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## REPORT

# Accident investigation following the Vest Tank explosion at Sløvåg

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Police District Hordaland, Kripos, and DSB

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Abstract:

*This report describes the accident investigation performed by GexCon AS following the tank explosion and subsequent fire that occurred at Vest Tank AS at Sløvåg Industrial Area on 24<sup>th</sup> May 2007. An atmospheric storage tank exploded, and the subsequent fire destroyed the remaining tanks in the tank farm, as well as some buildings and trucks near the tank farm. The extent of the work presented in this report includes revealing the direct causes of the accident, as well as evaluating plausible courses of events in light of the extent of the accident, witness observations, and a literature study on similar events. Chapter 7 summarizes the main conclusions, a plausible course of events, and some general recommendations for improved safety at similar tank facilities.*

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# 1 Introduction

On the 24<sup>th</sup> of May 2007, about 10 am, an explosion occurred in a storage tank on the facilities of the company Vest Tank AS, on the Sløvåg industrial area, in the municipality Gulen, in the county council district of 'Sogn og Fjordane', on the west coast of Norway. This report describes the results of an accident investigation undertaken by GexCon AS for Hordaland Politidistrikt (the local Police authorities in the county council district of Hordaland), the Norwegian National Criminal Investigation Service (Kripos), and the Norwegian Directorate for Civil Protection and Emergency Planning (DSB). This chapter contains a general introduction to the issues addressed in the remaining parts of the report. Section 1.1 describes the background for the work, section 1.2 introduces some fundamental concepts associated with fires and explosions, section 1.3 describes the tank facilities of Vest Tank at Sløvåg and summarizes the course of events during the accident, and section 1.4 provides an overview of the remaining parts of the report.

## 1.1 Background

The extent of the work undertaken by GexCon was defined in a commissioning letter from the Police (The Norwegian Police, ref. 0723.11705a, 2007), and by two meetings arranged during the project: a kick-off meeting at Fantoft on Friday 6<sup>th</sup> July 2007, and a regular project meeting at the police headquarters in Bergen on 13<sup>th</sup> September 2007. GexCon presented the Norwegian version of this report at a press conference at the police headquarters in Bergen on Wednesday 31<sup>st</sup> October 2007.

## 1.2 Basic concepts

This section defines a few concepts that are essential for understanding the course of events that took place during the accident at Sløvåg.

In a **fire**, chemical energy is released through non-premixed combustion as fuel and oxidizer mix and react in the flame zone. Figure 1-1 shows the so-called *fire triangle* that illustrates the three factors that must be present for a fire to occur:

- **Fuel:** combustible material – solid, liquid or gas.
- **Oxidizer:** usually oxygen from the air.
- **Ignition source:** the origin of the energy that initiates the self-propagating combustion reactions.

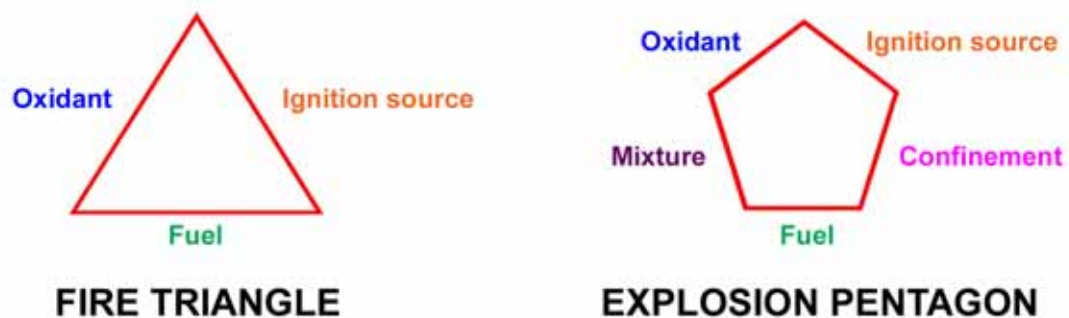
Because the mixing process in the flame zone is relatively slow, the reaction products usually escape without creating significant pressure build-up in the system.

In contrast to a fire, an **explosion** is generally associated with the sudden release of energy, resulting in the formation of a pressure wave. Depending on the source of the accumulated energy, it is customary to classify explosions in the following categories:

- Physical explosions.
- Chemical explosions.
- Nuclear explosions (of no relevance in the current context).

An example of a **physical explosion** is the rupturing of a closed container with compressed gas when the internal pressure exceeds the design strength of the container. The high pressure can be a result of over-filling, gas generation from materials inside the container (e.g. through phase transitions or chemical reactions), and/or thermal expansion of the gas. Heating of the gas can be due to exothermic chemical reactions or an external fire load. A borderline case occurs when the pressure increase is

due to combustion reactions inside the container, but for such incidents it is customary to use the term chemical explosion (see the next paragraph). Several factors may cause a container to rupture at significantly lower pressures than the original design pressure, e.g. fatigue fracture, material damage due to corrosion, or reduced material strength at elevated temperatures. For a closed container, even slow rates of pressure rise can result in a physical explosion. However, if the rate of heat release and/or phase transitions is sufficiently high, physical explosions may occur even if the container is not fully closed. An example of physical explosions that can occur in relatively open systems are the so-called vapour explosions that result from the rapid and intense heat transfer that can take place when a cold volatile liquid, like water, comes in contact with a hot liquid, like melted metal.



**Figure 1-1** The fire triangle (left) and the explosion pentagon (right) illustrate the various criteria that normally must be fulfilled to initiate a fire and a chemical explosion, respectively.

A **chemical explosion** is usually associated with premixed combustion. Figure 1-1 shows the so-called *explosion pentagon* that illustrates the five factors that normally must be present to cause this type of chemical explosions:

- **Fuel:** a combustible material, either gas, vapour droplets, dust particles, or an explosive.
- **Oxidizer:** usually oxygen from the air (explosive materials contain both fuel and oxidizer).
- **Mixture** of fuel and oxidizer within certain concentration limits (flammability limits).
- **Ignition source:** the initial energy release that initiates self-propagating combustion reactions.
- **Confinement or congestion;** although chemical explosions in the open can generate significant overpressures for very reactive mixtures, a certain degree of confinement or congestion is usually required to generate high overpressures in most hydrocarbon fuel-air mixtures.

The release of chemical energy through exothermic reactions, and hence thermal expansion of the combustion products, are the primary cause of pressure build-up in chemical explosions. Since the flame propagates through a mixture of fuel and oxidizer, chemical reactions can take place quite rapidly, and even relatively low degrees of confinement or congestion may result in high explosion pressures. Premixed combustion is however only possible when the mixture composition is within certain concentration limits:

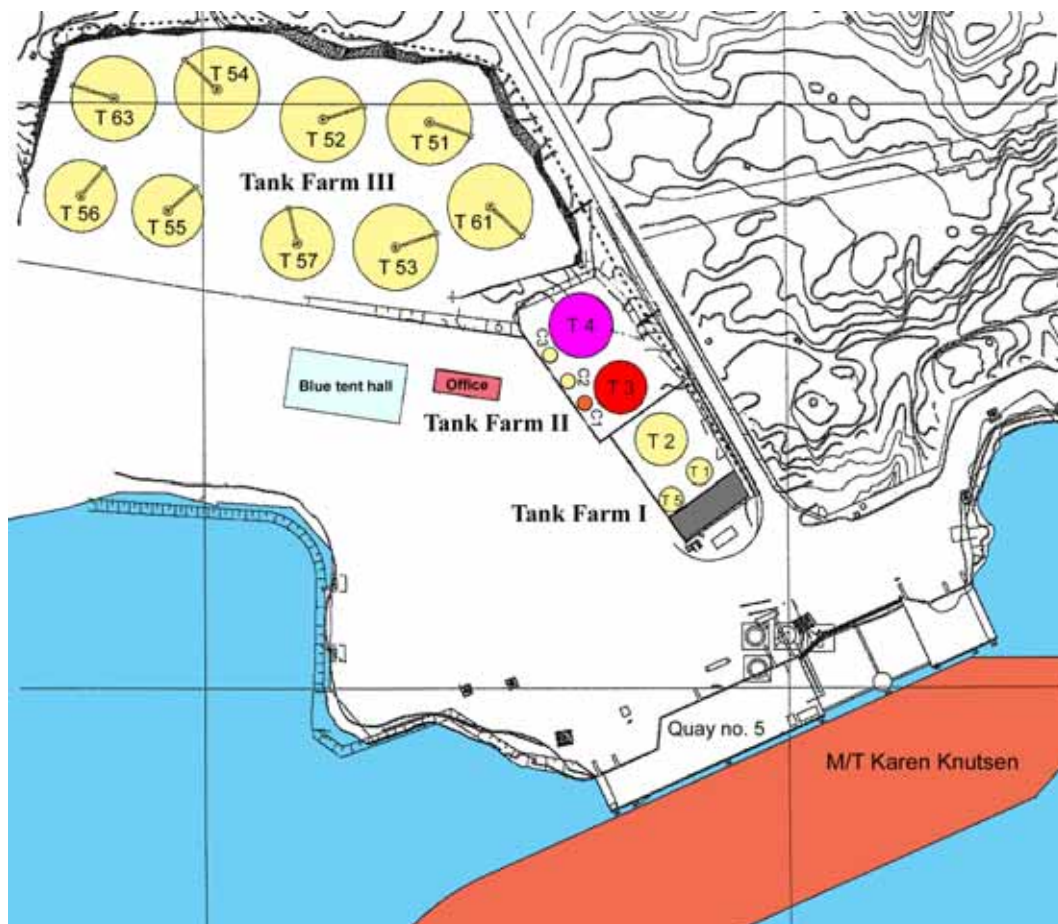
- Lower Flammability Limit (LFL), and
- Upper Flammability Limit (UFL).

The effect of the ignition source on the course of the explosion is usually restricted to a limited volume of the explosive mixture, and as long as the flame propagates outwards from the point of ignition, the volumetric rate of consumption of unburnt mixture increases steadily. In most situations, thermal expansion of the combustion products will generate turbulent flow conditions in the fresh mixture ahead of the flame front, and the rate of combustion increases significantly due to increased heat and

mass transport in the reaction zone. The positive feed back loop between increased turbulence and more rapid combustion leads to flame acceleration and increased rates of pressure rise.

### 1.3 The accident

Sløvåg is a community in the municipality Gulen, in the county council district of 'Sogn og Fjordane', on the west coast of Norway. The accident took place at the tank facility of the company Vest Tank AS on 24<sup>th</sup> May 2007. The company treated wastewater from the shipping and offshore sector. Figure 1-2 illustrates the layout of the tank facility prior to the accident. The first explosion took place in tank T3 around 10 am in the morning; subsequent explosions and fires destroyed Tank Farm II, the office building, and some tank trucks positioned outside the tank farm. There were no casualties in the accident, but at least two people received medical treatment for injuries sustained during the incident. This section of the report describes the course of events that led to the accident, and briefly how the initial explosion led to an extensive fire scenario in the tank farm. Chapter 3 describes further details concerning the tank facility and the course of events prior to and during the accident.



**Figure 1-2** Schematic illustration of the Vest Tank facility prior to the accident on 24<sup>th</sup> May 2007. The first explosion took place in tank T3, and tanks T4 and C1 exploded somewhat later. The illustration is based on drawing 3124-T-L-8 ('Sløvåg bunkringsanlegg tank kapasiteter' from Bergen Engineering, rev. 1, 22.05.05). The positions of the tanks C1-C3 are estimated according to a modified version of the original drawing from a preliminary accident report by Vest Tank AS (Berland, 2007). M/T Karen Knutsen was moored alongside Quay no. 5, but the figure does not take into account the actual dimensions or position of the tanker.

Prior to the accident, Vest Tank AS had treated, or 'purified', an oil product called *coker gasoline* (Pemex, 2005); coker gasoline is apparently a common ingredient in gasoline, and various witnesses referred to the product as 'naphtha', 'gasoline naphtha', 'light gasoline' or 'blended gasoline'. This activity started in October 2006, and continued until March 2007. In this period, the company treated some 6-7 tanker loads, each containing about 32 000 m<sup>3</sup> coker gasoline. The processing of one tanker load took about 5-7 days of round-the-clock processing in two tanks, T3 and T4.

The purpose of the treatment was to reduce the content of sulphur containing organic components, especially mercaptans (thiols). Coker gasoline from the tanker was pumped to the onshore tanks, and simultaneously mixed with sodium hydroxide (30 % NaOH dissolved in water); Figure 1-3 shows the lye tank and the flexible tubes. The process utilized the fact that the solubility of the relatively polar mercaptan molecules is significantly higher in an alkaline solution of water and NaOH, compared to less polar liquids such as coker gasoline. Pumps would circulate the content of the tanks for some time, before the force of gravity separated the liquid phases: the denser NaOH solution with dissolved mercaptans and precipitated sludge settled in the bottom of the tank, while the top layer of treated coker gasoline could be transferred back to the tanker.

The total amount of impurities removed from the coker gasoline by this process was typically about 0.15 % of the total volume. For 6 tanker loads of 32 000 m<sup>3</sup> coker gasoline each, or 192 000 m<sup>3</sup> in total, this amounts to about 290 m<sup>3</sup>. Assuming a density of coker gasoline of about 0.72 tons per cubic metre, the total mass of 6 tanker loads would be 138 240 tons, and 0.15 % of this corresponds to about 210 tons. The impurities that remained in the tanks after the treatment consisted of a liquid part (presumably NaOH solution with some remnants of coker gasoline), and a more or less solid substance referred to as waste or 'crystallized lye'.

Although Vest Tank transferred most of the liquid waste from tanks T3 and T4 to three smaller tanks (C1-C3), the amount of accumulated solid waste in the bottom of the two tanks eventually reached a level where it was impossible to treat additional tanker loads of coker gasoline. Prior to further treatment of the solid waste, Vest Tank conducted a small-scale pilot project where they diluted the solid waste with water and hydrochloric acid. This process served two purposes: it dissolved the precipitated waste, and it reduced the pH of the solution to levels in accordance with the discharge permit for the facility (SFR, 2001). Figure 1-3 shows the apparatus used in these experiments. The dilution of the solid waste with water and acid resulted in the generation of gas (referred to as 'acid vapour'), and the formation of a thin layer of an oily liquid on the surface of the solution. Subsequent testing of liquid from this surface layer showed that it was flammable.

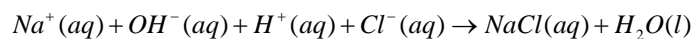


**Figure 1-3** The small-scale apparatus used to investigate the effect of adding hydrochloric acid solution to the solid waste (left); the tank facility seen from the quay, with the lye tank ('De Rijke'), and the flexible tubes used for transferring coker gasoline from the tanker to the tanks (centre); the remaining substance on the ground inside Tank Farm II after the accident (right); pictures provided by the Norwegian Police.

Prior to further treatment of the precipitated waste, Vest Tank transferred most of the liquid in tank T3 (about 30–40 m<sup>3</sup>) to tank T4, and some liquid residue to tank C1. Over several days, up to about 2-3 days prior to the accident, a vacuum pump was used to suck additional liquid from a depression in the remaining material (described as a 'spongy substance'). After several failed attempts at igniting a sample of the liquid last removed from the tank with an open flame, it was assumed that the liquid was not flammable.

Mercaptans are disreputable for being highly malodorous compounds, and to limit the release of such substances to the environment, both tank T3 and tank T4 were fitted with activated carbon canisters, i.e. air filters where the filter medium is granules of activated carbon (finely divided forms of carbon). These filters stood by the railing on the roof of each tank, and flexible pipes connected the vent on the top of each tank to the inlet opening on the respective air filter. Hence, all exchange of air or vapour between the interior of the tanks and the environment had to pass through these filters. As part of the final preparations for the planned solid waste treatment, Vest Tank replaced the old filter media in the air filters on both tanks.

Before gradually adding hydrochloric acid, the remaining 50 m<sup>3</sup> of precipitated waste in tank T3 was diluted with about 205 m<sup>3</sup> wastewater from tank T61, resulting in about 255 m<sup>3</sup> solution. The intention was to add about 18 m<sup>3</sup> of acid solution (30-36 % HCl in water). As mentioned above, the purpose of this process was to dissolve the solid precipitants, and at the same time neutralize the alkaline solution (i.e. reduce the pH value):



It is worth noticing that this chemical balance does not consider chemical reactions, or shifts in chemical equilibriums, involving other substances than the pure sodium hydroxide solution, amongst the 50 m<sup>3</sup> of precipitated waste inside the tank.

The process of adding hydrochloric acid started in the afternoon on Wednesday 23<sup>rd</sup> May, and tank T3 exploded about 10 am the next morning (after adding 14-15 m<sup>3</sup> of acid solution). Shortly after, tank T4, containing residue of coker gasoline and solid waste, and tank C1, containing residue of oil and solid waste, also exploded. Tanks C2 and C3 were empty, but were both destroyed in the subsequent fire in the tank farm.

An extensive pool fire developed in Tank Farm II shortly after the first explosion. Figure 1-4 shows the fire in Tank Farm II about 45 minutes after the first explosion, when the fire had just reached the red office building. Figure 1-5 shows a series of pictures taken by the crew onboard M/T Karen Knutsen that clearly documents the escalation of the fire scenario. Figure 1-6 illustrates the extensive damage to Tank Farm II, the office building, and some tank trucks outside the tank farm.





**Figure 1-4** Picture taken from a helicopter from Norsk Luftambulans (Norwegian Air Ambulance) about 45 minutes after the first explosion, showing the tanker M/T Karen Knutsen, most of the tank facility, and the extensive fire in Tank Farm II. The fire in the red office building has started, presumably due to radiative heat transfer from the fire in the tank farm. The picture also shows where the air filter from tank T3 landed, as well as various details not included in Figure 1-2. Photograph provided by Lasse Fossedal from Norsk Luftambulans.



First picture, a few minutes after the first explosion



Second picture, approximately 4 minutes after the first picture



Third picture, approximately 13 minutes after the first picture

Sløvåg 24.05.2007  
Photos by Glenn Rogers  
Chief Engineer M/T Karen Knutsen

**Figure 1-5** A series of pictures taken from M/T Karen Knutsen that illustrates how the fire in Tank Farm II developed during the first minutes after the first explosion in tank T3 on 24<sup>th</sup> May 2007. Photographs provided by Glenn Rogers, Chief Engineer, M/T Karen Knutsen.



