37.1 INTRODUCTION

Sulfur trioxide (SO₃) and oleums are generally aggressive materials with complicated properties. They are widely used in the process industries. Their main feature is the violent reaction of SO₃ and water that occurs in both the liquid and the vapor phase. Oleum (or fuming sulfuric acid) is a solution of sulfur trioxide in 100% sulfuric acid. Its strength is expressed as weight percentage free SO₃; thus 30% oleum contains 30% SO₃ and 70% H₂SO₄ by weight. The most commonly industrially used strengths are 65%, 30%, and 20% oleum; their hazardous potential increases with increasing strength.

37.1.1 Uses—Main Properties

Sulfur trioxide is a clear, oily, colorless liquid. As shipped, it may contain a haze and be off-white to light brown in appearance. Oleum is normally turbid and off-white in appearance. Their main uses are in the production of plastics, detergents, and dyestuffs (Kirk-Othmer, 1983; Duecker and West, 1971).

The properties of these substances are complicated and are dependent on the percentage free SO₃ and the temperature. Some of these properties are summarised in Table 37.1. Their

<table>
<thead>
<tr>
<th>Properties</th>
<th>SO₃</th>
<th>65% oleum</th>
<th>30% oleum</th>
<th>20% oleum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point (°C)</td>
<td>17</td>
<td>2</td>
<td>19</td>
<td>-10</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>45</td>
<td>58</td>
<td>121</td>
<td>142</td>
</tr>
<tr>
<td>Density at 30°C (kg m⁻³)</td>
<td>1,880</td>
<td>1,975</td>
<td>1,920</td>
<td>1,880</td>
</tr>
<tr>
<td>Heat capacity at 20°C (kJ kg⁻¹ K⁻¹)</td>
<td>2.70</td>
<td>1.85</td>
<td>1.43</td>
<td>1.41</td>
</tr>
<tr>
<td>Vapor pressure at 20°C (atm)</td>
<td>0.228</td>
<td>0.141</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Vapor pressure at 50°C (atm)</td>
<td>1.316</td>
<td>0.789</td>
<td>0.049</td>
<td>0.021</td>
</tr>
<tr>
<td>Viscosity at 20°C (cP)</td>
<td>2.2</td>
<td>55</td>
<td>48</td>
<td>39</td>
</tr>
</tbody>
</table>
boiling and freezing curves are shown in Fig. 37.1. More detailed descriptions can be found elsewhere (Kirk-Othmer, 1983; Duecker and West, 1971; Du Pont Chemicals, 1988).

**37.1.2 Legislation**

The hazardous nature of SO\(_3\) and oleum is recognized in various items of legislation relating to industrial safety. In the United Kingdom, SO\(_3\) is included in the Notification of Installations Handling Hazardous Substances Regulations (NIHHS, 1982) and in the list of substances covered by the Control of Industrial Major Accident Hazards Regulations (CIMAH Regulations, 1984). Under the new Seveso II European Union (EU) Directive, all substances that react violently with water or liberate toxic gases when in contact with water, are described as major hazards and should be included in the list of substances covered by this directive (European Union, 1996). Therefore, each member state should include not only SO\(_3\) but all strengths of oleums in its new regulations on major hazards. This EU Directive has been implemented in the United Kingdom as the COMAH Regulations, which came into force on April 1, 1999 (COMAH Regulations, 1999).

**37.2 EFFECTS ON HUMANS AND THE ENVIRONMENT**

On escape to the atmosphere, SO\(_3\) reacts violently and highly exothermically with water, producing fumes of sulfuric acid mist. Information on the acute effects of exposure to sulfuric acid mist is available from animal studies and from studies on human volunteers involving both healthy and asthmatic subjects. A detailed review of the health effects of sulfuric acid aerosols can be found in an IChemE monograph (Griffiths, 1996). This review is mainly concerned with acute effects, as is appropriate for the accidental exposures of interest in major hazards. With regard to long-term exposures, it is noteworthy that a report of the International Agency for Research on Cancer concludes that long-term occupational exposure to strong inorganic mists containing H\(_2\)SO\(_4\) is carcinogenic to humans (IARC, 1992).
37.2.1 Human Toxicity Data

From volunteer studies, it was shown that irritant responses to $H_2SO_4$ mist generally occur at exposure concentrations above 1 mg m$^{-3}$. It was also shown that this response is strongly dependent on droplet size, with droplets less than 1 $\mu$m in diameter producing no respiratory effects. Studies using aerosols with droplet diameters in the range of 1 to 1.54 $\mu$m have produced a variety of concentration-dependent respiratory changes and symptoms of irritancy. It should be noted, though, that the studies with submicron-sized mists of sulfuric acid were conducted for exposures of short duration (usually 15 minutes) and at very low concentrations (0.1 to 1 mg m$^{-3}$). Thus, no clear conclusion can be drawn concerning the possible effects of mists of submicron particle size at higher exposure concentrations and longer times. Human responses observed during these tests are summarized in Table 37.2.

37.2.2 Animal Toxicity Data

Most of the work on toxicity data of $H_2SO_4$ mist has been done using the guinea pig because it appears to be a better model for man than other rodents. Consistent with evidence from human studies, the toxicity of $H_2SO_4$ mist in animals is also dependent on the ambient humidity and the aerosol particle size. The relative humidity affects particle size due to the hygroscopic nature of the acid droplets (Wolff et al., 1979).

There is little doubt in the literature that the guinea pig is considerably more sensitive to the effects of inhalation of $H_2SO_4$ mist than other laboratory species and other larger animals.

