness length is absorbed by the pool [1]. It has also been assumed that the parameter  $H'$ (m) is not constant; it is a function of the pool radius  $R$  (m), and the percentage free SO<sub>3</sub> ( $p$ ) of the liquid in the pool. The equation used is [1]:  $H' = (R/30) * (p/100)$ .

As discussed in Section 2.1, the atmospheric water is a relatively significant water source and it becomes the dominant water source when the amount of free water lying on the ground is low. It was also shown that its significance increases with increasing spill strength. Therefore, the model sensitivity was checked for spills of 16 kg s<sup>−1</sup> for 600 s of 65% oleum (release duration = 1800 s,  $u^* = 0.2 \text{ m s}^{-1}$ ) at a free ground water film thickness equal to 0.00005 m and 0.001 m. The results of the analysis are summarised in Table 3. The spill scenarios under investigation correspond to the following assumptions: Scenario A:  $H' = (R/20) * (p/100)$ ; Scenario B:  $H' = (R/30) * (p/100)$  (adopted in the model); Scenario C:  $H' = (R/40) * (p/100)$ .

As shown in Table 3, the model results become sensitive to the assumption concerning the atmospheric water only at low values of free ground water film thickness. Generally, the model sensitivity increases with increasing spill strength and decreasing ground water availability. In other words, the model becomes sensitive in cases where the atmospheric water is the dominant water source ( $w_g < 0.0005 \text{ m}$ ). For spills of lower strengths (20 or 30% oleum) or when the amount of ground water is not low ( $w_g > 0.0005 \text{ m}$ ), the model is not sensitive to the assumption concerning the atmospheric water that is being absorbed by the pool. Since such low values ( $w_g < 0.0005$

Table 3  
Model sensitivity to the atmospheric water assumption

Scenario	Free water film thickness (m)	Percentage change from the adopted value	Total amount of H <sub>2</sub> SO <sub>4</sub> evolved (kg)	Percentage change from scenario B
A	0.00005	+ 33.33%	2513.38	+ 37.6%
B	0.00005	0	1826.1	0
C	0.00005	– 25%	1429.37	– 21.7%
A	0.001	+ 33.33%	3108.32	+ 7.5%
B	0.001	0	2891.87	0
C	0.001	– 25%	2786.97	– 3.6%

m) are rarely encountered, the general conclusion is that in the majority of the accidental spill cases the model results are not sensitive to this assumption.

#### 4. Discussion and further improvements

The main conclusions and observations have been discussed in Section 2. Generally, the results are very satisfactory in indicating critical aspects of the pool behaviour. They are generally not sensitive to the two assumptions concerning the water concrete content and the atmospheric water entering into the pool, as discussed in Section 3.

In the model, it is assumed that the pool composition, temperature and properties are uniform (average values are calculated). It is supposed that all the energy input is equally distributed to the pool area. As already mentioned, the main energy input is the heat of reaction between SO<sub>3</sub> and water. The most significant water source is the free water lying on the ground and the reaction that occurs between this water and SO<sub>3</sub> takes place at the spreading edges of the pool. Therefore, most of the energy input comes from the pool edges. Inside the pool, there will be a heat flux directed from the edges (highest temperature area,  $T_{\text{smmin}}$ ) to the centre (lowest temperature area  $T_{\text{smmax}}$ ). Apart from this, the liquid at the pool edges will have a lower percentage free SO<sub>3</sub> ( $p$ ) due to the consumption of SO<sub>3</sub> and the subsequent production of H<sub>2</sub>SO<sub>4</sub>. Thus, the liquid at the pool centre will have the highest value of free SO<sub>3</sub> ( $p_{\text{max}}$ ) and at the edges the lowest ( $p_{\text{min}}$ ). A representation of the temperature and composition profiles inside the pool is shown in Fig. 7.

Most of the properties of the liquid in the pool depend on both the pool temperature and the percentage free SO<sub>3</sub> and they increase with increasing temperature and percentage free SO<sub>3</sub>. Therefore, the properties of the liquid in the pool are probably not highly variable, as the areas of higher temperature have lower percentage free SO<sub>3</sub>. Although, for example, the pool temperature is the highest at the edge that does not mean that the edge evolution rate is the highest, because the local percentage free SO<sub>3</sub> is the lowest, and the liquid vapour pressure depends on both parameters.

Thus, it can be argued that the assumption concerning the pool temperature and composition uniformity may not significantly alter the results. Incorporation of tempera-

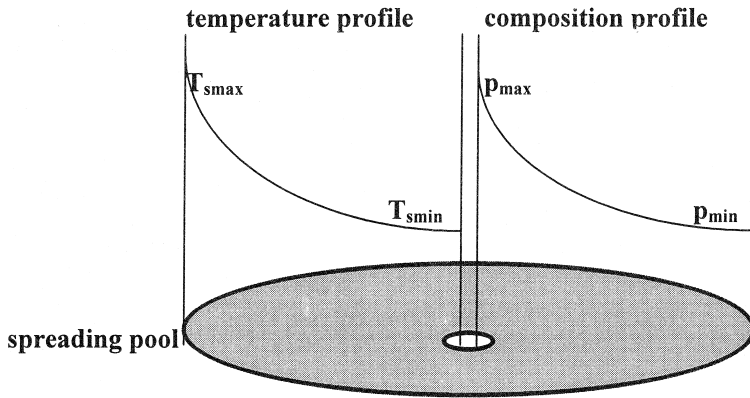


Fig. 7. Temperature and composition profiles inside the pool.

ture and composition profiles and the associated heat fluxes will make the model more complicated, increasing the running times significantly (3-D equations would have to be solved).

The model is mainly based on theoretical information as there are no experimental data relevant to the modelling requirements. Further improvement and validation depends on the availability of experimental data. Therefore, it is strongly recommended that experiments should be carried out to establish the necessary data for model validation.

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