**Figure 1-6** Overview pictures illustrating the tank facility at Sløvåg after the accident on 24<sup>th</sup> Mai 2007: Tank farm II viewed from the quay (25<sup>th</sup> May 2007); the remains of tank T3 viewed from the road (26<sup>th</sup> May 2007); Tank farm II with Tank farm I and M/T Karen Knutsen in the background (25<sup>th</sup> May 2007); damages to the trucks and the red office building (25<sup>th</sup> May 2007); photographs from the Norwegian Police.

## 1.4 Extent of work

This report describes the investigation by GexCon into the course of events that led to the accident at Sløvåg on 24<sup>th</sup> May 2007, in accordance with the commissioning letter from Hordaland Politidistrikt, Kripos, and DSB (The Norwegian Police, ref. 0723.11705a, 2007). The work is limited to revealing the direct physical and chemical factors that resulted in the first explosion in tank T3. The fact that the first explosion escalated to additional tank explosions and an extensive fire in the tank farm is typical for this type of accidents, and the report does not address details of such secondary events. Furthermore, the report does not address underlying causes such as human or organizational factors, possible legal matters that tend to arise after this type of incidents, and possible long-term damages to health or environment caused by the release of harmful substances during and after the incident.

Although most of the evidence suggests that it was a chemical explosion that occurred in tank T3, this report also considers the possibility of a physical explosion. A hypothetical accident scenario for a physical explosion involves chemical reactions and/or rapid phase transitions caused by adding hydrochloric acid to the alkaline solution in the tank. If the openings in the tank were either totally blocked, or too small to prevent effective mitigation of the increasing internal overpressure, the tank would eventually rupture. Hot surfaces, or mechanical sparks originating from the deformation of steel plates in the tank walls, could then ignite combustible gases or vapours. Hence, Chapter 4 of this report investigates the possibility of a physical explosion in light of possible mechanisms that could have resulted in sufficiently high rates of gas generation or heat release, for the given openings in the tank, to raise the internal pressure to unacceptably high levels.

Assuming the available evidence does not substantiate a hypothesis involving a physical explosion, it is reasonable to assume that it was a chemical explosion that took place in tank T3, and hence to identify likely candidates for the five causal factors in the explosion pentagon illustrated in Figure 1-1:

- **Fuel:** It seems clear that there was an explosive atmosphere inside tank T3 prior to the explosion, but it is nevertheless important to clarify the origin and chemical composition of the fuel.
- **Oxidizer:** The manhole covers on tank T3 had been open for several days prior to the addition of hydrochloric acid, and the oxidizer was presumably oxygen from the air inside the tank.
- **Explosive mixture:** The total volume of tank T3 was 4000 m<sup>3</sup>, and since there was only about 270 m<sup>3</sup> of liquid in the bottom of the tank (i.e. less than 7% of the total volume); most of the tank was initially filled with air. Combustible gases or vapours released from the liquid surface may have mixed with air and eventually created an explosive mixture in either the entire, or parts of, the free volume of the tank. The report also considers whether combustible mixture that escaped from openings in the tank could have reached ignition sources outside the tank.
- **Ignition source:** A chemical explosion scenario requires an ignition source, either inside the tank, or outside the tank but within reach of explosive mixture escaping from openings in the tank. A significant part of the report is therefore devoted to the analysis of potential ignition sources.
- **Confinement:** The internal volume of tank T3 provided ample degree of confined, and there would normally not be sufficient relief of the overpressure generated by a chemical explosion through the available openings in the tank: a six-inch inspection hatch (normally closed) and venting through the air filter with activated carbon.

Hence, to account for scenarios involving a chemical explosion, it is of primary interest to explain the origin of the fuel, and hence the chemical composition of the explosive atmosphere, as well as the type and position of the ignition source.

This report aims at revealing the direct causes of the accident at Sløvåg on 24<sup>th</sup> May 2007. The work has primarily consisted of the following activities:

### **Literature study**

*Chapter 2* presents a brief literature study concerning related accidents in similar facilities, and results from relevant research.

### **System description and summary of the course of events**

*Chapter 3* describes the tank facility and the course of events prior to the accident, as well as witness observations describing the actual accident.

### **Assessing the likelihood of a physical explosion as the initiating event**

*Chapter 4* explores the possibility of realizing a physical explosion in tank T3 by evaluating plausible mechanisms of generating or expanding sufficient volumes of gas, in light of both the available openings in the tank and observations by witnesses.

### **Studying possible ways of generating the explosive atmosphere**

*Chapter 5* looks at possible mechanisms of generating an explosive atmosphere inside the tank, and to what extent it is reasonable to assume that explosive mixtures could escape from openings in the tank and reach ignition sources outside the tank. Simulations with the CFD code FLACS imitate the generation of explosive mixtures inside the tank, and the dispersion of vapours escaping from openings in the tank.

### **Assessing potential ignition sources**

*Chapter 6* explores possible ignition sources, such as electrostatic discharges, electrical or mechanical equipment, hot work, and self-ignition in the filter media (i.e. pellets of activated carbon). The work includes measurements of the electrical conductivity of relevant liquid samples to assess the possibility of accumulating electrostatic charge on the liquid surface, and thereby the possibility of generating electrostatic discharges that could ignite an explosive atmosphere inside the tank.

*Chapter 7* summarizes the main conclusions from the accident investigation, provides a brief summary of a plausible course of events that is consistent with the main conclusions, and lists some general recommendations for risk reducing measures applicable to the type of process that took place at Vest Tank prior to the accident on 24<sup>th</sup> May 2007.

## 2 Literature study

The purpose of this literature study is to summarize previous accidents at tank facilities similar to the one at Sløvåg, and to identify other relevant issues that may explain the course of events during the accident on 24<sup>th</sup> May 2007.

### 2.1 Explosions in atmospheric storage tanks

A significant fraction of the accidents that take place in the process industries are associated with atmospheric storage tanks, because of overfilling, internal underpressure, or explosions (Kletz, 1988):

*“No item of equipment is involved in more accidents than storage tanks, probably because they are fragile and easily damaged by slight overpressure or vacuum. Fortunately, the majority of accidents involving tanks do not cause injury, but they do cause damage, loss of material, and interruption of production.”*

Historical data suggests a probability of explosions in atmospheric storage tanks of about once in 1000 years per tank (Kletz, 1988; Mannan, 2005). There are several reasons for this relatively high frequency:

- Storage tanks in the process industry contain large volumes of flammable liquids, and explosive mixtures of vapours and air are therefore present in the vapour space of many storage tanks.
- It is very difficult to prevent all ignition sources in storage tanks: lightning is one of the most frequent sources, and electrostatic discharges constitutes a hazard whenever the liquid in the tank has low enough electric conductivity for electrostatic charges to accumulate on the liquid surface.
- The design pressure of typical storage tanks is usually very low.
- Although most storage tanks are designed to fail at the roof/wall weld (thereby limiting the spill of liquid to the tank farm), it is often the base/wall weld that fails due to corrosion.

Chang & Lin (2006) reviewed 242 accidents involving storage tanks, and found that fire and explosion could account for 85 % of the accidents. They found 80 accidents (33 %) caused by lightning and 72 (30 %) caused by human errors. Figure 2-1 shows a fishbone diagram that summarizes the various causes of storage tank accidents.

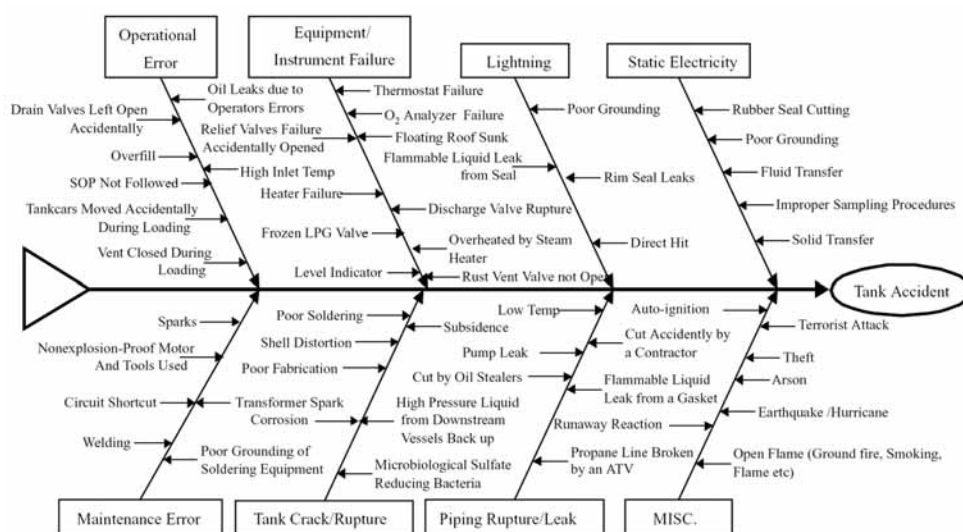


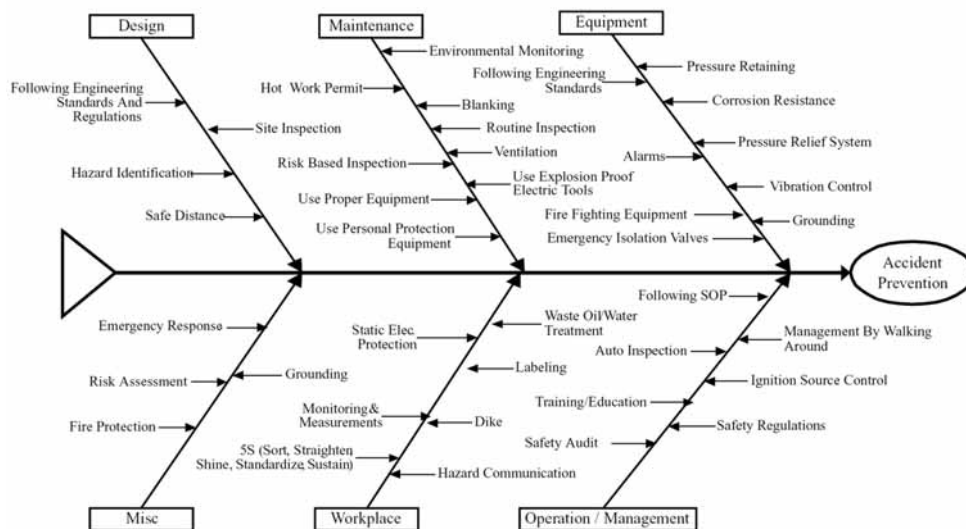
Figure 2-1 Fishbone diagram illustrating known causes of tank accidents, from Chang & Lin (2006).

Common methods of reducing the risk associated with tank explosions are (Kletz, 1988, 1990; DBE, 1994; EPA, 1997abcd, 2001; BP, 2006ab; Mannan, 2005; Chang & Lin, 2006):

- Use of floating roof tanks, thereby eliminating the formation of a confined explosive atmosphere.
- Blanketing with an inert gas (usually nitrogen) to prevent the formation of an explosive atmosphere inside the tank, thereby eliminating the ignition hazard due to electrostatic discharges.
- Antistatic additives that increase the conductivity of the liquid, thereby preventing electrostatic charges from accumulating on the liquid surface.
- Minimising the formation of static electricity during filling of the tank by maintaining low flow velocities during pumping (typically below  $3 \text{ m s}^{-1}$  for pure liquids, and below  $1 \text{ m s}^{-1}$  when water is present), avoiding splash filling, and including long lengths of tubing after restriction like filters or orifice plates to allow charges to decay.
- Sensible layout of tank farms, such as sufficient spacing between the tanks, separate bunds for each tank to capture liquid spills, placing pumps and other equipment outside the bunds, etc.
- Flame arresters on all vents for tanks containing flammable liquids.
- Hazardous area classification: preventing ignition sources by dictating design requirements for electrical equipment according to relative explosion risks in defined zones.

Figure 2-2 shows a fishbone diagram that summarizes the various means of preventing tank accidents. It is worth noticing that incorrect design, operation, or maintenance of the various types of safety equipment may nevertheless result in accidents (Kletz, 1988; Kletz, 1990).

In situations where chemical reactions take place intentionally in the liquid phase inside a tank, and especially when the reactions are strongly exothermic or produce significant amounts of gas, it is more appropriate to classify the vessel as a chemical reactor rather than an atmospheric storage unit. Chemical reactions may also occur unintentionally, for instance if incompatible substances mix, impurities enter the system, or if certain process parameters, such as pressure or temperature, get out of control (Mannan, 2005).



**Figure 2-2** Fishbone diagram illustrating means of preventing storage tank accidents, from Chang & Lin (2006).

## 2.2 Previous accidents and relevant research

Sources available in the open literature contain limited information on accidents bearing a strong resemblance to the one that occurred at Sløvåg. There are very few descriptions of explosion accidents involving mercaptans, or the hazards associated with treating coker gasoline with sodium hydroxide. The literature study nevertheless revealed a fair amount of information on related issues.

### Ignition by electrostatic discharges

Historical records from explosion accidents show that electrostatic discharges on many occasions have ignited flammable mixtures of vapour and air in storage tanks. The ability of a liquid to accumulate static charge is closely related to the electrical conductivity of the liquid, and the electrical conductivity is closely related to the presence of ions in the liquid (Mannan, 2005; BP, 2006c). Most hydrocarbons have lower conductivity than other liquids (typical exceptions are substances with symmetric molecules such as diethyl ether and carbon disulphide), and most water-soluble liquids are conductive enough to not raise problems of electrostatic discharges.

Ignition by electrostatic discharges poses a hazard for liquids with conductivities below  $5 \times 10^{-11}$  Siemens per meter (Babrauskas, 2003; BP, 2006c). However, if the conductivity is extremely low, typically less than  $1 \times 10^{-13} \text{ S m}^{-1}$ , the ionized components that can contribute to charge accumulation are practically non-existing. Hence, the real electrostatic ignition hazard is associated with conductivities in the range  $1 \times 10^{-13} - 5 \times 10^{-11} \text{ S m}^{-1}$  (see Figure 6-2 in Chapter 6).

Electrostatic discharges can ignite flammable mixtures of gas, vapour, or dust (Mannan, 2005; Babrauskas, 2003; BP, 2006c). Mannan discusses ignition in systems containing liquids, and various mechanisms for generating and discharging static electricity in such systems. Klinkenberg & van der Minne (1958) describe methods of estimating the magnitude of the electrical field inside storage tanks. The transfer of liquid into a tank generates a charging current that transports charge into the tank (Mannan, 2005). Some factors that influence this charge transport are:

- The diameter and material of the pipe.
- The viscosity and electrical conductivity of the liquid.
- The flow velocity or restrictions in the pipeline.
- Impurities, especially water (Klinkenberg & van der Minne, 1958).

The presence of a small amount of water in the product can increase the electrostatic charging effect by up to a factor of 50. High flow velocities, splash filling, or vigorous stirring of the contents in the tank also promote charge separation. Mannan (2005) describes the risk associated with electrostatic discharges in tanks for oil and chemicals, and during fire fighting in large storage tanks.

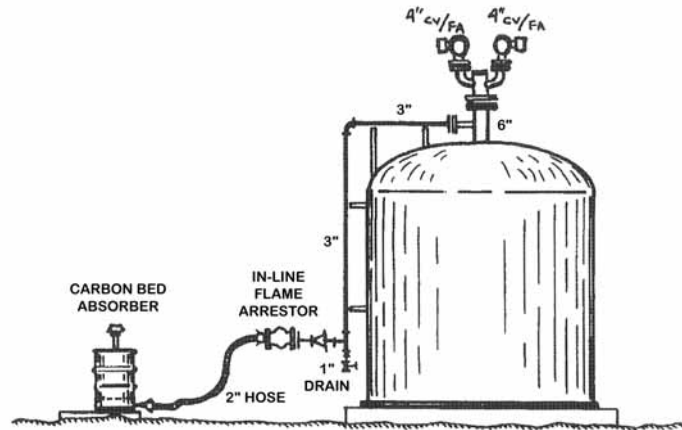
Kletz (1988) describes a 'typical' tank explosion where a large tank blew up 40 minutes after the start of a blending operation where one grade of naphtha was added to another. The fire was put out, and the next day the blending resumed in another tank – after 40 minutes this tank also exploded. The tanks were not nitrogen blanketed and there was an explosive mixture of naphtha vapour and air above the liquid in the tanks. High pumping rates resulted in significant charge generation, and the ignition source was electrostatic discharges between the liquid surface and either the top or wall of the tank.



## Self-ignition in filters with activated carbon

It is quite common to limit the release of volatile organic compounds, especially malodorous substances, by venting fixed-roof tanks through air filters that use activated carbon as the filter media. However, the combination of activated carbon and certain flammable compounds, like methyl mercaptan, ketones, and aldehydes, may result in self-ignition reactions in the filter media and subsequent ignition of the flammable vapour-air mixture inside the tank (EPA, 1997e; Zerbonia *et al.*, 2001). Both EPA, Zerbonia *et al.*, and Babrauskas (2003) describe the reaction between certain hydrocarbons and activated carbon as an exothermic adsorption process that may release sufficient heat for the temperature to exceed the ignition temperature of the activated carbon particles.

Figure 2-3 shows an installation where malodorous vapours from a tank are vented through a filter containing activated carbon (Harrell *et al.*, 1978). The flame arrester prevents a flame from propagating from the air filter to the tank, and the filter is placed at ground level to accommodate easy access and quick replacement in case of a smouldering fire in the filter media.



**Figure 2-3** Tank vented through a filter containing activated carbon, from Harrell *et al.* (1978).

## 3 System description and course of events

The purpose of this chapter is to summarize the course of events that led to the accident at Sløvåg on 24<sup>th</sup> May 2007. The system description and quotation of witness observations focus primarily on Tank farm II where the accident occurred. Of particular interest is information that can shed light on the composition of the explosive atmosphere inside tank T3 (discussed in Chapter 5), and conditions that influence the assessment of various ignition sources inside or outside the tank (Chapter 6).

### 3.1 The tank facility prior to the accident

The tank facility of Vest Tank AS was situated at the Sløvåg Industrial Area in the municipality Gulen on the west coast of Norway. The company treated oily or polluted water from the shipping and offshore industry, and released treated water to the sea according to a discharge permit from the Norwegian Pollution Control Authorities (SFT, 2001). Since October 2006, the company had also treated a petroleum product called coker gasoline in order to reduce the content of mercaptans.