### TABLE 37.2 Human Toxicity Data

<table>
<thead>
<tr>
<th>Exposure conditions</th>
<th>Human responses</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 mg m$^{-3}$ for 4 hours</td>
<td>No changes in pulmonary function in normal subjects (Kerr et al., 1981).</td>
</tr>
<tr>
<td>0.35 mg m$^{-3}$ for 5 to 15 minutes</td>
<td>Decreases in tidal volume and increases in respiratory rate (Amdur et al., 1952a).</td>
</tr>
<tr>
<td>0.4 mg m$^{-3}$ for 1 hour</td>
<td>No changes in pulmonary function attributable to $H_2SO_4$ mist were seen; subjects undertook alternate 10-minute periods of exercise and rest during exposures (Linn et al., 1986).</td>
</tr>
<tr>
<td>0.45 mg m$^{-3}$ for 16 minutes</td>
<td>Increases in airway resistance in asthmatics (Utell et al., 1983).</td>
</tr>
<tr>
<td>1 mg m$^{-3}$ for 10 minutes</td>
<td>No changes in pulmonary function were seen in normal and asthmatic subjects (Sackner et al., 1978).</td>
</tr>
<tr>
<td>1 mg m$^{-3}$ for 5 to 15 minutes</td>
<td>Odor threshold (Amdur et al., 1952a).</td>
</tr>
<tr>
<td>1 and 2 mg m$^{-3}$ for 1 hour</td>
<td>Normal and asthmatic subjects undertook three 10-minute exercise periods during exposure; no changes in pulmonary function were seen at 1 mg m$^{-3}$; slight effects and symptoms of irritancy at 2 mg m$^{-3}$ (Avol et al., 1988).</td>
</tr>
<tr>
<td>1 to 5 mg m$^{-3}$ for 5 to 15 minutes</td>
<td>Irritation, coughing, rapid shallow breathing (Amdur et al., 1952a; Sim and Pattle, 1957).</td>
</tr>
<tr>
<td>1.4 mg m$^{-3}$ for 2 hours</td>
<td>No pulmonary changes were seen, but throat irritation and coughing were experienced; subjects undertook intermittent exercise during exposure (Horvath et al., 1981).</td>
</tr>
<tr>
<td>20.8 mg m$^{-3}$ for 30 minutes</td>
<td>Initially intolerable with intense coughing, lacrimation and rhinorrhea which did not cease entirely throughout the exposure period (Sim and Pattle, 1957).</td>
</tr>
<tr>
<td>39 mg m$^{-3}$ for 1 hour</td>
<td>Bronchoconstriction, rales, coughing; increases in airway resistance up to 100% above normal (Sim and Pattle, 1957).</td>
</tr>
</tbody>
</table>
The mouse, rabbit, monkey, cat, sheep and donkey have all been subjected to a variety of exposure regimes and are all less responsive to H\textsubscript{2}SO\textsubscript{4} mist than the guinea pig (Cameron, 1954; Treon et al., 1950). Overall, the 8-hour LC\textsubscript{50} for the guinea pig lies in the range 18 to 30 mg m\textsuperscript{-3}. At a concentration of 8 mg m\textsuperscript{-3}, there was no lethality to the guinea pig, even with an exposure duration of 72 hours (Amdur et al., 1952b). A more detailed overview of animal toxicity data can be found in the IChemE monograph (Griffiths, 1996).

### 37.2.3 Relationship between Animal and Human Toxicity

It should be noted that there are no quantitative data concerning human exposures to acutely toxic or lethal concentrations of H\textsubscript{2}SO\textsubscript{4} mist. Animal studies indicate that only the guinea pig shows a degree of respiratory tract sensitivity to H\textsubscript{2}SO\textsubscript{4} mist similar to human responses. However, the guinea pig appears to be particularly susceptible to the lethal effects of H\textsubscript{2}SO\textsubscript{4} mist due to an intense bronchoconstriction and possible laryngospasm mechanism that occurs in the species. After detailed investigation of the toxicity data, the working party of the IChemE monograph concluded that the combinations of airborne concentrations and exposure times leading to 50\% lethality in the guinea pig correspond to conditions which would cause severe and possibly disabling respiratory tract irritancy in humans and a possible low rate of deaths in the more vulnerable (asthmatic or bronchitic) members of the population (Griffiths, 1996).

### 37.2.4 Toxicity in the Context of Major Hazards

There is continuing debate on how to establish a description of a set of exposure conditions that properly represents those likely to be encountered in the event of accidental releases and reflects an appropriate level of concern for human populations in relation to such hazards. This issue has been examined in detail in a report by the European Chemical Ecology and Toxicity Centre (ECETOC, 1991).

The U.K. Health and Safety Executive (HSE) has published a document on the toxicology of H\textsubscript{2}SO\textsubscript{4} mist (Turner and Fairhurst, 1992). This document is one of a series of reports on the toxicology of substances, which are primarily directed at establishing toxicity values for use in land-use planning decisions involving major hazards and are based on an approach set out in related publications by the same authors (Turner and Fairhurst, 1993; Fairhurst and Turner, 1993). In this scheme, toxicological data are reviewed and used to derive a measure referred to as the dangerous toxic load (DTL). The DTL is generally a combination of concentration, $c$, and duration of exposure, $t$, in the form $ct^n = \text{constant}$, where the index $n$ takes values typically in the range 1 to 4. The DTL is associated with a level of effect, which is designated the specified level of toxicity (SLOT). The effects associated with the SLOT are:

- Severe distress to almost everyone
- A substantial fraction requires medical attention
- Some people are seriously injured, requiring prolonged treatment
- Any highly susceptible people might be killed

For H\textsubscript{2}SO\textsubscript{4} mist, the DTL is based principally on an examination of LC\textsubscript{50} data from the guinea pig, and is given a value:

$$\text{DTL} = c^2t = 2.16 \times 10^5 \text{ (mg m}^{-3})^2 \text{ min}$$

where $c$ is in mg m\textsuperscript{-3}, $t$ in minutes and the index $n = 2$. The concentration corresponding to the above DTL for an exposure duration of 60 minutes is 60 mg m\textsuperscript{-3}. 
The American Industrial Hygiene Association (AIHA) has derived Emergency Response Planning Guidelines (ERPGs) for oleum, SO₃, and H₂SO₄ (AIHA, 1989). Three levels of ERPG are defined, the ERPG-3 (the highest of the three) being the “maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening effects.” The concentrations are expressed as H₂SO₄ mist, the ERPG-3 being set at 30 mg m⁻³, based on animal data as well as human experience; it is recognized that unusually sensitive individuals in the population may be affected more severely.

The AIHA ERPG-3 and the HSE DTL differ in their basis; the former asserts that for nearly all individuals the specified one-hour exposure would not be life-threatening, whereas the DTL is possibly fatal to very susceptible individuals and is intended to apply over a range of durations. It is noteworthy that the concentrations corresponding to these two reference levels for a 60-minute exposure (30 mg m⁻³ and 60 mg m⁻³, respectively) differ by a factor of only 2.

### 37.3 BEHAVIOR ON RELEASE

When SO₃ or oleum is spilled onto the ground, a highly exothermic and violent reaction between SO₃ and water takes place. The products of the reaction are H₂SO₄ and SO₃. The volume of SO₃ that reacts per unit volume of water depends on the percentage of free SO₃ in the pool (Hermann, 1941). The energy produced by the reaction increases the temperature of the pool and thus increases its vapor evolution rate. Depending on the pool temperature and composition (expressed as % free SO₃ 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 pool composition and temperature are not constant; they change continuously, and so do all the properties of the liquid, such as the boiling and freezing points. When the spill is onto a concrete surface, another exothermic reaction occurs between H₂SO₄ and calcium hydroxide (Plum and Hammersley, 1984). The pool contains SO₃, H₂SO₄, and water (when there is an excess of water). SO₃ and possibly H₂SO₄ vapor will evolve from the pool, the amount of which depends on the composition, the temperature, and other characteristics of the liquid.

There are three sources of water available for reaction: as the pool spreads it meets free groundwater; it also absorbs atmospheric moisture and it extracts substrate water. Apart from SO₃, which has a high vapor pressure, H₂SO₄ may also evolve under certain conditions (pool composition <35% free SO₃ and pool temperature >333 K) and always in smaller amounts than the SO₃ vapor (due to its much lower vapor pressure) (Kirk-Othmer, 1983). The main interactions that occur in the liquid phase inside the pool are depicted in Fig. 37.2.

![FIGURE 37.2 Main interactions occurring in the pool (some dimensions are exaggerated).](image)
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FIGURE 37.3 Behavior and processes that occur in a cloud generated from pools of SO$_3$ and oleum.

The evolved SO$_3$ and H$_2$SO$_4$ vapors will react with the atmospheric moisture in a complicated way. The final product of these reactions is H$_2$SO$_4$ aerosol. In most cases the cloud will initially be denser than air, with numerous processes occurring in it. Only after some distance of travel downwind, allowing adequate dilution with air, will transition to passive behavior occur. By this point, all the SO$_3$ and H$_2$SO$_4$ vapor is consumed and only H$_2$SO$_4$ aerosol is present in the cloud. The processes that occur in the cloud can be considered in three stages, as shown in Fig. 37.3.

SO$_3$ or oleums are usually stored and transported in their liquid form. Therefore, almost all of the accidents that have occurred involved the generation of a liquid pool (with the exception of the Richmond accident [Basket et al., 1994]). Although there are numerous pool evolution models in the literature, most of them deal with nonreactive liquids, with boiling points either much lower or much higher than typical ambient temperatures. The regime of behavior is then clearly either that of a boiling pool or the evaporation of a liquid of low volatility.

The behavior of pools of liquids with boiling points close to ambient temperatures presents a more complicated modeling problem, especially if the liquid properties are critical, as is the case here, where the temperature range between boiling and freezing points is quite narrow. The chemical reactions that are involved add further to this complexity.

37.4 SPILL TESTS, MITIGATION TECHNIQUES, ACCIDENTS, LESSONS LEARNED

Almost all the experiments that have been conducted with SO$_3$ or oleum have been designed to test the effectiveness of substances that are used to control such spills. The mitigation techniques that were mainly tested are the application of water spray, foam, and Spill-X-A agent.
37.4.1 Spill Tests and Mitigation Techniques

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, U.K. (Braley, 1980). The purpose of the trials was to examine the effectiveness of different treatments and remedies for spills of corrosive acid materials, to study the effectiveness of fume knockdown using water spray systems, and to find the most effective way of dealing with the residues of the treatment. Although SO$_3$ was not tested, up to 750 kg of 65% oleum were spilt onto both asphalt and concrete trays.

A variety of treatment methods was checked. The most effective was the rapid addition of Kemsol (anhydrous sodium sulfate) to the pool. It was observed that the initial vapor cloud traveled 6 to 7 km downwind and dispersed very slowly. The conditions of the tests were very humid (relative humidity $\approx$ 84%). It took 13 minutes of application of Kemsol to suppress the fumes (the rate of application was not specified). Treatment of the cloud with water spray seemed to be ineffective. Addition of water to the pool produced very large quantities of fume, and this method appeared to be suitable only for handling small spills.