Prior to the accident, the tank facility at Sløvåg contained three tank farms with 17 storage tanks (see Figure 1-2). The total volume, inner diameter (ID), and height (TT) of the individual tanks, according to drawings from Bergen Engineering, are summarized below. The content of the tanks at the time of the accident, according to statements from key witnesses, is also described.

- **Tank farm I** was used for storage, treatment, and recovery of liquids. The tank farm had a low bund wall and controlled run-off for drain water to the sea. None of the three tanks were destroyed during the accident on 24<sup>th</sup> May 2007:
  - **T1** (580 m<sup>3</sup>) contained cargo from M/T 'Probo Emu' and possibly 50 m<sup>3</sup> of acidic water.
  - **T2** (4000 m<sup>3</sup>) contained non-flammable mud/slurry from North Sea offshore activities.
  - **T5** (1000 m<sup>3</sup>) contained approximately 750 m<sup>3</sup> mud/slurry.
- **Tank farm II** was used for storage, treatment, and recovery of liquids, including coker gasoline. The tank farm had a bund wall and controlled run-off for drain water to the sea. All of the five tanks were destroyed in the accident on 24<sup>th</sup> May 2007 (see Figure 3-2 and Figure 3-3):
  - **T3** (4000 m<sup>3</sup>, ID 18 m, TT 16 m) contained about 270 m<sup>3</sup> liquid at the time of the accident: 50 m<sup>3</sup> precipitated waste from the treatment of coker gasoline, 205 m<sup>3</sup> waste water from tank T61, and 14-15 m<sup>3</sup> hydrochloric acid (filling of acid from a tank truck was going on when the accident occurred). It should be pointed out that some sources estimate the total volume of the liquids in T3 to 255 m<sup>3</sup> (including the 14-15 m<sup>3</sup> of acid), but this does not significantly influence analysis in this report. Tank T3 was the first to explode during the accident. Figure 3-1 shows a sketch of the tank prior to the accident.
  - **T4** (5000 m<sup>3</sup>, ID 22 m, TT 13 m) contained 350 m<sup>3</sup> of residue from the treatment of coker gasoline, including combustible liquid from tank T3. This tank exploded shortly after tank T3.
  - **C1** (120 m<sup>3</sup>) contained approximately 60 m<sup>3</sup> liquid waste from the treatment of coker gasoline in T3 and T4, and transfer of this liquid to a tank truck had started 10 minutes before the first explosion). Figure 3-2 shows that the top of the tank blew off during the accident.
  - **C2** (120 m<sup>3</sup>) was empty at the time of the accident, but the tank was nevertheless destroyed during the fire (see Figure 3-2).
  - **C3** (120 m<sup>3</sup>) was empty at the time of the accident, but the tank was nevertheless destroyed during the fire (see Figure 3-2).

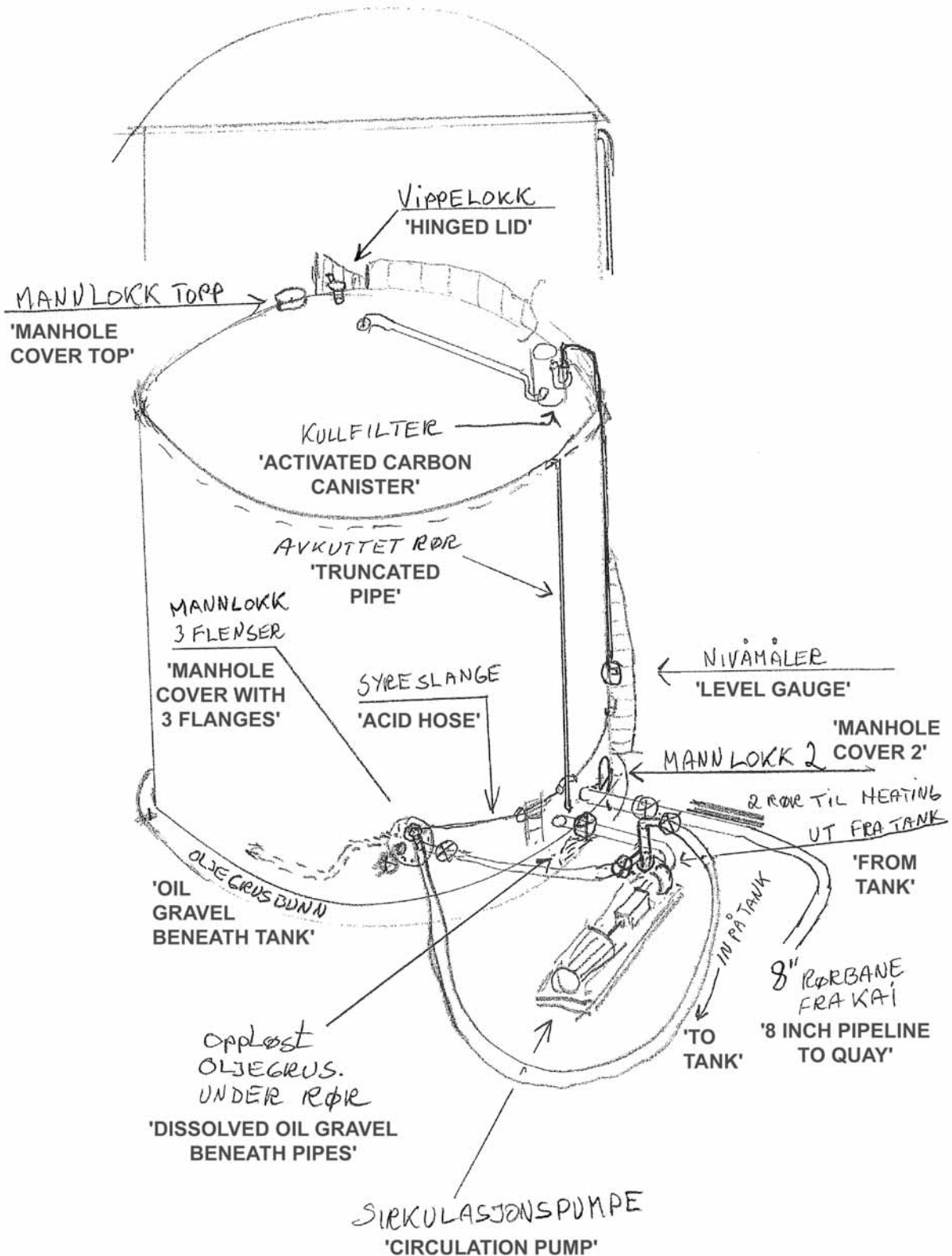
- **Tank farm III** was used for receiving waste from the offshore and shipping industry. The tank farm had a bund wall and pipe drainage ducts. None of the nine tanks were significantly damaged in the accident on 24<sup>th</sup> May 2007:
  - **T51** (12290 m<sup>3</sup>) contained slop water and mud.
  - **T52** (12290 m<sup>3</sup>) contained acidic water from Mongstad (almost empty).
  - **T53** (11060 m<sup>3</sup>) contained slop water.
  - **T54** (11060 m<sup>3</sup>) was not in use.
  - **T55** (8534 m<sup>3</sup>) contained slop water with a fraction of mud.
  - **T56** (8534 m<sup>3</sup>) contained a mixture of water and flushing water from cleaning of other tanks.
  - **T57** (8534 m<sup>3</sup>) had contained acidic water, but was empty at the time of the accident.
  - **T61** (12290 m<sup>3</sup>) contained 2000–2500 m<sup>3</sup> waste oil and water from C1.
  - **T63** (12290 m<sup>3</sup>) contained slop water with a fraction of mud.

Of primary interest for the accident investigation described in this report are circumstances relating to Tank farm II, and in particular tank T3.

Figure 3-1 is a schematic illustration made by one of the witnesses that shows tank T3 and the system for adding hydrochloric acid while circulating the contents of the tank. The following points should be noted, since they are relevant for the discussion in chapters 4 to 6:

- The tank was vented through an activated carbon canister to limit the release of malodorous gases; a six-inch flexible hose connected the canister to an opening in the centre of the tank top.
- The sketch shows the various openings in the tank; although all manhole covers were closed prior to the accident, the six-inch hinged lid was repeatedly used to inspect the processes inside the tank during the night before the accident, and to some degree this opening served the function of a pressure release valve since it would open at a certain internal pressure in the tank (estimated to about 11 mbar).
- A one inch pipe entered through the wall of the tank just below the tank top, and was truncated about 0.5 m above the ground, where it had been sealed with adhesive tape shortly before the process of adding hydrochloric acid started.
- The heating system in the bottom of the tank was not in use.

Section 3.2 contains a more detailed discussion of the course of events prior to and during the accident at Sløvåg on 24<sup>th</sup> May 2007.



**Figure 3-1** Schematic sketch illustrating tank T3 prior to the accident. The drawing shows the openings in the tank, the truncated pipe sealed with adhesive tape, the system for adding acid while circulating the content on the tank, and the air filter on top of the tank. Witness C (Table 3-1) made the drawing during an examination at Masfjorden Police Station on 13<sup>th</sup> June 2007, and the authors added the printed text during the translation of the English version of this report.

## 3.2 The course of events during the accident

This section describes the course of events during the accident, according to the witness observations. The intention is to shed light on the possible extent of flammable mixture prior to ignition, as well as possible ignition sources.

Table 3-1 summarizes the observations by the various witnesses. There are several similarities between the statements:

- About half of the witnesses heard two separate explosions within a short time period.
- Four witnesses heard a sound they describe as a gas leak shortly before the first explosion.
- Several witnesses saw flying objects (projectiles).
- Several witnesses observed smoke or steam from the air filter prior to the accident.

Some witness observations stand out from the others:

- Two witnesses report a relatively long time delay between the first two explosions:
  - One witness estimates the delay to significantly more than 10-15 seconds.
  - One witness estimates the delay to about 20-30 seconds.
- Two witnesses saw flames near tank T3 prior to the first explosion.

There can be several explanations for the apparent contradictions in the observations concerning the first explosions. It is plausible that the perception of time during this type of incident varies from person to person. Furthermore, a statement referring to 'the second explosion' by one witness may refer to a different explosion, or loud bang, compared to a similar statement from another witness (i.e. if one witness perceives two consecutive explosions as one single explosion).

Figure 3-2 and Figure 3-3 illustrate the damage to Tank farm II after the accident on 24<sup>th</sup> May 2007:

- Tank T3 exploded first: the base/wall weld ruptured, and the upper part of the tank was launched up in the air and landed in the north-eastern corner of Tank farm II, leaving the base of the tank on the ground; the roof of the tank landed even further away.
- Tank T4 exploded shortly after; it is likely that projectiles from tank T3 hit it.
- The roof on tank C1 blew off during the subsequent fire, and tanks C2 and C3 collapsed.
- Parts of the bund wall collapsed.
- Two of the three tank lorries outside the bund wall were more or less completely burnt-out: the lorry delivering the hydrochloric acid and an old vacuum truck placed near the office building; in addition, there was some damage to the blue tank lorry collecting waste liquid from tank C1.

The overall agreement between the various witness observations is reasonably good, and the physical evidence from the tank facility after the accident supports these observations.

**Table 3-1** Summary of witness observations describing the course of events during the accident at Vest Tank on Sløvåg on 24<sup>th</sup> May 2007; the reader should refer to Table 3-2 for a brief chronological summary of key events prior to the accident, Figure 1-2 for the layout of the tank facility, and Figure 3-1 for details concerning tank T3. Note that a reference to 'Witness Z' in the text corresponds to the respective witness ('Z') in this table.

Witness	Location and movement	Description of the accident
<p><b>Witness A</b></p>	<p>The witness stood together with <i>Witness K</i> between Tank farm II and the tank lorry delivering the acid (near the winding staircase); escaped towards the quay, and thereafter towards the quarry (Figure 1-4).</p>	<p>The witness describes the explosion as 'launching of a space shuttle'; cannot tell whether there were one or two explosions. According to <i>Witness K</i>, the witness was thrown to the ground by the explosion; however, the witness has no recollection of this.</p>
<p><b>Witness B</b></p>	<p>The witness and five others were inside the red office building; escaped behind the blue tent hall and then along the quayside northwards.</p>	<p>The witness perceived two consecutive explosions, managed to move into the shower room, was thrown to the ground, observed flying objects, a pressure wave, and windows breaking. The witness finally managed to get out of the office building, and noticed that tank T3 was gone, and flames issuing from the north side of T4.</p>
<p><b>Witness C</b></p>	<p>The witness was not present when the accident occurred.</p>	<p>The witness had been monitoring the process of adding hydrochloric acid to tank T3 (together with <i>Witness Q</i>). Three times during the night, the witness observed the processes inside the tank through a 6-inch hinged lid on the roof of the tank; the first two inspections indicated that the solid waste dissolved according to plan, but the third inspection (about 5 am) revealed circulating structures of oil drops floating on the surface. Around 6 am the witness noticed a strong malodorous smell, similar to what had been observed in the small-scale pilot study, and around 8:00 the witness saw steam/smoke issuing from the air filter on the roof of the tank. <i>Witness K</i> relieved the witness, and the witness went home between 9:00 and 9:30 in the morning.</p>

Witness	Location and movement	Description of the accident
<b>Witness D</b>	The witness was inside the red office building when the accident occurred (together with <i>Witness H</i> ); escaped behind the blue tent hall and further along the quayside northwards.	The witness arrived at Vest Tank around 8:00, and was told that everything had gone according to plan during the night; there was no indication of abnormal heat generation in tank T3. However, due to the observation of smoke from the air filter, the addition of acid had paused for 20-30 minutes just after 8:00. It was assumed that the smoke from the filter was steam, since it dissolved very quickly, and the process of adding hydrochloric acid resumed. The witness heard a rumbling sound, before the office building shook and fractured. Outside the red office building, the witness noticed flying objects and flames from various directions.
<b>Witness E</b>	The witness was in the coffee room inside the red office building when the accident occurred; escaped a few hundred meters towards the west.	Immediately before the explosion, the witness heard a sound that resembled a gas leak from a hose or a tank; the sound lasted for 1-2 seconds.
<b>Witness F</b>	The witness was not present when the accident occurred.	The witness was at Ågotnes when the accident occurred, and arrived at Sløvåg around noon.
<b>Witness G</b>	The witness was not present when the accident occurred.	The witness described previous maintenance work on tanks inside Tank farm II.
<b>Witness H</b>	The witness was in an office inside the red office building when the accident occurred (together with <i>Witness D</i> ). The witness escaped behind the blue tent hall, ran over to the basin with the drain cocks from Tank farm II and closed the drains, continued to the fire station and started the sprinkler system, and finally evacuated southward along the seashore.	The witness heard a loud bang (a 'heavy hollow sound') that shook the building; as the witness was running out from the building, there came an even stronger explosion (some 20-30 seconds after the first one). The witness waited inside, as scrap metal fell down around the building. The witness noticed that a lot of smoke developed outside, and went back for two respirators (gave one to <i>Witness E</i> ).

Witness	Location and movement	Description of the accident
<p><b>Witness I</b></p>	<p>The witness stood on the quayside, some 700-800 meters away from the tank facility; drove away towards the incineration plant.</p>	<p>The witness heard a loud boom ('more powerful than a blast in the quarry'), and observed that the upper part of a tank lifted off and dissolved in several parts; three large projectiles landed in the sea north of M/T Karen Knutsen. Immediately after, a flame ball emerged more than 100 meters above ground, and 2-3 seconds later were another flame ball about 50 meters high. The flames from the subsequent fire reached 10-20 meters above ground, and after 5-10 minutes, there was another weak explosion.</p>
<p><b>Witness J</b></p>	<p>The witness sat inside a semi-trailer, some 40 meters away from the tank facility; jumped under the truck, and ran southwards along the quayside towards Baker Oil.</p>	<p>Heard a loud bang and saw the top of the tank (T3) lift off and split into several parts; scrap metal fell down for some 20-30 seconds, and some weaker bangs followed during the subsequent fire.</p>
<p><b>Witness K</b></p>	<p>The witness stood together with <i>Witness A</i> between Tank farm II and the tank lorry delivering the acid (near the winding staircase leading into Tank farm II); jumped under the tank lorry, before heading towards the red office building, but continued to the fire station and started the sprinkler system (together with <i>Witness H</i>).</p>	<p>The witness arrived at Vest Tank around 8:00, and received an update from <i>witnesses A, C, L, and Q</i> concerning the process that went on in tank T3: the malodorous smell had decreased from 6:00 to 8:00, and white smoke from the air filter had resulted in a temporary pause in the addition of acid. <i>Witness C</i> had been on the roof of T3 without noticing anything out of the ordinary. The witness entered Tank farm II to check the hose connections on the pump, and continued to gather tools outside the tank farm. Some 15-20 seconds after the witness left the tank farm there came a loud hissing sound for 3-5 seconds, and then the first explosion occurred. The witness was thrown to the ground by the explosion, and observed tank T3 lift off in smoke and flames, before scrap metal started falling down. The witness did not notice any sign of flames or fire outside the tank farm prior to the first explosion. The second explosion, believed to be tank T4, took place some 10-15 seconds later.</p>
<p><b>Witness L</b></p>	<p>The witness arrived at Vest Tank at 08:50, and was inside the red office building when the accident occurred. The witness escaped behind the blue tent hall, and then along the quayside northwards.</p>	<p>The witness heard a loud bang and observed flying objects, some penetrating the roof of the building.</p>



Witness	Location and movement	Description of the accident
<b>Witness M</b>	The witness and a colleague stood inside tank farm III when the accident occurred, about 50 meters from T3; both evacuated towards the quay, away from the tanks.	The witness felt the ground shaking, and then a gust of wind about 1 second after the first explosion. Small pieces of scrap metal started falling down, and a large piece of the roof from a tank flew through the air ('it looked like a tarpaulin').
<b>Witness N</b>	The witness and two colleagues stood approximately 60 meters from the tank facility, about 10 meters north-west of the blue container. The witness took cover, but later got a camera from the car and took some pictures before leaving the area.	The witness heard a load bang ('like to cars colliding'), and noticed flames in front of the blue tank (T3); the tank exploded some 2-4 seconds later, and a large metal plate (about 2 m <sup>2</sup> ) and some railing rotated through the air above the witness; then the large tank (T4) collapsed.
<b>Witness O</b>	The witness was onboard M/T Karen Knutsen when the accident occurred. A tugboat pulled the tanker away from the quay.	Heard a bang and felt vibrations at 09:55.
<b>Witness P</b>	The witness arrived at Vest Tank 8:30, and stood by the blue tank truck when the accident occurred.	The witness noticed that gas started flowing from the top of tank T3 immediately prior to the first explosion, and observed flames and smoke near the ground before the tank launched into the air.
<b>Witness Q</b>	The witness was not present when the accident occurred.	The witness had been monitoring the process of adding hydrochloric acid to tank T3 (together with <i>Witness C</i> ). Went home around 08:30, and noticed white smoke from the air filter on the roof of the blue tank (T3); the smoke dissolved almost immediately.
<b>Witness R</b>	The witness stood on the ferry quay in Sløvåg, about 1.5 km north of the tank facility (Figure 3-5).	The witness heard two loud consecutive bangs (about 09:58), and observed a cloud of black and white smoke.
<b>Witness S</b>	The witness was not present when the accident occurred.	The witness described previous maintenance work inside Tank farm II.
<b>Witness T</b>	The witness stood in the office of the company Wergeland Halsvik AS, approximately 800 meters from Vest Tank.	The witness noticed a strong vibration and a pressure pulse, and observed a fireball; interpreted the sound as two consecutive explosions.
<b>Witness U</b>	The witness was not present when the accident occurred.	The witness had provided advice to Vent Tank concerning the process of dissolving the precipitated waste by adding hydrochloric acid.