After the trial, the concrete tray was eroded by 2 mm and the asphalt tray by 25 mm. It seemed that the upper surface of the trays was rapidly attacked, but at depth erosion proceeded very slowly.

In 1990, the Ansul Company tested its product Spill-X-A (magnesium oxide blended with other chemical additives) on mitigating spills of SO$_3$, 65% oleum, and chlorosulfonic acid (Behnke, 1999). Six tests that involved spillages of 65% oleum and SO$_3$ have been carried out. In each test, 55 gallons of SO$_3$ or 65% oleum were spilled into a 50 ft$^2$ (4.6 m$^2$) test pan. The generated pool was 1.75 in (4.1 cm) deep. The choice of a confined spill (rather than onto flat ground) was made because this would be a more severe test of the effectiveness of Spill-X-A agent. In the test report summary, it is stated that some previous testing on small (one to five gallons) flat spills showed that application of Spill-X-A is an effective way of mitigating and neutralizing acid vapor releases in a one-step process. It was found that application of Spill-X-A agent along with an intermittent water fog spray proved to be a fast and effective means of dealing with spills of these acids. As shown in Table 37.3, it was most effective on chlorosulfonic acid, followed by 65% oleum, and then sulfur trioxide.

The reaction efficiency was taken as the percentage ratio of the mass of reacted acid to the mass of acid spilled. During the sulfur trioxide test series, a test of an existing control technique (direct application of water spray) was run to examine acid cloud generation during application. This profile was compared with Spill-X-A agent application. This comparison showed that both techniques increase the mist concentration during initial application. However, the concentration spike from the Spill-X-A agent application was less intense and shorter in duration than the water fog application. Visual examination during several tests showed a large reduction in the fuming five minutes after the Spill-X-A agent application began. Complete control, with no potential for fuming, was accomplished in 10 to 20 minutes.

In the summary of this test report it is stated that reaction coefficients and control times will improve for flat spills normally encountered during an accidental release. The advantage

<table>
<thead>
<tr>
<th>Acid tested</th>
<th>Reaction efficiency range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorosulfonic</td>
<td>78 to 86%</td>
</tr>
<tr>
<td>65% oleum</td>
<td>44 to 63%</td>
</tr>
<tr>
<td>Sulfur trioxide</td>
<td>38 to 54%</td>
</tr>
</tbody>
</table>
of this technique is that it mitigates and neutralizes in one step, leaving a nonhazardous waste to dispose of after cleanup (in compliance with the Resource Conservation and Recovery Act).

The Du Pont Specialty Chemicals company carried out field tests on mitigation methods for small spills of chlorosulfonic acid and oleum at the Liquefied Gaseous Fuels Spill Test Facility in Nevada during April and May 1992. Sixteen different tests were conducted by spilling about 25 U.S. gallons of 65% oleum. Three different control agents were tested: water spray, two new types of foam, and Spill-X-A agent. The pan was 1.5 in. deep. The results of these tests are summarized in Table 37.4.

It should be noted that the control time was taken as the time from the start of the mitigation to the point at which fuming has essentially stopped. The following conclusions were drawn from these mitigation tests:

• High temperatures (over 260°C) may result from the mitigation/neutralization of 65% oleum.

• Both types of foam were very effective on 65% oleum (control time was 50% of the water spray mitigation).

• The temperatures on foam mitigation tests were lower than on water mitigation tests.

• Mitigation with Spill-X-A agent resulted in higher temperatures and longer control times. This technique has been reported as probably best suited for small spills spread out over a larger area.

The generated plume had the appearance of an opaque white cloud even though the prevailing relative humidity was quite low (about 15%). The heat of reaction of SO₃ with the applied mitigating agent resulted in large temperature rises in the pan, as shown in Table 37.4. These field tests further demonstrated that the reaction between SO₃ and water is extremely violent and that application of the control agent should be made with all the necessary precautions by an experienced person wearing protective equipment.

The application of water spray and foam produced a hot nonfuming solution of H₂SO₄ at the end of the mitigation procedure. This solution should be neutralized before disposal. Different substances, such as lime, soda ash, pot-ash, lime stone, and Spill-X-A, could be applied for this purpose. Spill-X-A neutralization was selected in these tests because of the ease of application into the solution and also because it has been formulated to minimize the heat of reaction and result in a nonhazardous waste.

The U.K. Health and Safety Executive (HSE) carried out some small-scale (a few kg) spillage trials at their Buxton site, in Derbyshire (Carter, 1996). The trials were conducted by spilling 20%, 30%, and 65% oleum in concrete trays. Although the scale of the tests was

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3CSA/oleum mitigation tests, 4, 5/92 (file no. 179-08-92), obtainable in VHS format at U.S. $15 per copy, PAL or C-CAM format at U.S. $30 per copy, from W. Lazor, Du Pont Specialty Chemicals, Chestnut Run Plaza, P.O. Box 80709, Wilmington, DE 19880–0709, U.S.A.
very small, it was observed that the pool was gaining weight rather than losing it because the SO₃ in the pool was absorbing atmospheric water. The conclusion was that there must be a flux of moisture entering the pool from the windfield. Particle size measurements were made, and they showed that the diameter of the H₂SO₄ mist droplets was around 0.65 μm. This small value of the droplet diameter is the cause of the great opacity observed. The vapor release from the spillages of 20% and 30% oleum ceased very quickly. The visible plume from the spillage of 65% oleum extended 200 m downwind of the release point.

37.4.2 Accidents

Accidental releases also give an indication of the behavior of spillages of SO₃ or oleum. There have been several incidents, and a few of the most important are described in this subsection. It should be noted that the level of detail in the accident reports is highly variable, limiting the usefulness of the information. More detailed descriptions of accidents involving these substances can be found elsewhere (Griffiths, 1996; Kapias and Griffiths, 1998a–e; Kapias, 1999).

On December 4, 1985, in Delhi, India, a tank containing 65% oleum collapsed due to corrosion of the metal supports (Singh et al., 1990). This resulted in a leakage from a 3-in. diameter pipe. According to eyewitness estimates, a liquid pool about 4 m in diameter was formed. The leak continued for about 40 minutes, during which 55 tons of oleum were released. In an attempt to minimize the toxic effects of the leakage, large quantities of water, lime, and other alkalis were added to the spillage. The process generated sufficient heat to produce a buoyant plume. As a result, people in the factory complex and immediate vicinity remained relatively unaffected. However, the toxic fumes dispersed into highly populated areas of the city due to the prevailing wind direction. Medical reports show that 297 persons reported for treatment to various hospitals in the city and 15 of them were detained. Singh and coworkers presented a mathematically modeled simulation of this spillage (Singh et al., 1990).

A leak of 35% oleum occurred from a 100-ton rail tanker in Richmond, California, in July 1993 (Basket et al., 1994). The cause of the leak was the application of heat to reduce the viscosity of oleum for ease of pumping. As a result, a safety valve ruptured on a tank car. SO₃ was released to the air under high pressure and quickly condensed to a whitish H₂SO₄ mist due to the prevailing values of relative humidity (78 to 92%). The release formed a visible cloud 300 m high stretching for about 15 to 20 km. The leak occurred in a densely populated industrial area and more than 20,000 people sought hospital treatment. The responsible company received claims for compensation from more than 60,000 people and it paid out about $180 million. A dispersion modeling simulation of this accident was published by the Atmospheric Release Advisory Capability (ARAC) (Basket et al., 1994).

In August 1995, in Kentucky, a cast iron pipe on an oleum storage tank sheared off from a connecting valve, releasing more than 23,000 U.S. gallons of oleum over four hours. Between 1,000 and 1,400 people in two counties were evacuated and 50 to 70 sought hospital treatment. The company was prosecuted on the grounds that it failed to design and maintain a safe operation for handling hazardous substances. It also failed to contain the leak once it occurred and to notify the authorities promptly. Nearly 250 people filed federal suits. The company spent nearly $600,000 on penalties and improvements at the plant (Washington dateline general news, 1997).

37.4.3 Lessons Learned

The following are the main lessons learned from field tests and accidental releases of SO₃ and oleum:
• The direct application of water to mitigate vapors from accidental spills of SO\(_3\) and oleum is shown to be ineffective except on very small spills (less than 20 kg).
• The application of foam or Spill-X-A agent is a generally effective technique in handling such spills.
• The reaction between SO\(_3\) and water is extremely violent and therefore mitigation and neutralisation procedures should be carried out by experienced personnel, wearing the right protective equipment.

### 37.5 REVIEW OF PREVIOUS APPROACHES TO THE MODELING OF SPILLS

Early work on hazard assessment of spillages of SO\(_3\) and oleum was prepared by the Technology Division of the HSE with assistance from the Safety and Reliability Directorate of the UKAEA and was published in 1990 (Grint and Purdy, 1990). This article contains descriptions of both the pool and the cloud behavior. The pool model consists of two different models, RASP for spills of SO\(_3\) and 65% oleum and TOEM for spills of 20% oleum. For spills of SO\(_3\) and 65% oleum, it has been assumed that there are two different evaporation mechanisms, one due to the reaction between SO\(_3\) and water on the ground and the other due to the wind flow. The pool-spreading behavior is not taken into account, and the pool radius is calculated simply from the volume of the liquid present in the pool. It is assumed that the pool temperature remains constant and is arbitrarily set equal to an extremely low value (no energy balance is incorporated). It is also assumed that the pool composition remains constant throughout the release duration. The heat generated by the reaction with water on the ground is a function of the percentage-free SO\(_3\), and it is assumed to be entirely used in the vaporization process. Boiling, solidification, interaction with the substrate, and H\(_2\)SO\(_4\) evolution are not included. The wind-driven evaporation rate is estimated by Sutton’s correlation. For spillages of 20% oleum, the heat generated by the reaction is assumed to be used entirely in warming up the bulk liquid. For those spillages, evolution of vapor occurs only due to the wind flow. For spills of different strengths of oleum (other than 20%, 65% oleum, and pure SO\(_3\)), interpolation of results is necessary. Grint and Purdy assumed that there is always enough atmospheric moisture above the pool for complete and rapid reaction of the SO\(_3\) vapor to H\(_2\)SO\(_4\) aerosol. They also assumed that the cloud will behave as passive for purposes of dispersion modeling, that it contains only H\(_2\)SO\(_4\) aerosol, and that it has reached its chemical end point instantaneously. The conventional Gaussian plume model is used to describe the dispersion behavior. Gravitational settling and deposition effects are ignored. Although this work was a useful first step, it described the behavior in a very oversimplified manner.

In 1990, Singh and coworkers published a mathematical model developed to describe the 65% oleum leakage that occurred in Delhi in 1985 (Singh et al., 1990). Their modeling approach is composed of two stages. The first stage deals with a possible mechanism that led in this particular accident to a rapid initial plume rise. In this stage, they estimated a temperature rise through thermodynamic heat-exchange relationships. The plume rise is calculated by a process that includes some very approximate assumptions. In the second stage, a time-dependent advection–diffusion equation is solved analytically in order to estimate the downwind aerosol concentration. The authors adopted the basic assumption that the dispersing vapor is H\(_2\)SO\(_4\) mist, ignoring interactions and processes that occur in the vapor phase. It was also assumed that the cloud will behave passively. The model incorporated the particular local topographical and meteorological conditions of the place where the spill occurred.