<b>Witness</b>	<b>Location and movement</b>	<b>Description of the accident</b>
<b>Witness V</b>	The witness stood on the premises of the company Baker Oil Tool, some 500 meters from Vest Tank.	The witness watched the top of the tank (T3) being lifted by a gas column, heard a loud bang some 3-5 seconds later, and saw lots of flames and black smoke.
<b>Witness W</b>	The witness stood on the premises of the company Baker Oil Tool, some 500 meters from Vest Tank.	The witness noticed a hissing sound immediately prior to the first explosion; something was projected into the air, followed by flames, a loud bang, and black smoke; another bang followed a few seconds later.
<b>Witness X</b>	The witness was onboard M/T Karen Knutsen when the accident occurred. A tugboat pulled the tanker away from the quay.	The witness observed small flames between the bund and the blue tank (T3), then flames behind the blue tank lorry, and immediately thereafter T3 exploded; estimates the time between the first observation of flames and the first explosion to 2-3 seconds.

**Table 3-2** Key activities and events that took place at the tank facility of Vest Tank AS at Sløvåg prior to the accident on 24<sup>th</sup> May 2007.

Time period	Activities and events
2006	Autumn Three new tanks installed in Tank farm II: C1, C2, and C3.
	Oct. – Nov. Air filters with activated carbon installed on tanks T3 and T4.
	Oct. – Nov. Treatment of coker gasoline from tankers initiated.
	Late autumn Electrical cabinets installed outside Tank farm II (not Ex-equipment, but outside Ex-zone).
2007	March Service on a pump inside Tank farm II (Ex-equipment).
	April Meeting at Vest Tank, addressing the further treatment of waste from the cleaning of coker gasoline. Two methods considered: adding hydrochloric acid, or adding oxygen and heat (so-called WAO process) – the first alternative was chosen.
	April – May Laboratory-scale experiments, HCl added to waste from T3; tests considered successful.
May 2007	9 <sup>th</sup> Meeting at Vest Tank, discussing the procedures for adding hydrochloric acid to T3.
	18 <sup>th</sup> Ordering of the hydrochloric acid.
	21 <sup>st</sup> Safe Job Analysis (SJA) at Vest Tank; decided to change the filtering media in the air filters to limit the release of malodorous compounds.
	22 <sup>nd</sup> Fresh activated carbon in the air filters on T3 and T4 (15-20 sacks, 25 kg each).
23 <sup>rd</sup> May	15:30 Addition of hydrochloric acid to T3 initiated; contains 50 m <sup>3</sup> precipitated waste and 205 m <sup>3</sup> wastewater from tank T61 (255 m <sup>3</sup> in total); 18 m <sup>3</sup> HCl to be added over an 18 hour period.
	19:30 <i>Witness C</i> observes the process through a 6-inch hinged lid at the roof of T3; notices no smell, and observes that some oil has separated from the solution.
24 <sup>th</sup> May	00:30 – 01:30 <i>Witness C</i> observes that more oil has separated from the solution.
	05:00 <i>Witness C</i> observes even more oil floating on the aqueous solution; oil drops stick together like 'frogspawn'-like agglomerates that circulate inside the tank; no extraordinary smell.
	06:00 Malodorous smell; a neighbouring company complains to Vest Tank.
	07:00 The malodorous smell diminishes.
	08:00 White smoke or steam observed from the air filter on the roof on tank T3; assumed to be steam, since it dissolves very quickly; the feed of acid stops temporarily for 20-30 minutes; <i>Witness C</i> observes the process again from the roof of the tank, without noticing anything out of the ordinary. <i>Witness K</i> takes over for <i>Witness C</i> ; notices a nauseating smell.
	08:30 <i>Witness Q</i> goes home; notices that white smoke is still coming out of the air filter.
	08:30 – 08:45 The addition of hydrochloric acid resumes.
	09:15 – 09:30 Leaking coupling near tank lorry replaced; the feed of acid stops temporarily.
	09:55 – 10:00 The first explosion in tank T3.



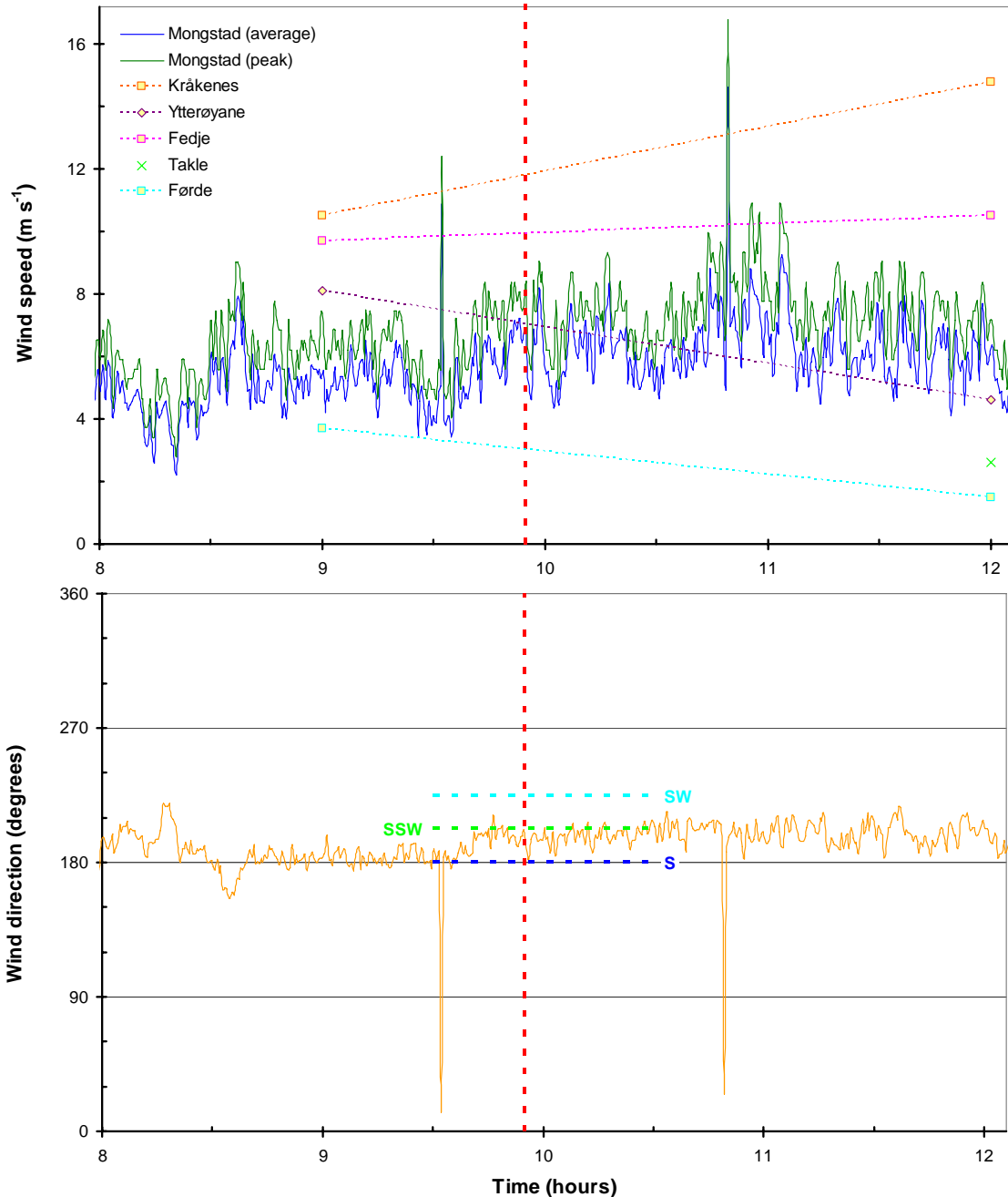
**Figure 3-2** Tank farm II viewed from the south (pictures taken from the roof of tank T2, see Figure 1-2). The upper picture shows the three smaller tanks C1-C3 along the bund, the upper part of T3 thrown partly out of the tank farm, and T4 collapsed; the base of T3 is below the water (The Norwegian Police, 25<sup>th</sup> May 2007). The lower picture shows the base of tank T3 with the heating system (The Norwegian Police, 31<sup>st</sup> May 2007).



**Figure 3-3** Various pictures of Tank farm II viewed from the north, illustrating the damage to the 5 tanks, the bund, the office building, the two tank lorries, and the vacuum truck; pictures from The Norwegian Police, taken 25<sup>th</sup> May 2007 (above and centre) and 31<sup>st</sup> May 2007 (below).

### 3.3 Weather data and maps

The CFD-simulations of gas dispersion outside tank T3, discussed in section 5.3, require information about the weather conditions at Sløvåg on 24<sup>th</sup> May 2007, as well as the topology of the terrain near the tank facility. Figure 3-4 summarises weather data from various sources for the relevant period, and Figure 3-5 shows two topographical maps of the area from the Geological Survey of Norway (NGU, www.ngu.no).



**Figure 3-4** Weather data: wind speeds (above) and wind directions (below); observations at the Mongstad oil refinery (provided by Terje Palmesen, Statoil Hydro; received from DSB) and various weather stations (provided by Anne Haaland Simonsen, Government Meteorologist, The Norwegian Meteorological Institute, Forecasting Division of Western Norway; received from Masfjorden Police Station).



**Figure 3-5** Topographical maps illustrating the area described by the weather data presented in Figure 3-4: overview showing Fedje, Mongstad, and Sløvåg (above), and a more detailed map showing the oil refinery at Mongstad, and Sløvåg (below). The tank facility was located at 'Stongeneset', about 1.5 km south of Sløvåg.

## 4 Physical explosion

The purpose of this chapter is to assess whether the conditions prior to the accident, and the course of events described by the witnesses, are consistent with a physical explosion in tank T3.

A physical explosion in tank T3 could only occur through an increase in the internal pressure caused by production of gas inside the tank and/or by a significant temperature rise in the gas inside the tank (thermal expansion). Furthermore, these processes would have to take place within a relatively short period to prevent efficient pressure relief through the openings in the tank. Assuming the tank could withstand the static pressure exerted by a 12.5-meter liquid column with density  $720 \text{ kg m}^{-3}$ , corresponding to 80% filling with coker gasoline, the tank should at least withstand an internal overpressure of 0.88 bar. The damages to the tank indicate that the wall/roof and the wall/base welds had approximately the same strength: apparently, the roof came off shortly after the upper part of the tank lifted from the ground.

To achieve an internal overpressure of at least 0.88 bar, the rate of increase in pressure had to exceed the rate of pressure relief by outflow through the openings in the top of the tank. Assuming the hinged lid closed ('worst case scenario'), leaving only the six-inch opening through the air filter for effective pressure relief, an internal overpressure of 0.88 bar corresponds to a mass flow rate of  $9.3 \text{ kg s}^{-1}$  for a gas with molecular weight of pentane ( $72 \text{ g mol}^{-1}$ ), and  $5.9 \text{ kg s}^{-1}$  for a gas with average molecular weight of air ( $29 \text{ g mol}^{-1}$ ). Additional pressure relief through the hinged lid would increase the corresponding flow rates significantly.

To achieve an internal overpressure in the tank that could cause it to rupture, the rate of vapour production from the liquid surface should exceed the rate of outflow through the openings in the tank. For tank T3, with inner diameter 18 m, this corresponds to a rate of vapour production from the liquid surface of  $23\text{--}36 \text{ g m}^{-2} \text{ s}^{-1}$ , or  $83\text{--}131 \text{ kg m}^{-2} \text{ hr}^{-1}$ . For comparison, the rate of vapour production from pentane is  $27.1 \text{ kg m}^{-2} \text{ hr}^{-1}$  at  $25 \text{ }^\circ\text{C}$  (Kawamura & MacKay, 1987); the boiling point of pentane is  $36.1 \text{ }^\circ\text{C}$ . Hence, the rate of vapour production from the liquid surface that would be consistent with a physical explosion scenario is very high; assuming a linear relation between the rate of evaporation and the vapour pressure, boiling of pentane inside the tank would not be sufficient.

Several witnesses noticed a sound that resembled the outflow of gas from a pressurised tank immediately prior to the first explosion, but the sound lasted for only 1-2 seconds (Table 3-1). Potential mechanisms for generating gas in amounts that would be consistent with a physical explosion would therefore have to occur within a very limited period. Based on these witness observations and the above estimates of rates of vapour production, it seems highly unlikely that a physical explosion caused the accident. It can nevertheless be of interest to investigate various mechanisms that could result in rapid release of gas from the liquid surface: evaporation of hydrocarbon liquids, boiling of water, or very rapid release of sulphur containing components because of adding hydrochloric acid to the alkaline solution in the tank.

The manhole covers on the roof of tank T3 had been kept open over a period of about 4 weeks (up to a few days prior to the accident), and it seems reasonable to assume that only a limited amount of low molecular weight hydrocarbons remained in the liquid phase. Furthermore, most of the flammable liquid had been removed prior to the process of adding hydrochloric acid. Evaporation of heavier hydrocarbons (higher molecular weight than air) will typically produce a dense vapour layer that covers the liquid surface. The resulting equilibrium between evaporation and condensation, between the liquid surface and the dense vapour layer, will limit the net rate of evaporation from the surface. Hence, rapid evaporation of hydrocarbons from the liquid surface is not consistent with a scenario involving a physical explosion.



Evaporation of water could only yield the required rate of vapour production if the temperature in the liquid exceeded the boiling point of water (100 °C). A vapour pressure of 0.88 bar can be achieved at a temperature of approximately 95 °C in a closed container. It is highly unlikely that chemical reactions between the hydrochloric acid and the alkaline solution could release enough energy to raise the overall temperature of the solution to temperatures in this range (see section 5.2). Furthermore, it is practically impossible that such a process should take place within a sufficiently short period to explain the course of events at Sløvåg on 24<sup>th</sup> May 2007, as described by the witnesses (Table 3-1).

There is significant uncertainty associated with the rate of gas production that followed from reduced solubility of sulphur containing components when the pH value in the solution was reduced from more than 11 to about 9 by adding hydrochloric acid (see the discussion in section 5.1). Estimates based on evaporation experiments performed in open beakers by the police (The Norwegian Polices ref. 0723.11705b, 2007) suggest a rate of gas production of about 1 kg s<sup>-1</sup> in tank T3. However, the relative amounts of acid added in these experiments were probably somewhat lower than in the process that took place in tank T3 prior to the accident (section 5.1). Furthermore, it is not clear to what extent the results were influenced by evaporation of water (since the beakers were open), and the concentration of mercaptans measured above the liquid surface was quite low (about 12 ppm). Finally, there is significant uncertainty associated with extrapolating results from a laboratory scale experiments to actual large-scale industrial situations. It nevertheless seems highly unlikely that a change in solubility could take place within a sufficiently short period to explain a physical explosion in tank T3.

Based on the presumed chemical composition of the liquid inside tank T3, and witness observations during the accident, it is highly unlikely that a physical explosion, resulting from excessive gas production inside the tank, caused the accident at Sløvåg on 24<sup>th</sup> May 2007. Hence, it seems justified to assume that it was a chemical explosion that took place inside the tank, and the next two chapters explore such scenarios.

## 5 Formation of explosive atmosphere

From the analysis in the previous chapter, it seems highly unlikely that a physical explosion took place in tank T3, and it seems reasonable to assume that it was a chemical explosion that caused the accident at Sløvåg on 24<sup>th</sup> May 2007. A realistic description of plausible courses of events must therefore account for the composition of the fuel, the formation of the explosive atmosphere, and potential ignition sources. This chapter focuses on potential fuels and the formation of an explosive atmosphere, and Chapter 6 considers the most likely ignition sources.

### 5.1 Combustible material inside tank T3

There is considerable uncertainty associated with the actual composition of the solution inside tank T3 prior to the accident, but several of the components were without doubt combustible. The purpose of the following paragraphs is to assess the amounts of the various components that may have been present, and to summarize characteristic explosion properties of the most relevant substances.

#### Vapour from remains of coker gasoline or related flammable liquids

Although the majority of the flammable liquid from tank T3 was removed prior to adding the hydrochloric acid (see section 1.3), it seems reasonable to assume that there may have been traces of coker gasoline in the tank. Table 5-1 summarizes the composition and properties of coker gasoline, according to the available material safety data sheet (Pemex, 2005), as well as measured values of mercaptanic sulphur before and after the treatment with sodium hydroxide (from the statement of *Witness L*). It should be noted that the measured values indicate a significantly higher content of mercaptans than indicated by the data sheet (about three orders of magnitude higher), and the reason for this deviation is not clear. It is possible that the data sheet applies to the finally treated product, but according to the values in Table 5-1, a significant further reduction of the content of mercaptanic sulphur would then be required (i.e. from more than 500 ppm to 1 ppm). Another explanation could be that other sulphur containing compounds influenced the measurements of mercaptanic sulphur.