The Atmospheric Release Advisory Capability (ARAC) team has used a dispersion model to simulate the behavior of the accidental release of 35% oleum that occurred in 1993, in Richmond, California (Basket et al., 1994). In their report, ARAC provides some information
on the topographical and meteorological conditions of the site and of the conditions and reasons for the accident. It should be noted that the authors revised the initial source estimate of 97.5 tons of 35% oleum over 90 minutes to a final estimate of 8 tons of SO₃ over 225 minutes. The SO₃ vapor was assumed to condense immediately into a fine sulfuric acid mist with a median particle diameter of 1 μm (initial estimate). In their final assessment, the value of the median particle diameter of the mist was revised to 0.4 μm. A three-dimensional, diagnostic, finite-difference dispersion modeling system for estimating consequences of accidental atmospheric releases was employed. This system is used by ARAC for any accidental atmospheric release. However, this general approach ignores the complexity of the behavior of releases of SO₃ and oleum. A number of the release characteristics were revised in order to approximate the measurements of mist concentration from a monitoring station located at about 2.3 km downwind.

In more recent work, Kapias improved the initial RASP and TOEM pool models (Kapias, 1996). The basic improvements presented, compared to RASP and TOEM, were the incorporation of a more recent and reliable evaporation model (Brighton, 1987), the introduction of a flux of atmospheric moisture entering the pool, and the use of more reliable values for the properties of the liquids. It was also shown that there is not usually enough atmospheric moisture above the pool for complete and rapid reaction of the SO₃ vapor to H₂SO₄ aerosol. Therefore, the cloud will initially be denser than air with gradual reactions taking place, and it will become passive only after some distance downwind. This work identified the particular requirements for the new modeling procedure described in Section 37.6.

The IChemE monograph (Griffiths, 1996) reviews the hazards of accidental releases of SO₃ and oleum. The monograph gives a detailed review of the relevant literature on toxicity and challenges the assumption that there is enough atmospheric moisture in the wind flow above the pool for complete and rapid conversion of the SO₃ vapor to H₂SO₄ aerosol.

### 37.6 ASTO: A NEW MODEL FOR ACCIDENTAL SPILLS OF SULFUR TRIOXIDE AND OLEUM—BRIEF DESCRIPTION

Kapias and Griffiths have developed ASTO, a new model that describes accidental spills of SO₃ and oleum. Detailed description of the model and its results can be found elsewhere (Kapias and Griffiths, 1998a–e; 1999a; Kapias, 1999a). This model describes both the pool and the cloud behavior. It can be used for releases of different strengths of oleums, either continuous or instantaneous, and under varying values of input parameters. This model incorporates and describes realistically the phenomena that occur in the liquid and vapor phase.

#### 37.6.1 Model Description

The pool model consists of different submodels that describe different features of the behavior of the liquid:

- **Pool spreading**: The spreading behavior of the pool is described by differential equations that are based on the principles of mass, momentum, and energy conservation (TNO, 1992; Leonelli et al., 1994).
- **Availability of water**: The amount of water available for reaction is estimated by calculating the available amount from each source. The free water lying on the ground is modeled according to previous work (Grint and Purdy, 1990), while the atmospheric and substrate water fluxes are estimated by a new procedure (Kapias and Griffiths, 1998a; Kapias, 1999).
- **Reaction of SO₃ and water**: The volume of SO₃ liquid that reacts per unit volume of water depends on the percentage free SO₃ in the pool (Hermann, 1941).
• **Reaction of SO₃ and H₂SO₄ with the substrate:** Both these liquids are highly aggressive and could react with some of the components of any type of substrate (i.e., in the case of concrete, H₂SO₄ reacts exothermically with calcium hydroxide: Plum and Hammersley, 1984).

• **Energy balance:** An energy balance that takes into account all the possible energy sources is implemented and the pool temperature is calculated (Kawamura and MacKay, 1987).

• **Evaporation:** The evaporation rate is calculated by Brighton’s model, which is an analytical model that accounts for high vapor pressures (Brighton, 1987).

• **Boiling and solidification:** The boiling and solidification scenarios are described by new methods (Kapias and Griffiths, 1998a; Kapias, 1999).

The cloud modeling procedure includes the following submodels (Kapias and Griffiths, 1999a):

• **Thermodynamics:** A new thermodynamic model that describes all the significant processes and interactions that occur in the vapor phase has been developed. It includes an energy balance in order to calculate cloud temperature.

• **Dense-gas dispersion:** The dense-gas regime is described by the thermodynamic model and a box-type dispersion model (Raj et al., 1987; Mohan et al., 1994).

• **Transition:** Different criteria are used to check whether transition to passive behavior occurs. When transition takes place, a transition model is used to match the final dense-gas cloud characteristics to those of the initial passive cloud (Jagger, 1981).

• **Passive dispersion:** The passive regime is described by the partial reflection model, which is a Gaussian-based model that accounts for gravitational settling and deposition effects (Overcamp, 1976).

A summarized algorithm of the modeling procedure is depicted in Fig. 37.4.