Table 5-2 summarizes some properties of coker gasoline, as well as the corresponding properties of some components in coker gasoline. Coker gasoline and pentane have similar flammability limits and boiling points, and it is therefore a reasonable assumption to use properties of pentane for estimating the amount of coker gasoline required for generating an explosive atmosphere in the free volume above the liquid surface in tank T3. Table 5-3 summarizes the amounts of various fuel vapours that, when mixed with air, would produce various flammable mixtures inside T3. For pentane, 152 kg could fill the tank with a homogeneous mixture at the lower flammability limit (LFL), 227 kg could produce a stoichiometric mixture, and 847 kg would be required to reach the upper flammability limit (UFL). However, it is highly unlikely that a homogeneous fuel-air mixture filled the entire free volume of the tank prior to the accident, and it is possible that the explosive atmosphere only occupied a certain fraction of the free volume.

*Witness C* observed the formation of an 'oily layer' on the surface of the aqueous solution when the hydrochloric acid was added to the tank (Table 3-1). Since a sample of the presumably similar liquid that was formed during the small-scale pilot experiments proved flammable (see section 1.3), the oily liquid formed inside tank T3 was most likely also flammable. Although the composition of this liquid

layer is unknown, it seems reasonable to assume that many of the components originated from coker gasoline.

There were also several flammable components in the liquid waste added from tank T61 to dilute the precipitated waste in tank T3. The composition of this liquid has been investigated by gas chromatography (The Norwegian Police, ALS Analytica NUF, 29. August 2007), and although the main component was water, there were also several flammable components: methanol, mercaptans (e.g. methanethiol, ethanethiol, 1-propanethiol, 2-propanethiol, 1-butanethiol, and 2-butanethiol), dichloromethane, methyl tert-butyl ether (MTBE, or 2-methoxy-2-methylpropane), and disulphides (e.g. dimethyl disulphide, methyl-ethyl-disulphide, ethyl-1-methyldisulphide, ethyl-n-propyl-disulphide, 1-methyl-ethyl-propyldisulphide, as well as several unspecified disulphides).

Coker gasoline has lower density than water, and a potential trace that remained after removing flammable liquid prior to the addition of hydrochloric acid could form a surface layer on the alkaline solution inside the tank. It is not clear how much the oily liquid observed by *Witness C* resembles coker gasoline, but since both liquids are flammable, evaporation from the surface layer would contribute to the explosive atmosphere inside the tank. For a tank diameter of 18 meters, or a liquid surface of 254 m<sup>2</sup>, the thickness of the hypothetical surface layers that corresponds to 152 kg (LFL), 277 kg (stoichiometric mixture), and 847 kg (UFL), is 0.95 mm, 1.73 mm, and 5.28 mm, respectively. Limited mixing is however likely to prevent the evaporation of such layers from forming a homogeneous mixture inside the tank, at least within a relatively short period. The lighter components would evaporate continuously from the surface layer, and this process had presumably gone on since the manhole covers were closed prior to diluting the content of T3 with wastewater from T61 (see Table 3-2). The addition of acid would typically result in an increase in temperature due to exothermic acid-base reactions (see section 5.2), and this would in turn increase the rate of evaporation of heavier components, and hence contribute to the formation of the explosive atmosphere. Although the explosive atmosphere only occupied parts of the tank, there could still be a chemical explosion provided the flammable mixture reached an ignition source.

**Table 5-1** Composition of coker gasoline, according to the data sheet from Pemex (2005) and relevant witness observations (*Witness L*).

Component	Concentration
Alkanes (paraffins)	56.08 vol%
Alkenes (olefins)	23.43 vol%
Cycloalkanes (naphthenes)	10.57 vol%
Aromatics	4.80 vol%
Not identified	5.12 vol%
Hydrogen sulphide liquid	< 5 ppm wt
Total sulphur content	8500 ppm wt
Mercaptanic sulphur according to data sheet:	1 ppm wt
Mercaptanic sulphur according to witness L – prior to the treatment at Vest Tank	1200 ppm wt
Mercaptanic sulphur according to witness L – after the treatment at Vest Tank	500 – 900 ppm wt

**Table 5-2** Properties of selected components of coker gasoline: molecular weight  $M_w$ , boiling point  $T_b$ , specific gravity SG of liquid at ambient conditions relative to density of water at 4 °C, lower flammability limit LFL, stoichiometric concentration  $C_{stoic}$ , upper flammability limit UFL, auto-ignition temperature  $T_{AIT}$ , and flash point  $T_{FP}$ . Data from Kuchta (1985), Babrauskas (2003), Perry (1997) and material safety data sheet for coker gasoline (Pemex, 2005). According to the data sheet, the vapour pressure of coker gasoline is 0.52 bar (7.6 psi). Missing values (NA) are due to one of three reasons: the value is not possible to define unambiguously (e.g.  $T_b$  for 'paraffins'), the value is non-existent (e.g. SG of  $H_2S$  in the liquid phase at ambient conditions), or the value was not found in the literature (e.g.  $C_{stoic}$  for coker gasoline).

Component	$M_w$ (g mol <sup>-1</sup> )	$T_b$ (°C)	SG (–)	LFL (vol%)	$C_{stoic}$ (vol%)	UFL (vol%)	$T_{AIT}$ (°C)	$T_{FP}$ (°C)
Paraffins	> 216	NA	NA	1.3	NA	8.1	242	NA
Pentane	72.15	36.3	0.630	1.4	2.55	7.8	258	- 49
Methyl mercaptan	48.11	5.8	0.896	3.9	6.53	22	325	- 17
Methyl mercaptide	70.11	>210	1.34	NA	NA	NA	NA	NA
Ethyl mercaptan	62.13	36	0.839	2.8	4.53	18	295	- 20
Hydrogen sulphide	34.08	- 59.6	NA	4.0	12.25	44	270	NA
<b>Coker gasoline</b>	NA	33	0.718	1.3 – 1.4	NA	7.1 – 7.6	280	- 45

**Table 5-3** Data for fuels that are relevant for the explosion in tank T3: density of pure fuel vapour  $\rho_{amb}$  (1 bar, 25 °C), and the required mass of fuel that, when mixed with air, would produce homogeneous explosive mixtures, occupying the entire free volume of the tank (3730 m<sup>3</sup>), with concentrations corresponding to LFL,  $C_{stoic}$ , and UFL, respectively.

Component	$\rho_{amb}$ (kg m <sup>-1</sup> )	LFL (vol%)	$m_{LFL}$ (kg)	$C_{stoic}$ (vol%)	$m_{stoic}$ (kg)	UFL (vol%)	$m_{UFL}$ (kg)
Pentane	2.91	1.4	152	2.55	277	7.8	847
Methyl mercaptan	1.94	3.9	282	6.53	473	22	1 593
Ethyl mercaptan	2.51	2.8	262	4.45	416	18	1 683
Hydrogen sulphide	1.37	4.0	205	12.25	628	44	2 256
Coker gasoline	NA	1.4	NA	NA	NA	7.6	NA

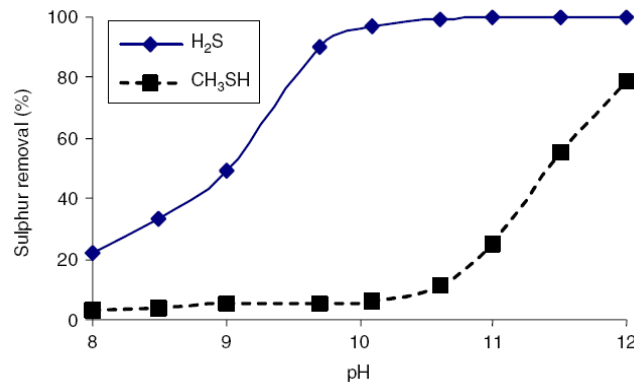
## Reduced solubility of mercaptans in less alkaline solutions

An alternative source of fuel inside tank T3 was the mercaptans, and possibly hydrogen sulphide, originating from the treatment of coker gasoline. The difference in the measured content of mercaptans, before and after the treatment at Vest Tank (see Table 5-1), provides a rough estimate for the total mass of mercaptanic sulphur removed from coker gasoline from October 2006 to April 2007. Assuming a reduction from 1200 to 900 ppm (i.e. 300 ppm by weight removed), in six tanker loads of coker gasoline (32 000 m<sup>3</sup> each), the total amount of mercaptans removed becomes:

$$6 \text{ tanker loads} \times 32\,000 \text{ m}^3 \text{ (tanker load)}^{-1} \times 0.000300 \times 720 \text{ kg m}^{-3} = 41\,470 \text{ kg}$$

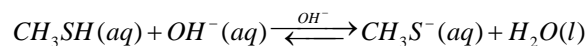
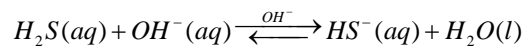
According to Table 5-3 it would be sufficient to mix 282 kg of methyl mercaptan with air to fill tank T3 (free volume 3 730 m<sup>3</sup>) with a mixture of the lowest flammable concentration ( $LFL = 3.9\%$ ), and 473 kg to fill the tank with a stoichiometric mixture ( $C_{stoic} = 6.53\%$ ). Hence, only 0.7 % of the mercaptans removed from the coker gasoline would be sufficient to reach the lower flammability limit in the entire tank, and 1.1 % could fill the tank with a stoichiometric mixture (assuming methyl mercaptan).

A plausible mechanism for the release of mercaptans from the initially alkaline solution is the reduced solubility of mercaptans when the adding of hydrochloric acid lowers the pH value of the solution. Figure 5-1 illustrates the effect of lowering the pH on the solubility of hydrogen sulphide and methyl mercaptan in a NaOH solution (Couvert *et al.*, 2006).

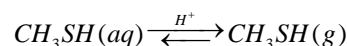


**Figure 5-1** Influence of pH in a NaOH solution on the removal of hydrogen sulphide (H<sub>2</sub>S) and methyl mercaptan (CH<sub>3</sub>SH) after 45 minutes, measured in a laboratory scale adsorption (scrubbing) column; gas temperature 25 °C and initial concentrations  $[H_2S]_i = [CH_3SH]_i = 7 \text{ ppm}$ ; from Couvert *et al.* (2006).

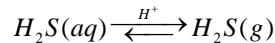
Higher pH in the solution results in increased solubility of the gases because both hydrogen sulphide (H<sub>2</sub>S) and methyl mercaptan (CH<sub>3</sub>SH) react as acids in the liquid phase reactions:



It should be pointed out that the experiments by Couvert *et al.* were performed in an adsorption column where hydrogen sulphide or methyl mercaptan were removed from the gas phase, i.e. 'the opposite' process of the one that presumably took place in tank T3 at Vest Tank. At Sløvåg, the added acid reduced the pH in the solution, and this resulted most likely in increased mass transport of methyl mercaptan (CH<sub>3</sub>SH) across the liquid-vapour boundary surface according to the equilibrium:



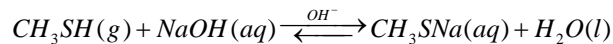
Provided the alkaline solution in T3 also contained significant amounts of hydrogen sulphide (H<sub>2</sub>S), a shift in the following equilibrium would also result in a release of this gas:



Consequently, it seems reasonable to assume that the addition of hydrochloric acid to the alkaline solution in tank T3 resulted in the release of fuel in the form of gaseous mercaptans, and possibly hydrogen sulphide, and that these gases mixed with air to form an explosive atmosphere inside the tank. The solubility of methyl mercaptan (CH<sub>3</sub>SH) in water at 25 °C is 23.30 kg m<sup>-3</sup> (MTC, 2001), but the solubility is significantly higher in solutions of 1 N sodium hydroxide (ATOFINA, 2001).

Although most of the original liquid was removed prior to the process of diluting the precipitated waste with water from tank T61, it is highly likely that the remaining waste in tank T3 was saturated with mercaptan salts, disulphides (RSSR), or related components. Reduced pH after the addition of hydrochloric acid to the diluted solution would most likely cause a shift in the equilibrium that resulted in more mercaptans in the solution. The solubility of mercaptans in both water and sodium hydroxide solutions decreases rapidly with increasing molecular weight (ATOFINA, 2001), so it is possible that the precipitated waste contained significant amounts of heavy mercaptans, mercaptan salts, and disulphides.

The sodium salt of methyl mercaptan (sodium methyl mercaptide, CH<sub>3</sub>SNa) form when bubbles of methyl mercaptan pass through a solution of sodium hydroxide:

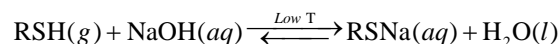


Higher pH shifts the equilibrium towards more methyl mercaptide in the solution, and lower pH shifts the equilibrium towards more gaseous methyl mercaptan. According to the *Mercaptans/Thiols Council* (MTC, 2001), the ratio between CH<sub>3</sub>SNa and CH<sub>3</sub>SH is 1:1 in a solution at 25 °C at pH 10.7, and shifts by a factor 10 for each unit change in pH:

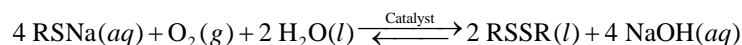
- 100:1 for pH 8.7 (primarily methyl mercaptan).
- 10:1 for pH 9.7
- 1:1 for pH 10.7 (equal amounts of methyl mercaptan and methyl mercaptide in the solution).
- 1:10 for pH 11.7
- 1:100 for pH 12.7 (primarily methyl mercaptide).

Hence, the addition of acid to an alkaline solution with high mercaptide content will result in the release of gaseous mercaptans.

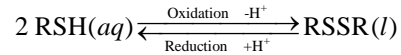
There exist many methods for removing sulphur-containing components like hydrogen sulphide and mercaptans from petroleum products (so called 'sweetening'), and several of these utilize the fact that low molecular weight mercaptans have low solubility in sodium hydroxide solutions. One example is the so-called Mercox™ process that removes mercaptans from liquid hydrocarbons in a two-step process (UOP, 2007). In the first step, the mercaptans (RSH) dissolve in the NaOH-solution, forming sodium mercaptides (RSNa):



The second step regenerates the NaOH-solution as the mercaptides oxidize to disulfides (RSSR), or 'disulfide oil':



According to UOP (2007), the catalyst is required for accelerating the process to an 'economically acceptable rate', and it is therefore difficult to predict the amount of disulfides that may have been formed over a relatively long time period during the treatment of coker gasoline at Vest Tank. However, the disulfide bond is a weak chemical bond, and can easily be reduced to give the mercaptan (Patai, 1974; Streitwieser *et al.*, 1992):



Hence, it is likely that some of the precipitated waste in tank T3 consisted of disulphides formed from mercaptans, and that the addition of hydrochloric acid to the solution reduced some of these disulfides back to mercaptans.

Provided the treatment at Vest Tank involved a significant reduction in the concentration of dissolved mercaptans in the coker gasoline, from about 1200 ppm to 900 ppm or less (*Witness L*), and assuming that a significant fraction of the precipitated material was still present in the solid waste inside tank T3, the potential amount of fuel present inside the tank was definitely more than enough to explain the accident that occurred on 24<sup>th</sup> May 2007.

### Laboratory experiments for estimating the rate of evaporation in tank T3

The police reported some preliminary results from experiments in open beakers (66 and 56 mm in diameter) that may indicate the rate of evaporation from the solution inside tank T3 (The Norwegian Police ref. 0723.11705b, 2007). Precipitated waste was diluted with either pure water, or wastewater from tank T61, and 0.054 grams of 36 % hydrochloric acid was added to 10 grams of the solutions. This corresponds to about 10 % of the relative amount of acid added to tank T3 prior to the accident ( $0.054 \text{ g} \div 10 \text{ g} = 0.0054$ , and  $14 \text{ m}^3 \div 255 \text{ m}^3 = 0.055$ ).

The rate of gas generation, measured as weight loss over time, indicated a near linear mass flux of  $1.85 \cdot 10^{-5} \text{ kg s}^{-1} \text{ m}^{-2}$  from a 4 mm high liquid column in the beakers. Assuming the same volumetric release of mercaptans from the  $255 \text{ m}^3$  of solution in T3 (i.e. approximately a 1 m high liquid column with diameter 18 m) suggests a mass flux of  $4.6 \cdot 10^{-3} \text{ kg s}^{-1} \text{ m}^{-2}$ , or a total estimated rate of gas generation of about  $1.16 \text{ kg s}^{-1}$ . The experiments also showed that the vapours above the liquid surface contained mercaptans, but not measurable amounts of hydrogen disulphide or hydrocarbons.

The amount of hydrochloric acid added in the experiments suggests that the pH of the solution was reduced to a level where mercaptans could become less soluble in an aqueous environment (pH about 11). However, according to Figure 5-1, more acid would be required to release significant amounts of  $\text{H}_2\text{S}$  from the solution. Hence, it not clear whether the results from these laboratory scale experiments provide a realistic estimate of the rate of gas release that took place in tank T3 prior to the accident on 24<sup>th</sup> May 2007.

### Possible contributions from other combustible gases

Technically, the explosive atmosphere in T3 may have contained other flammable gases, in addition to hydrocarbons, mercaptans, and possibly hydrogen disulphide. The investigation considered the possibility of generating significant amounts of hydrogen gas through reactions between exposed metal surfaces in the tank and acid (or lye), but no evidence was found to supported this hypothesis. On the contrary, the available sources on relevant corrosion processes suggest that only very limited amounts of gaseous hydrogen would form within the relevant period of time (e.g. Bengough *et al.*, 1931).

## Discussion of possible combustible material in tank T3

It is highly likely that the addition of hydrochloric acid to the solution in tank T3 triggered two mechanisms that contributed to the formation of an explosive atmosphere inside the tank:

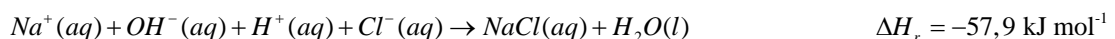
- The formation of a thin surface layer of coker gasoline and/or similar flammable liquids, and subsequent evaporation of low molecular weight hydrocarbon components.
- Reduced solubility of sulphur containing organic compounds in the alkaline solution following the addition of hydrochloric acid (reduced pH), and subsequent release of mercaptans and possibly hydrogen disulphide.

It is likely that both mechanisms influenced the course of events in T3, and it is not straightforward to estimate the relative contribution from each process. However, assuming that the original content of mercaptans in coker gasoline was of the order of magnitude indicated by *Witness L*, i.e. about 1200 ppm, it seems reasonable to assume that the primary contribution to the explosive atmosphere came from the release of mercaptans, and possibly also other sulphur containing components.