### 37.6.2 Model Inputs and Outputs

The inputs of the model are:

• The spill rate of SO₃ or oleum (\(M\) in kg s⁻¹) [or the quantity spilled (\(M\) in kg)]
• The time step (\(\delta t\) in s) (used by the pool model)
• The distance increment (\(dx\) in m) (used by the dispersion model)
• The spill duration (\(t_{s1}\) in s)
• The type of release (rel) (SO₃ or different strengths of oleum)
• The maximum duration of the release to the atmosphere to be modeled (\(t_{s2}\) in s)
• The maximum radius of the pool (\(r_{max}\) in m)
• The free water film thickness on the ground (\(w_g\) in m)
• The air temperature (\(T_a\) in K)
• The location defined by the longitude (\(LG\) in degrees) and the latitude (\(LA\) in degrees)
• The time and day (\(\tau\) and \(d\))
• The wind speed at a reference height of 10 m [\(U(10)\) in m s⁻¹]
• The type of surface (\(s\)) (whether it is concrete or asphalt, etc.)
• The roughness length of the surface (\(z_o\) in m)
• The atmospheric radiation and cloud cover factors (\(r\) and \(c\))
• The atmospheric relative humidity (% RH)
• The standard deviation of the horizontal wind direction ($\sigma_u$ in degrees)
• The average ground surface temperature ($T_{\text{grd}}$ in K)

The main outputs of the pool model are:
• The total mass of SO$_3$ vapor evolved in the three regimes (spreading duration, duration after spreading ceases, and total release duration)
• The total mass of $H_2SO_4$ vapor evolved in the three regimes
• The average pool temperature, radius, and vapor evolution rates in the three regimes
• The spreading duration (which can be different to the spill duration $t_{sp}$)
• The total amount of liquid left in the pool
• The % free $SO_3$ of the liquid left in the pool
• The pool temperature versus time, boiling point versus time, and freezing point versus time (indicating at which stages the pool boils or evaporates or solidifies)
• The pool radius versus time
• The vapor evolution rates versus time

The main outputs from the cloud model are:

• The cloud width and height in the dense-gas regime and the vertical and lateral dispersion coefficients in the passive regime
• The total mass rate of the toxic substances ($SO_3$, $H_2SO_4$, and $H_2SO_4$ aerosol) versus distance in both regimes
• The cloud density and the Richardson number in the dense-gas regime
• The cloud composition in the dense-gas regime

For spills of liquid $SO_3$ or oleum, the pool model should be run first. The results of the pool model are automatically set as inputs to the dispersion model. The dispersion model is subsequently run. For releases of $SO_3$ vapor, the dispersion model should be run directly. For varying input parameters, the distance- or time-varying functions should be defined.

37.6.3 Model Results

The new model has been implemented in a computer code in Microsoft Visual Basic 5.0. The code has a user-friendly interface providing all the necessary help and information on the release behavior. Some representative results are given in Figs. 37.5 to 37.9. The pool behavior is governed by the amount of water available for reaction as shown in Fig. 37.5. This figure shows that the total sulfuric acid evolution rate usually increases with increasing free groundwater film thickness. The total sulfuric acid evolution rate is calculated by the following equation:

$$\text{Total } H_2SO_4 \text{ evolution rate: } \frac{H_2SO_4 \text{ evolved}}{\text{release duration}} + \frac{(98/80) \times (SO_3 \text{ evolved})}{\text{release duration}}$$

The most important water source is the free water lying on the ground. Atmospheric water is usually a less significant source, and its contribution to the total water used increases with decreasing values of film thickness of the free groundwater. Concrete water is usually the least significant source, and its contribution increases with decreasing film thickness of the free groundwater (Kapias, 1999; Kapias and Griffiths, 1998b). The wind speed also has a relatively strong effect, while the effect of the rest of the pool model input parameters is usually less significant.

The pool behavior during the pool spreading phase is quite different from that after spreading ceases. The vapor evolution rates are much higher during spreading due to the greater amount of water available for reaction, thereby generating higher pool temperatures, resulting in higher vapor pressures and vapor evolution rates. After spreading ceases, there are only two water sources available for reaction: atmospheric and substrate water. Moreover, in this phase, it is more likely that the pool will solidify, terminating the reaction between $SO_3$ and water (Kapias, 1999; Kapias and Griffiths, 1998b).
As mentioned, the pool composition (expressed as percentage-free \(\text{SO}_3\) in the liquid) changes continuously, and so do all the pool properties. Different composition profiles for continuous spills of \(\text{SO}_3\) under different values of free water film thickness lying on the ground are given in Fig. 37.6.

Whether the pool is predicted to boil or evaporate or solidify is a function of many parameters. One case that involves all three phenomena is depicted in Fig. 37.7. In this scenario, the pool boils in the early stage of the spill, then it evaporates during the rest of the spreading period, and just after spreading ceases, it solidifies. The pool temperature in this scenario varies from \(265 \text{ K}\) to \(330 \text{ K}\).

The cloud behavior is affected mostly by the wind speed, the vapor evolution rates from the pool, the atmospheric stability class, and the atmospheric relative humidity (Kapias, 1999; Kapias and Griffiths, 1999a). In the majority of the cases, the cloud will initially be denser...
than air and transition to passive dispersion behavior will occur only after some distance downwind. Only when the vapor evolution rates from the pool are very low and the wind speed quite high will transition to passive behavior occur rapidly. The duration of the dense-gas regime increases with decreasing wind speed and with increasing stability. It also increases with increasing values of free groundwater film thickness (or increasing strength of spilled liquid). In the dense-gas regime, SO$_3$ vapor, H$_2$SO$_4$ vapor, and H$_2$SO$_4$ aerosol are present in the cloud. Both the SO$_3$ and H$_2$SO$_4$ vapors interact with the atmospheric moisture, yielding H$_2$SO$_4$ vapor and H$_2$SO$_4$ aerosol respectively. The interactions that occur in the

**FIGURE 37.6** Pool composition profiles for spills of 16 kg s$^{-1}$ of SO$_3$ for 600 s [$U(10) = 5$ m s$^{-1}$].

**FIGURE 37.7** Temperature profile for a spill of 16 kg s$^{-1}$ of SO$_3$ for 600 s [$w_s = 0.001$ m, $U(10) = 5$ m s$^{-1}$].
cloud usually finish before transition to passive dispersion behavior occurs. Generally, the cloud composition in the dense-gas regime is affected mainly by the wind speed, the source strength, and the relative humidity (Kapias, 1999; Kapias and Griffiths, 1999a).

When transition to passive dispersion behavior occurs, only H$_2$SO$_4$ aerosol is present in the cloud and some of it is lost on the ground due to deposition and gravitational settling effects (Kapias, 1999; Kapias and Griffiths, 1999a).

The effects of wind speed and atmospheric stability class on the hazardous species centerline concentration in the cloud are depicted in Figs. 37.8 and 37.9. It should be noted that

**FIGURE 37.8** Wind speed effect on the hazardous species centerline concentration for spills of 16 kg s$^{-1}$ of SO$_3$ for 600 s (stability class D).

**FIGURE 37.9** Atmospheric stability class and wind speed effect on the hazardous species centerline concentration for spills of 16 kg s$^{-1}$ of SO$_3$ for 600 s.
the results depicted in these figures correspond to the period before spreading ceases (a little over 10 minutes in this case), where the vapor evolution rates from the pool are much higher. For the period after spreading ceases, the vapor evolution rates are much lower, transition to passive behavior occurs much faster, and the hazardous species centerline concentration is much lower (Kapias, 1999; Kapias and Griffiths, 1999a).

In Figs. 37.8 and 37.9, the dangerous toxic load (DTL) concentration, equal to around 147 mg m\(^{-3}\) for a period of 10 minutes, and the ERPG-3 (for exposures up to 60 minutes), equal to 30 mg m\(^{-3}\), are also shown for comparison. The exposure duration for calculating the DTL concentration was chosen equal to the spreading period of about 10 minutes because it is the period of main exposure (higher vapor evolution rates).

Overall, the hazardous species centerline concentration increases with decreasing wind speed, increasing stability, and increasing source strength. Figure 37.8 shows a very big effect of the wind speed on the centerline concentration as compared with simple Gaussian plumes, where for a decrease of 1 m s\(^{-1}\), the centerline concentration decreases by a factor of about 4. This big change shows the significance of the physical and chemical processes that occur in the initially dense-gas plume.

In the scenarios depicted in Figs. 37.5 to 37.9, some of the input parameters were constant and set equal to: \(M' = 16\) kg s\(^{-1}\), \(\delta t = 0.01\) s, \(dx = 0.01\) m, \(t_s = 600\) s, \(t_s = 1800\) s, \(r_{\text{max}} = 50\) m, \(T_a = 288\) K, location = Manchester, UK, \(\tau = 09:00\) hrs, day = October 25, \(s = \text{concrete, rough}, z_0 = 0.1\) m, RH = 70%, \(T_{\text{grd}} = 285\) K.

### 37.7 DISCUSSION, CONCLUSIONS, AND RECOMMENDATIONS FOR FURTHER INVESTIGATION

Sulfur trioxide and oleums of all strengths are important substances in the field of major hazards. Their main feature is the violent and exothermic reaction between SO\(_3\) and water that occurs in both the liquid and vapor phase.

With regard to available mitigation techniques, the application of water is appropriate only when handling small spills (less than 20 kg). The other available techniques (application of foam or other agents) are reported to be quite effective in mitigating spills of SO\(_3\) and oleum.

Previous models of spillage and dispersion behavior described the releases of these substances in an unrealistic way. The new model ASTO described in Section 37.6 is much more realistic and is suitable for use by industry and enforcing authorities in fulfilling the requirements of international legislation on major hazards risk assessment. The following are the main advantages of the new model.

- It describes the pool and the cloud behavior realistically, taking into account significant processes that occur in both the liquid and the vapor phases.
- Although the overall release behavior is very complicated, calculation times are very satisfactory (usually less than 15 minutes on a Pentium II).
- It can incorporate a wide variety of input parameters and can model both instantaneous and continuous releases (steady or varying in the latter case).
- It can be used for releases of any strength of oleum as a liquid spill or as a vapor released directly to the atmosphere.
- It can readily be adapted for use with other reactive chemicals, especially those with high affinity for water.
- ASTO is very easy to use. It has a user-friendly interface providing extensive help and information on the release behavior.
The pool model has been modified to include other water reactive chemicals such as phosphorus trichloride and oxychloride, silicon tetrachloride, chlorosulfonic acid, and acetyl chloride. REACTPOOL is a new model 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 or reactivity and it also describes pools consisting of more than one liquid that can have changing composition and properties (Kapias and Griffiths, 1999b; 2001a and b; Kapias et al., 2001a and b).

Unfortunately, although a number of accidents involving spillages of SO₃ and oleum have occurred, almost no experimental data on release behavior are available. Therefore, it is strongly recommended that experiments be carried out, especially to determine the following aspects, which are the main areas of uncertainty in order of importance:

1. Aerosol nucleation and growth under conditions of high concentrations of the aerosol components, including particle deposition behavior
2. More precise kinetics on the gas phase reaction of SO₃ and H₂SO₄ with water
3. Atmospheric water entering into the pool

### 37.8 REFERENCES


Control of Industrial Major Accident Hazards (CIMAH) Regulations. 1999. SI 1984, No. 1902, HMSO.

Control of Major Accident Hazards (COMAH) Regulations. 1999. SI 1999, No. 743, HMSO.