## 5.2 Formation of explosive atmospheres inside tank T3

The key prerequisites for a chemical explosion inside tank T3 on 24<sup>th</sup> May 2007 are the formation of an explosive mixture of flammable gas and air inside the tank, and an ignition source within reach of the flammable mixture. From the discussion in section 5.1, it seems clear that there were abundant amounts of gaseous fuel available inside the tank. Buoyancy due to a vertical temperature gradient (exothermal reactions presumably raised the temperature of the solution somewhat), diffusion due to a vertical concentration gradient, and/or convection due to the motion of the liquid surface (circulation during the addition of hydrochloric acid), may have promoted the transport and mixing of air and flammable gases released from the liquid surface. This section explores the creation of a vertical temperature gradient, and the subsequent formation of a flammable mixture inside the tank.

Release of vapours from a liquid surface with temperature above ambient may have created a vertical temperature gradient inside the tank. Heating of the solution could be due to exothermal acid-base reactions between hydrochloric acid and sodium hydroxide (Book of Data, 1984):



Assuming a total added volume of 14.5 m<sup>3</sup> of 36 % hydrochloric acid (HCl) with density 1179 kg·m<sup>-3</sup> (according to the material safety data sheet for 'hydrochloric acid 30-36 %'), the solution in tank T3 contained 6 153 kg pure HCl, or 168.8 kmol ( $M_{\text{HCl}} = 36.462 \text{ kg}\cdot\text{kmol}^{-1}$ ). If we further assume an excess amount of sodium hydroxide in the solution, and that the reaction ran to completion, the total amount of energy released would be  $57.9 \cdot 10^3 \text{ J}\cdot\text{mol}^{-1} \cdot 168.8 \cdot 10^3 \text{ mol} = 9.77 \cdot 10^9 \text{ J}$ . The corresponding increase in temperature becomes approximately  $9.77 \cdot 10^9 \text{ J} \div (4184 \text{ J}\cdot\text{kg}^{-1} \cdot \text{C}^{-1} \cdot 270 \cdot 10^3 \text{ kg}) = 8.7 \text{ }^\circ\text{C}$  for 270 m<sup>3</sup> solution (or 9.2 °C for 255 m<sup>3</sup> solution).

The calculations above assume that the density and specific heat of the solution are the same as for pure water, and that there is no heat loss to the environment. The results should nevertheless provide a reasonable worst-case estimate for the average temperature rise in the solution, although higher local temperatures ('hot spots') may have occurred if concentrated acid mixed with precipitated solid waste. It should be noted that the results do not deviate significantly from data reported by Vest Tank in a preliminary accident report (maximum temperature rise estimated to 10 °C), and that they are in



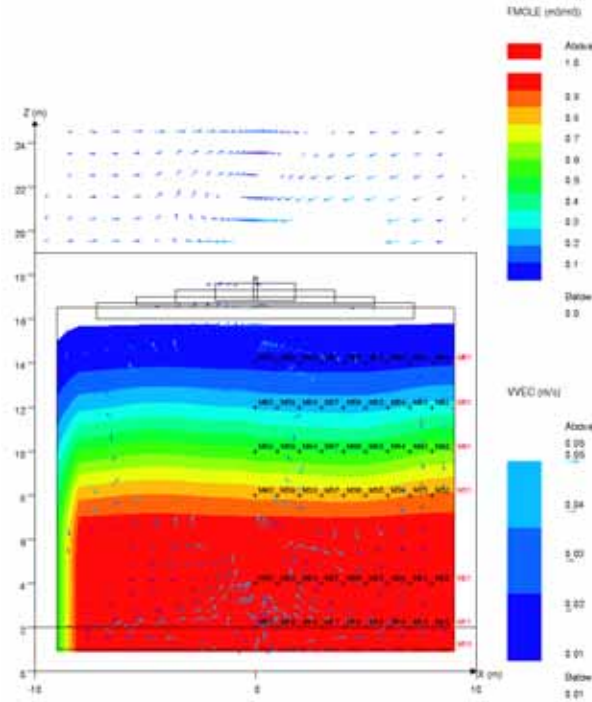
reasonable agreement with the measured temperature rise of 5 °C from the small-scale pilot experiments described in section 1.3 (Berland, 2007). However, there is considerable uncertainty associated with potential contributions from other exothermal reactions that may have taken place during the addition of hydrochloric acid to the alkaline solution containing precipitated waste.

Simulations with the CFD-code FLACS were performed to explore the process of mixing flammable vapour and air inside the tank. The purpose of this work was to explore reasonable locations for potential ignition sources, based on the extent of the flammable mixture. The analysis assumed ambient temperature of 12 °C, a total mass flow rate of 1 kg s<sup>-1</sup> evenly distributed over the liquid surface, and temperatures of the released vapours from the liquid surface of 35, 50, or 70 °C. A release rate of 1 kg s<sup>-1</sup> corresponds to a hypothetical release scenario involving boiling pentane (section 5.3). The same outflow through the six-inch opening to the air filter is consistent with an internal overpressure in the tank just below the pressure difference that would cause the hinged lid to open at an estimated pressure difference of 11 mbar, thereby doubling the vent area. However, the released vapour was modelled as propane, with a molecular weight of 44 kg kmol<sup>-1</sup>, since this corresponded reasonably well with both the lighter components in coker gasoline and the most relevant sulphur containing compounds: methyl mercaptan and hydrogen sulphide have molecular weights 48 and 34 kg kmol<sup>-1</sup>, respectively.

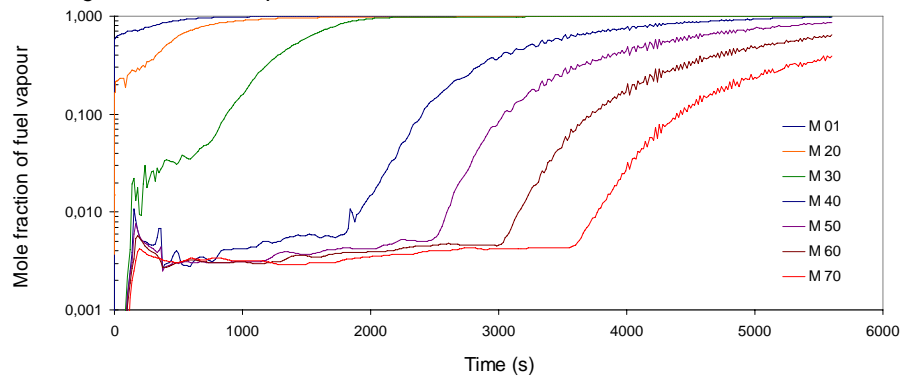
Figure 5-2 illustrates the simulated concentration gradient after 71 minutes in a vertical cross-section of the tank, for a release of vapour at 35 °C from a liquid surface. The flammable mixture has reached the top of the tank, while the concentration close to the liquid surface is above the upper flammability limit. The flow velocities resulting from buoyancy are approximately 4-5 cm s<sup>-1</sup>. Figure 5-3 shows how the simulated fuel concentration develops in the monitor points along the centre of the tank for the same simulation. Figure 5-4 illustrates the effect of decreasing the density of released vapour (by increasing the temperature, but reduced molecular weight would in principle have given similar results), on the simulated mole fractions of fuel vapour near the roof of the tank. Reduced density increases the buoyancy, and the flammable mixtures reach the top of the tank faster.

When the released vapour or gas is denser than the air inside the tank, the fuel concentration decreases gradually from the liquid surface and upwards. However, it is possible that increased temperature in the solution over time could have created a layer of less dense gas near the liquid surface, and that the resulting instability could have resulted in an inversion of the layers (convective mixing). Other effects may also have influenced the process, i.e. variations in the rate of release, liquid movement in the tank, or release of lower density gas (e.g. hydrogen sulphide) below a layer of more dense gas (e.g. mercaptans) as a result of reduced pH in the solution (see Figure 5-1).

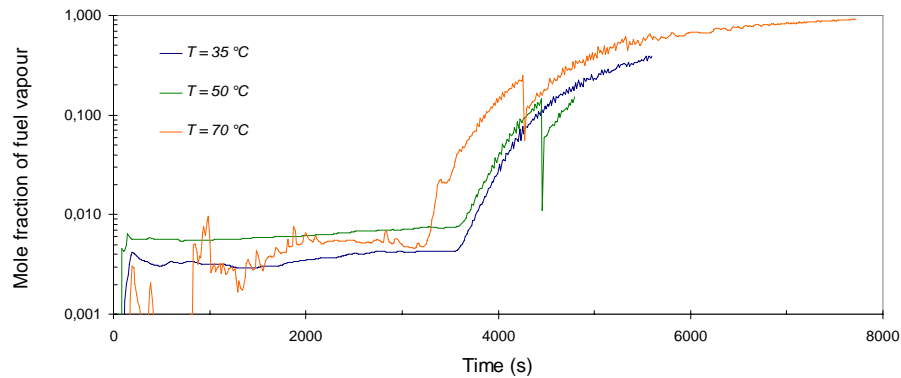
The simulations suggest that the entire free volume of the tank at some point in time would contain a flammable mixture. In the early stages, the explosive atmosphere would be limited to a zone just above the liquid surface. However, over time the zone with explosive mixture would move upwards, and probably reach the roof inside the tank within hours, while the fuel concentration near the liquid surface would exceed the upper flammability limit. Hence, it is not likely that the explosive mixture occupied the entire free volume of the tank at the same time, but this could nevertheless occur due to buoyancy driven flow or convective mixing, or by other means.



**Figure 5-2** Vertical cross-section of tank T3 illustrating the simulated mole fraction of fuel vapour and velocity vectors after a 71 minutes release from a liquid surface at elevated temperature; total release rate  $1 \text{ kg s}^{-1}$ ; release temperature  $35 \text{ }^\circ\text{C}$ .



**Figure 5-3** Simulated mole fractions of fuel vapour as a function of time at various elevations inside the tank; total release rate  $1 \text{ kg s}^{-1}$ , release temperature  $35 \text{ }^\circ\text{C}$ ; monitor points shown in Figure 5-2.



**Figure 5-4** Simulated mole fractions of fuel vapour near the roof of the tank as a function of time; monitor point M 70 in Figure 5-2; release rate  $1 \text{ kg s}^{-1}$ , and liquid temperatures of  $35$ ,  $50$ , and  $70 \text{ }^\circ\text{C}$ , respectively.

### 5.3 Formation of explosive atmospheres outside tank T3

The analysis in section 5.2 suggests that an explosive atmosphere, resulting from the release of flammable vapour or gas from the liquid surface, at some point in time filled most of the free volume inside tank T3. This section explores the possibility of releasing flammable mixtures through the openings in the tank, and thereby creating explosive atmospheres that could reach potential ignition sources outside the tank. The analysis is supported by simulations with the CFD-code FLACS.

Figures 5-5 to 5-7 illustrate the geometry model of the tank facility at Sløvåg that was implemented in FLACS for these simulations, and Figure 5-8 shows the simulated wind field in a horizontal cross-section 20 meters above the ground in Tank farm II. The wind data measured at the Mongstad oil refinery (see section 3.3) suggest wind from south at speeds around 6-8 m s<sup>-1</sup> at 10 am on 24<sup>th</sup> May 2007. Figure 5-8 illustrates that the simulated flow velocities are reduced on the leeward side of M/T Karen Knutsen, and downstream of the tallest tanks at Vest Tank.

To ensure conservative estimates of the simulated flammable gas clouds, the analysis assumed that pure fuel vapour (simulated as pentane) had replaced all the air in the tank, and the corresponding release rates are therefore high. Assuming a maximum temperature rise in the solution of 10 °C (see section 5.2), and an ambient temperature of 12 °C, the maximum temperature of the release should not exceed 22 °C. The exact composition of the fuel is unknown, but a model for pentane (molecular weight 72 kg kmol<sup>-1</sup>) nevertheless represented the fuel gas/vapour in the simulations. The maximum evaporation flux for pentane at 25 °C is 27 kg m<sup>-2</sup> h<sup>-1</sup> (Kawamura & MacKay, 1987), and this results in a total release rate of 1 kg s<sup>-1</sup> from tank T3.

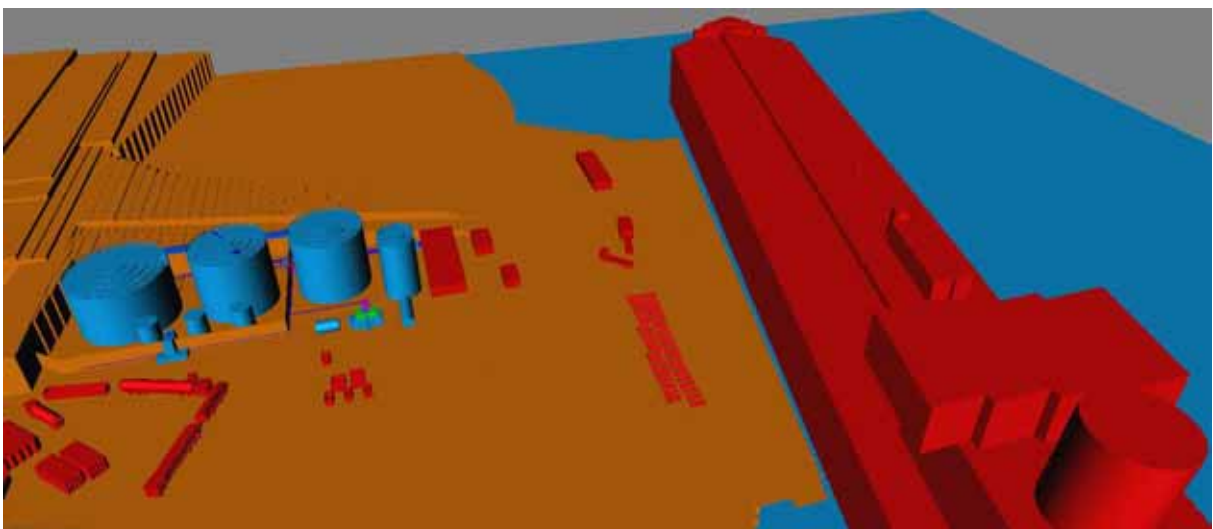
The first simulation involves a leak with release rate 1 kg s<sup>-1</sup>, pointing downwards from the position of the exit from the air filter, and wind from the south at a speed of 6 m s<sup>-1</sup>. Figure 5-9 shows a three-dimensional representation of the steady-state gas cloud formed by this release, and Figure 5-10 shows the cloud in a vertical cross-section through the tank. Figure 5-11 summarizes the simulated mole fractions of fuel vapour in the four monitor points shown in Figure 5-10. This simulation suggests that no traces of fuel reach the monitor point upstream of the tank, and that the concentrations in the monitor points downstream of the release are of the order 0.01-1 ppm, i.e. significantly lower than the lower flammability limit for the relevant fuels (Table 5-2 suggests LFL > 1.3 vol%). Since the wind field quickly dilutes the fuel gas with air, the explosive atmosphere is limited to a small region near the release point, and all concentrations at ground level are orders of magnitude lower than LFL.

Two additional simulations were performed to investigate the sensitivity of the results discussed above: one simulation with release rate 9 kg s<sup>-1</sup> and wind speed 6 m s<sup>-1</sup>, and one simulation with release rate 1 kg s<sup>-1</sup> and wind speed 3 m s<sup>-1</sup>. The 9 kg s<sup>-1</sup> release rate implies an internal overpressure exceeding the design pressure of the tank (for the given area of the outlet), and a wind speed of 3 m s<sup>-1</sup> is about half the characteristic wind speed measured at Mongstad (see Figure 3-4). Figure 5-12 shows the simulated gas cloud from the simulation with a release rate of 9 kg s<sup>-1</sup>, and Figure 5-13 summarizes the simulated mole fractions of fuel vapour in the four monitor points shown in Figure 5-10. Figure 5-14 shows the simulated gas cloud from the simulation with wind speed of 3 m s<sup>-1</sup>. Both scenarios produce significantly larger gas clouds than the scenario with release rate 1 kg s<sup>-1</sup> and wind speed 6 m s<sup>-1</sup>, but the fuel concentrations at ground level are nevertheless significantly below the lower flammability limit.

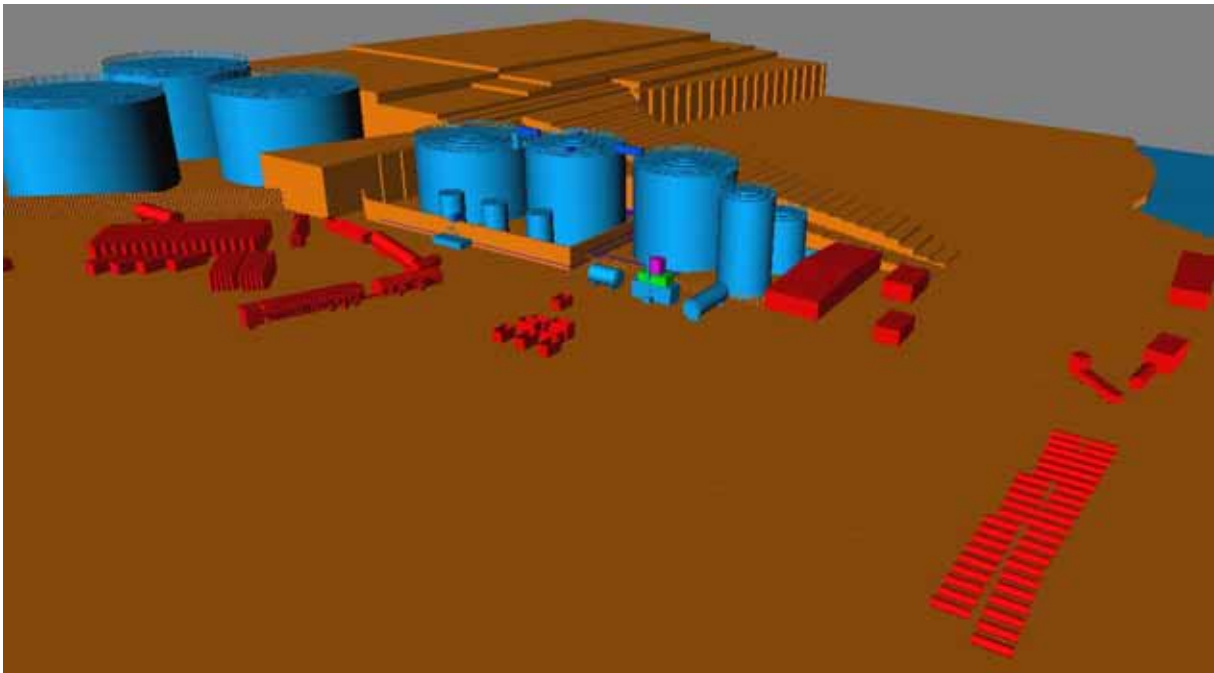
The fourth simulated scenario assumes that the hinged lid on top of the tank was open, in addition to the flow of flammable gas through the air filter. Based on the cross section of the opening and the weight of the lid, it was estimated that the lid would open at an internal overpressure of about 11 millibars, corresponding to a release rate of about  $1 \text{ kg s}^{-1}$  from a six inch opening. Hence, this simulation included two outlets with a release rate of  $1 \text{ kg s}^{-1}$  each. Figures 5-15 and 5-16 show the simulated gas clouds from the two leaks, and the simulated mole fractions of fuel vapour in the four monitor points shown in Figure 5-10. As for the previous simulations, the extent of the explosive atmosphere generated in this simulation is also quite limited, and all fuel concentrations near the ground are significantly below LFL.

A final simulation explored the potential release from a 1-inch pipe that went from the roof of the T3 tank, down to about 40-50 cm above the ground in the tank farm (Figure 3-1). This pipe served no purpose for the operations involved in treating the coker gasoline, but it had previously been in use for handling crude oil. Witness C had sealed the open end of the pipe, near the ground, with adhesive tape the day prior to the accident. However, it is conceivable that the tape might have fallen off, thereby admitting flammable gas into the tank farm at ground level. As discussed previously, an internal overpressure of 11 mbar would presumably be sufficient to open the hinged lid, and since a pressure difference of 11 mbar over a 1" opening corresponds to a release rate of about  $0.026 \text{ kg s}^{-1}$  (CPR 14E, 1997), this simulation assumed the same rate. The simulation domain was somewhat reduced compared to the previous simulations, and based on the previous simulations, the wind speed in the modified domain was reduced to  $1 \text{ m s}^{-1}$ . Figure 5-17 shows that the size of the simulated gas cloud is quite small, and based on the witness observations and the layout of the tank farm it is highly unlikely that there were any ignition sources within the volume covered by flammable mixture around 10 am on 24<sup>th</sup> May 2007.

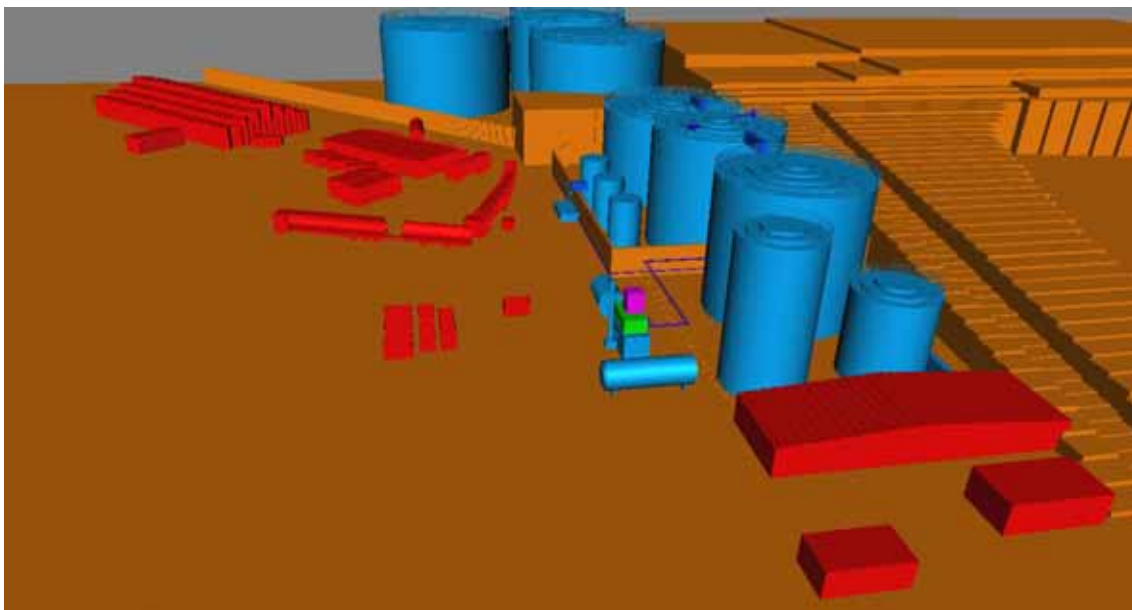
The simulation results presented in this section suggest that it is highly unlikely that an ignition source outside the tank ignited a release of flammable mixture from tank T3 on 24<sup>th</sup> May 2007. Even though the simulations involve quite conservative assumptions, i.e. high release rates or low wind speeds, the extent of the explosive atmosphere is very limited. The most likely ignition source on the roof of the tank would be a stroke of lightning, but there are no reports of lightning in the particular area on the particular day. The reader may refer to Chapter 6 for a further discussion of potential ignition sources.



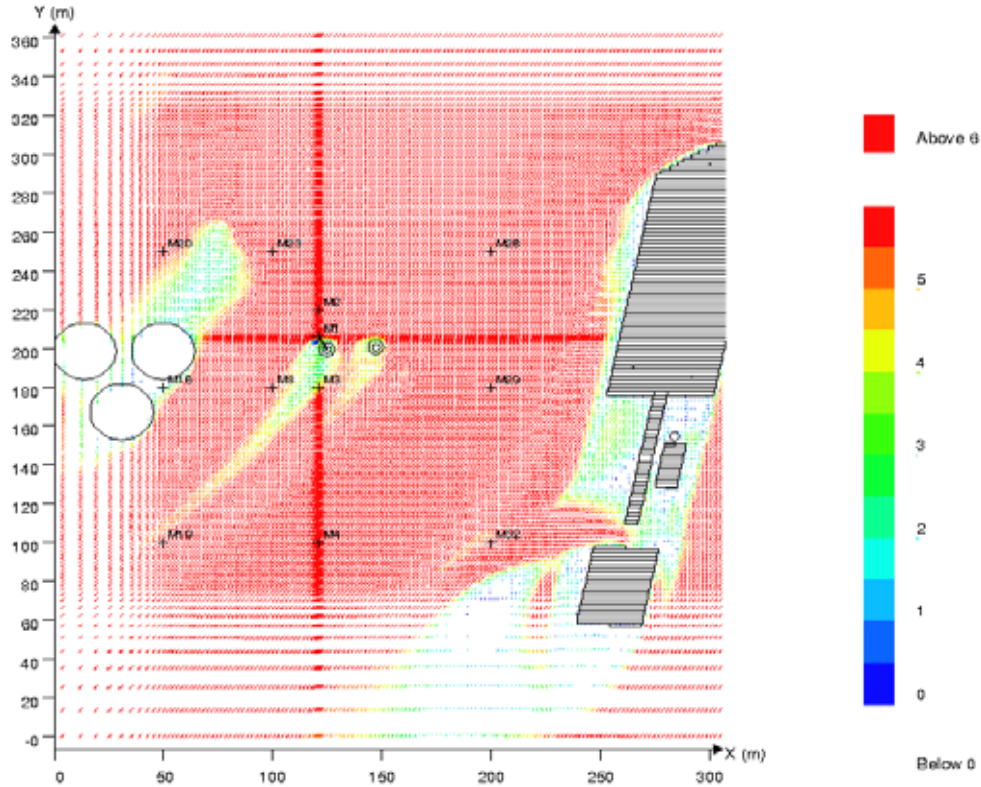
**Figure 5-5** Implemented geometry model for the FLACS simulations of potential release scenarios at Sløvåg: Tank farms I & II (on the left) and the tanker M/T Karen Knutsen moored alongside Quay no. 5 (on the right).



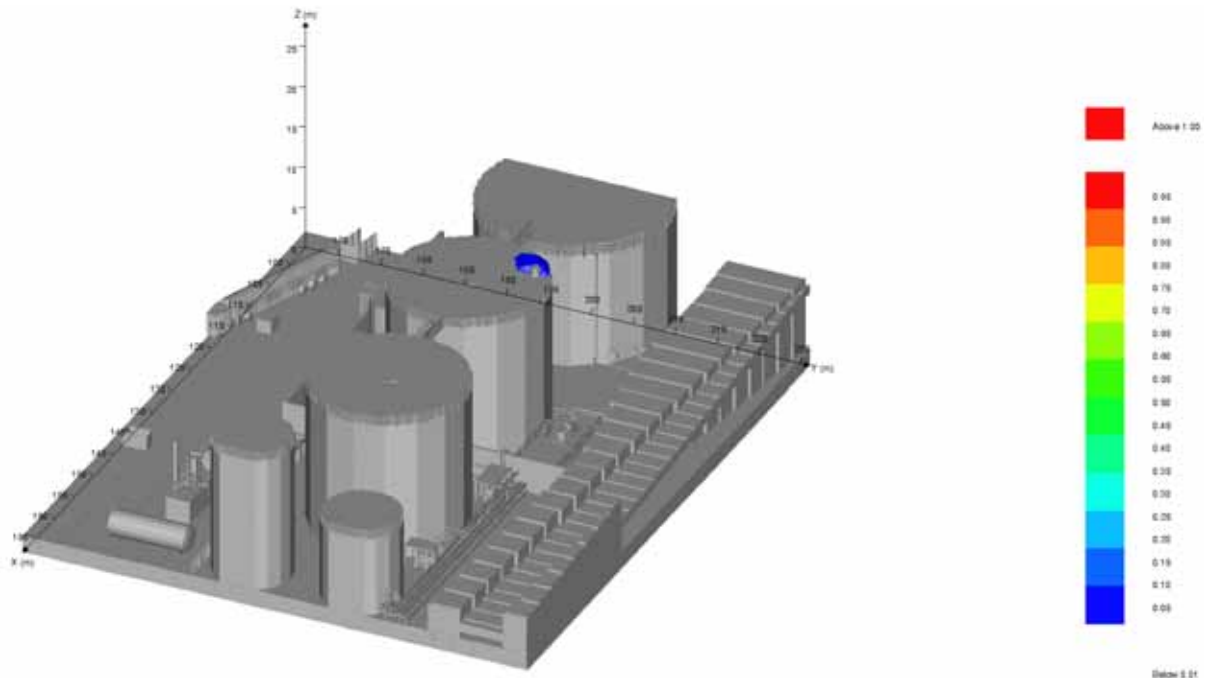
**Figure 5-6** Implemented geometry model for the FLACS simulations of potential release scenarios at Sløvåg: the three tank farms – Tank farm II with two large tanks (T3 and T4) and three smaller tanks (C1-C3) near the centre of the picture.



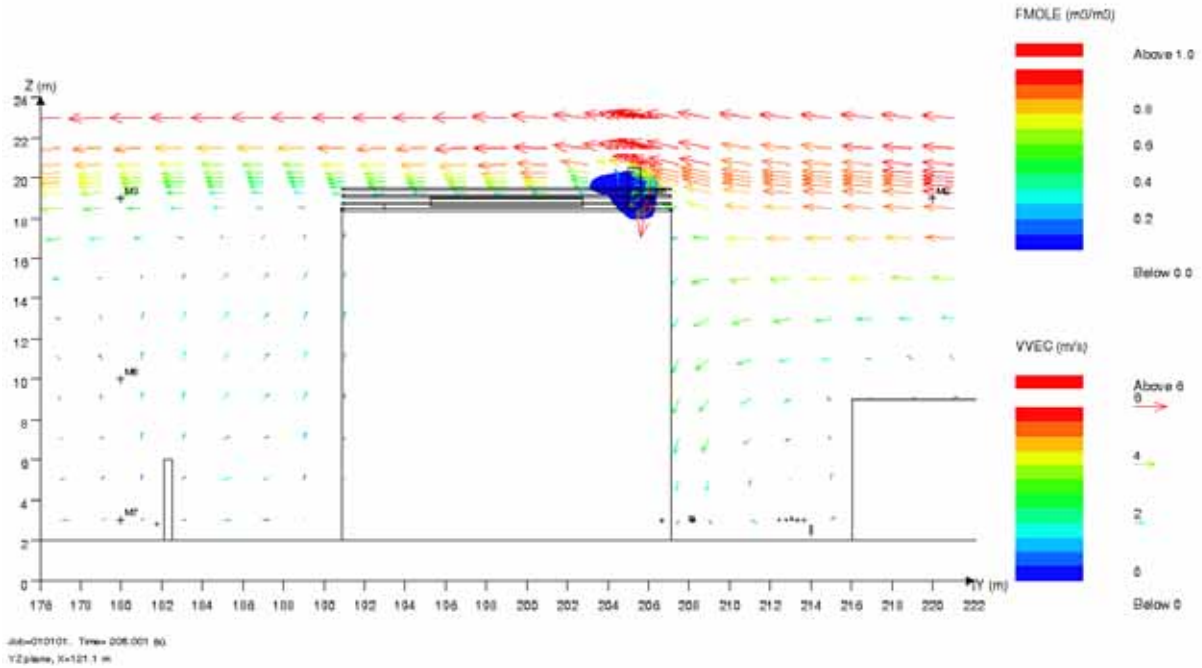
**Figure 5-7** Implemented geometry model for the FLACS simulations of potential release scenarios at Sløvåg: the tank farms viewed from the tanker M/T Karen Knutsen.



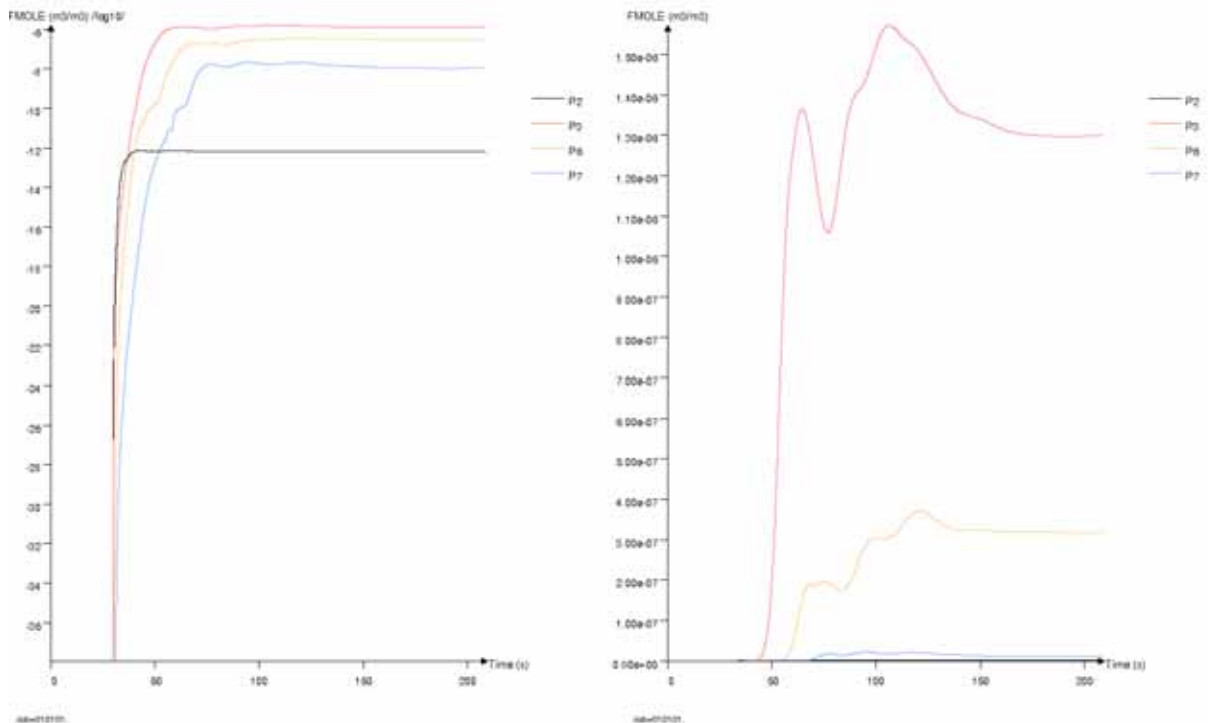
**Figure 5-8** Horizontal cross-section of the simulated wind field above the tank facility at Sløvåg around 10 am on 24<sup>th</sup> May 2007. Wind speed and wind direction according to measurements at the Mongstad oil refinery (see section 3.3) – the legend indicates wind speeds in units of  $m s^{-1}$ .



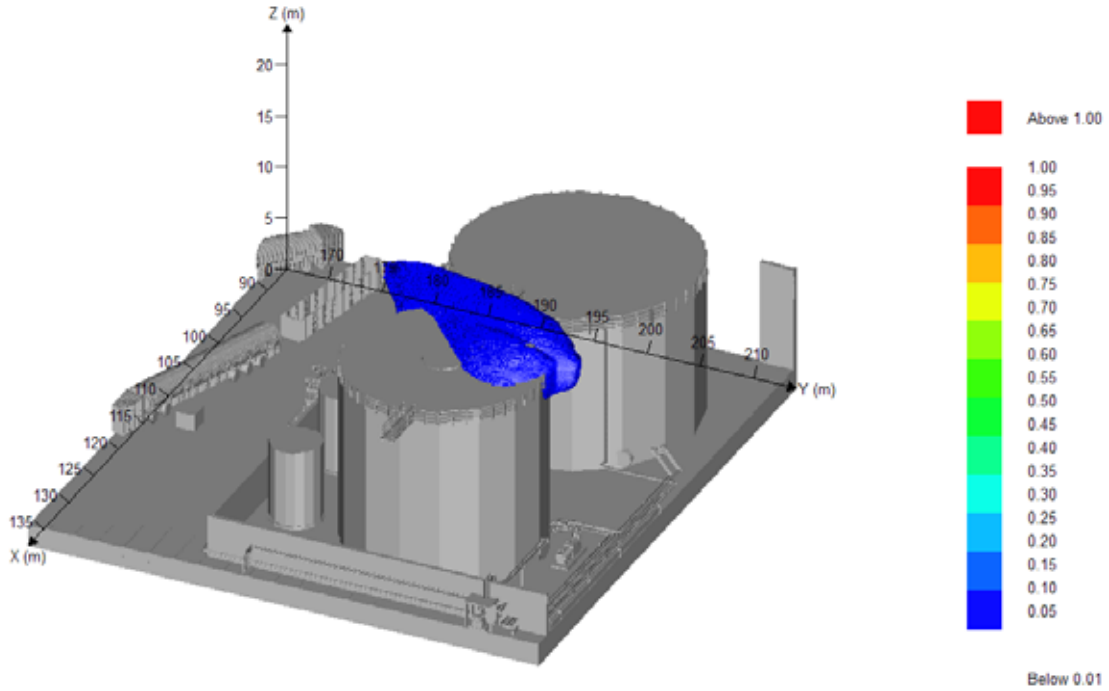
**Figure 5-9** Stabilised gas cloud on the roof of tank T3 after 3.5 minutes of a constant rate release ( $1 kg s^{-1}$ ) from the outlet of the air filter (wind speed  $6 m s^{-1}$ ). The picture shows Tank farm I in front, and Tank farm II in the background. The blue surface contour indicates 1 per cent by volume of fuel (i.e. presumably somewhat below LFL).



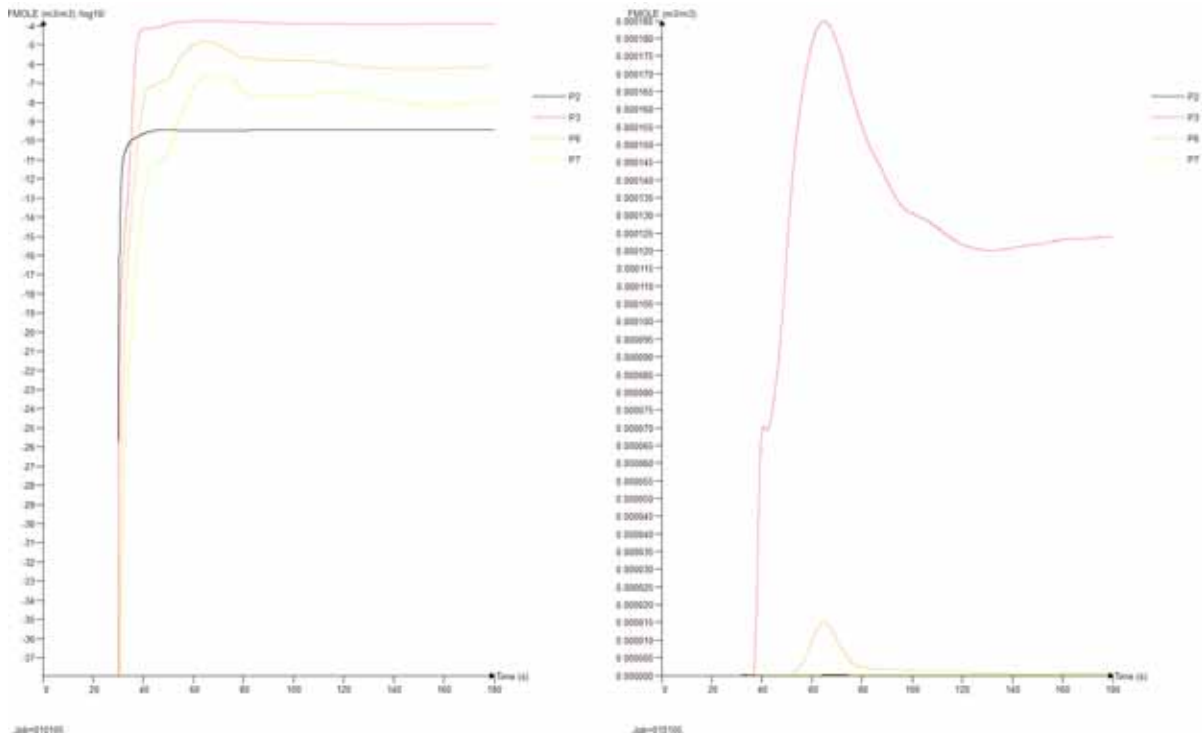
**Figure 5-10** Horizontal cross-section illustrating the stabilised gas cloud on the roof of tank T3 after 3.5 minutes of a constant rate release ( $1 \text{ kg s}^{-1}$ ) from the outlet of the air filter (wind speed  $6 \text{ m s}^{-1}$ ). The gas cloud indicated by blue colour has a fuel concentration of at least 1 per cent by volume, and is therefore representative for the extent of the explosive atmosphere near the release point.



**Figure 5-11** Simulated mole fractions of fuel vapour as a function of time during a constant rate release ( $1 \text{ kg s}^{-1}$ ) from the outlet of the air filter (wind speed  $6 \text{ m s}^{-1}$ ); the four monitor points are shown in Figure 5-10: M2 (P2), M3 (P3), M6 (P6), and M7 (P7). Note that the two plots show the same values, but with logarithmic scale (left) and linear scale (right) on the ordinate axis.

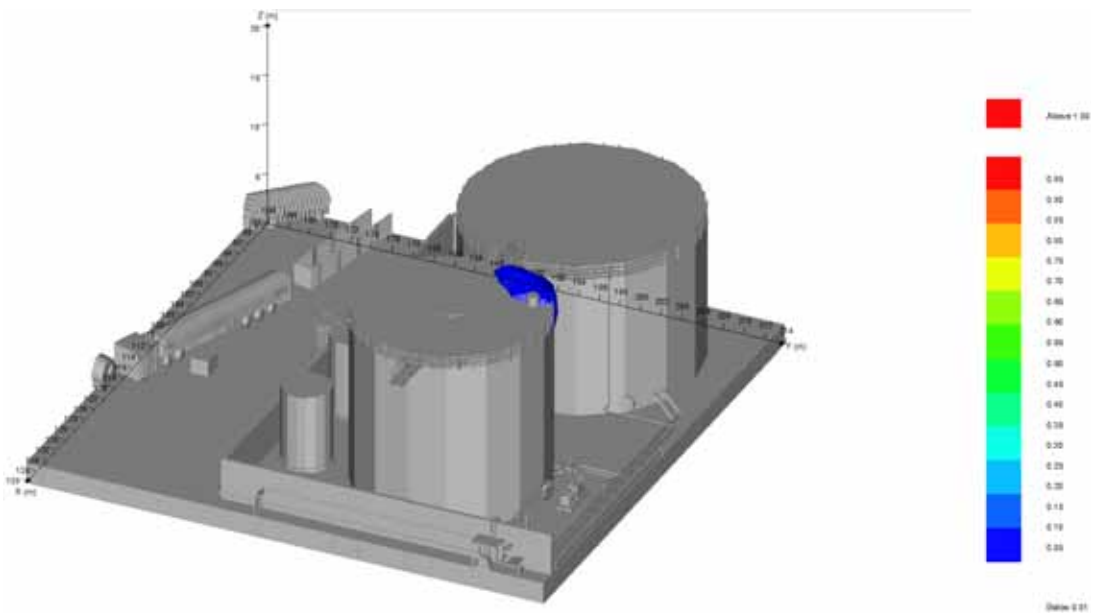


**Figure 5-12** Stabilised gas cloud on the roof of tank T3 after 3.5 minutes of a constant rate release ( $9 \text{ kg s}^{-1}$ ) from the outlet of the air filter (wind speed  $6 \text{ m s}^{-1}$ ). The gas cloud indicated by blue colour has a fuel concentration of at least 1 per cent by volume, and is therefore representative for the extent of the explosive atmosphere near the release point; the fuel cloud is significantly larger than for the scenario with a release rate of  $1 \text{ kg s}^{-1}$ , illustrated in Figure 5-9.

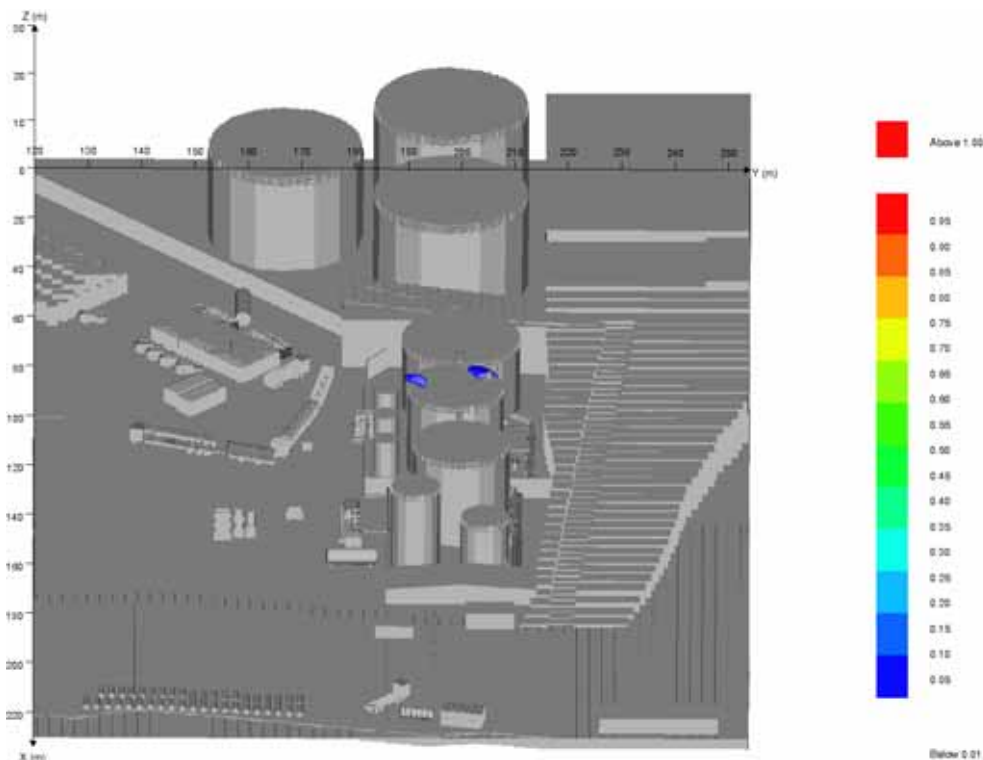


**Figure 5-13** Simulated mole fractions of fuel vapour as a function of time during a constant rate release ( $9 \text{ kg s}^{-1}$ ) from the outlet of the air filter (wind speed  $6 \text{ m s}^{-1}$ ); the four monitor points are shown in Figure 5-10: M2 (P2), M3 (P3), M6 (P6), and M7 (P7). Note that the two plots show the same values, but with logarithmic scale (left) and linear scale (right) on the ordinate axis.

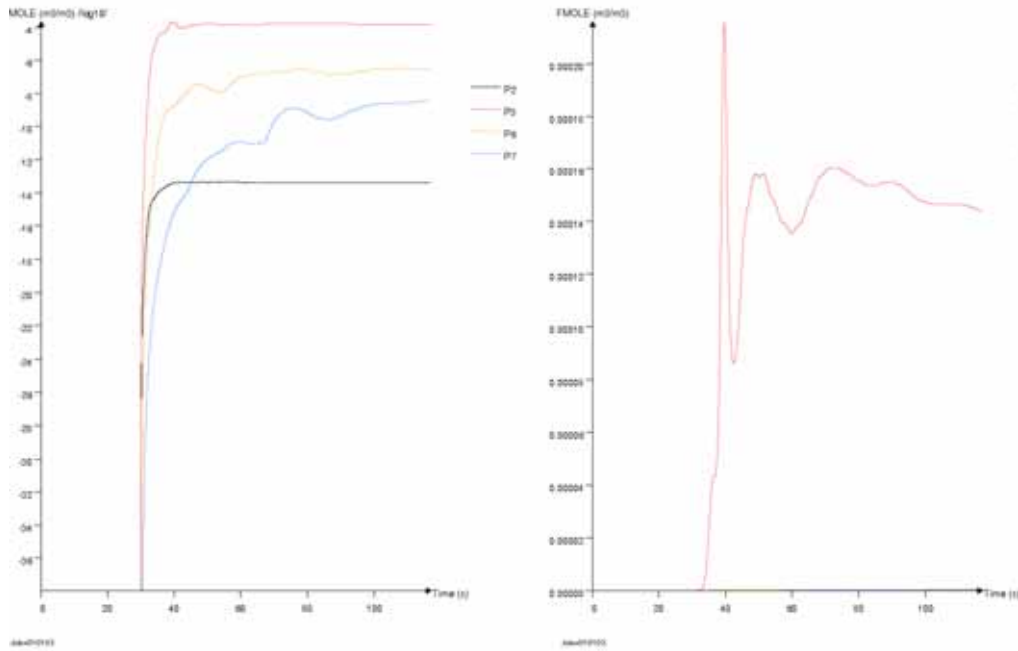




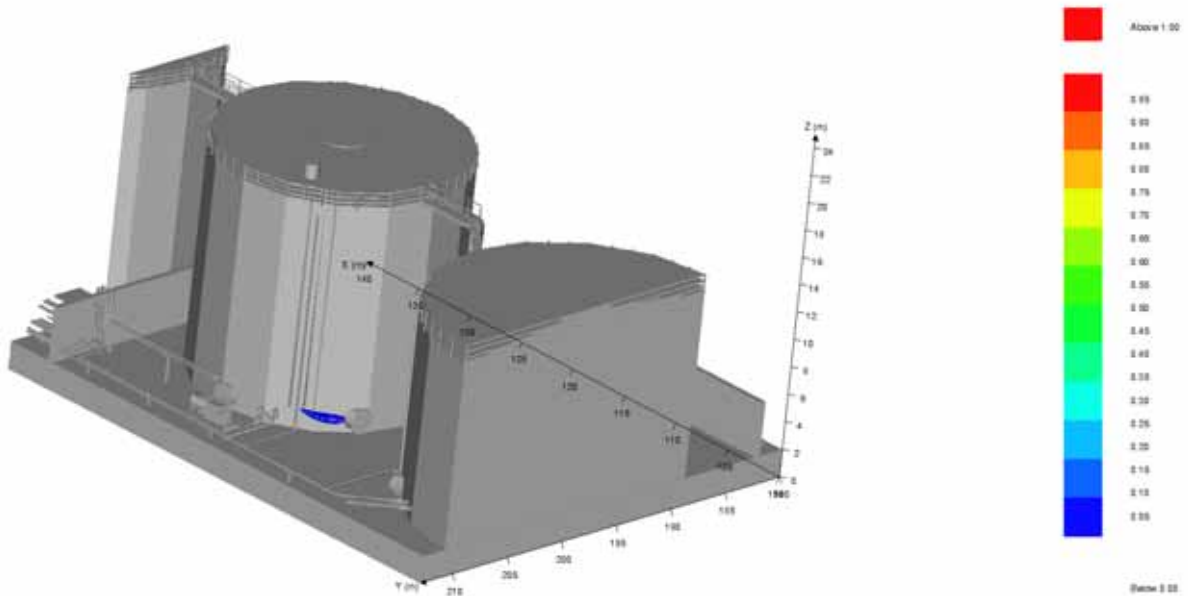
**Figure 5-14** Stabilised gas cloud on the roof of tank T3 after 3.5 minutes of a constant rate release ( $1 \text{ kg s}^{-1}$ ) from the outlet of the air filter (wind speed  $3 \text{ m s}^{-1}$ ). The picture shows only Tank farm II. The gas cloud indicated by blue colour has a fuel concentration of at least 1 per cent by volume, and is therefore representative for the extent of the explosive atmosphere near the release point; the fuel cloud is somewhat larger than for the scenario with wind speed  $6 \text{ m s}^{-1}$ , illustrated in Figure 5-9.



**Figure 5-15** Stabilised gas clouds on the roof of tank T3 after 3.5 minutes of two parallel constant rate releases (each  $1 \text{ kg s}^{-1}$ ) from the outlet of the air filter and from the outlet by the hinged lid (wind speed  $6 \text{ m s}^{-1}$ ). The picture shows all the three tank farms. The gas cloud indicated by blue colour has a fuel concentration of at least 1 per cent by volume, and is therefore representative for the extent of the explosive atmosphere near the release point; each fuel cloud is similar in volume to the cloud from the scenario with only one release, illustrated in Figure 5-9.



**Figure 5-16** Simulated mole fractions of fuel vapour as a function of time during two parallel constant rate releases (each  $1 \text{ kg s}^{-1}$ ) from the outlet of the air filter and from the outlet by the hinged lid (wind speed  $6 \text{ m s}^{-1}$ ); the four monitor points are shown in Figure 5-10: M2 (P2), M3 (P3), M6 (P6), and M7 (P7). Note that the two plots show the same values, but with logarithmic scale (left) and linear scale (right) on the ordinate axis.



J46=012107 Vu=FMOLE (m3/m3) Time= 130 500 (s)  
Xu101 120, Yu101 210, Zu03 24 m

**Figure 5-17** Stabilised gas cloud near the ground of tank T3 after 2 minutes of a constant rate release ( $0.026 \text{ kg s}^{-1}$ ) from the 1" pipe (local wind speed  $1 \text{ m s}^{-1}$ ). The gas cloud indicated by blue colour has a fuel concentration of at least 1 per cent by volume, and is therefore representative for the extent of the explosive atmosphere near the release point.

## 6 Potential ignition sources

The discussion in Chapter 5 suggests that an explosive atmosphere filled most of the free volume inside tank T3 prior to the accident on 24<sup>th</sup> May 2007. Furthermore, explosive atmospheres outside the tank were most likely present only in very limited zones near openings on the roof of the tank. This chapter explores potential ignition sources in light of the processes that went on inside the tank, witness observations describing the course of events during the accident, results from the simulations presented in Chapter 5, and discoveries made at the scene of the accident.

### 6.1 Potential ignition sources inside tank T3

This section looks at plausible ignition sources that may have ignited a flammable mixture inside tank T3. In this context, the term 'inside the tank' includes the interior of the air filter, as well as the flexible tube connecting the air filter to the tank. The most relevant ignition sources are then: electrostatic discharges, self-ignition in the activated carbon bed inside the air filter, and possible electrical or mechanical equipment inside the tank. The work includes an experimental investigation of the electrical conductivity of various relevant liquid samples, and a subsequent evaluation of the possibility of accumulating hazardous levels of electrostatic charge on the liquid surface inside the tank.

#### 6.1.1 Electrostatic discharges inside tank T3

Electrostatic discharges can ignite flammable vapour-air mixtures in storage tanks (e.g. Klinkenberg & van der Minne, 1958; Babrauskas, 2003; Mannan, 2005). However, the electrical conductivity of the liquid determines its ability to accumulate electrostatic charge, and ignition by electrostatic discharges poses a real hazard only for electrical conductivities below about  $50 \times 10^{-12} \text{ S m}^{-1}$  (see Chapter 2). Figure 6-1 shows the liquid conductivity meter, *Model L40* from Wolfson Electrostatics, which was used to measure the electrical conductivity of six selected liquid samples: three samples of coker gasoline, and three samples of alkaline waste. Table 6-1 summarizes the contents of the samples, as well as the measured values of electrical conductivity for each sample.



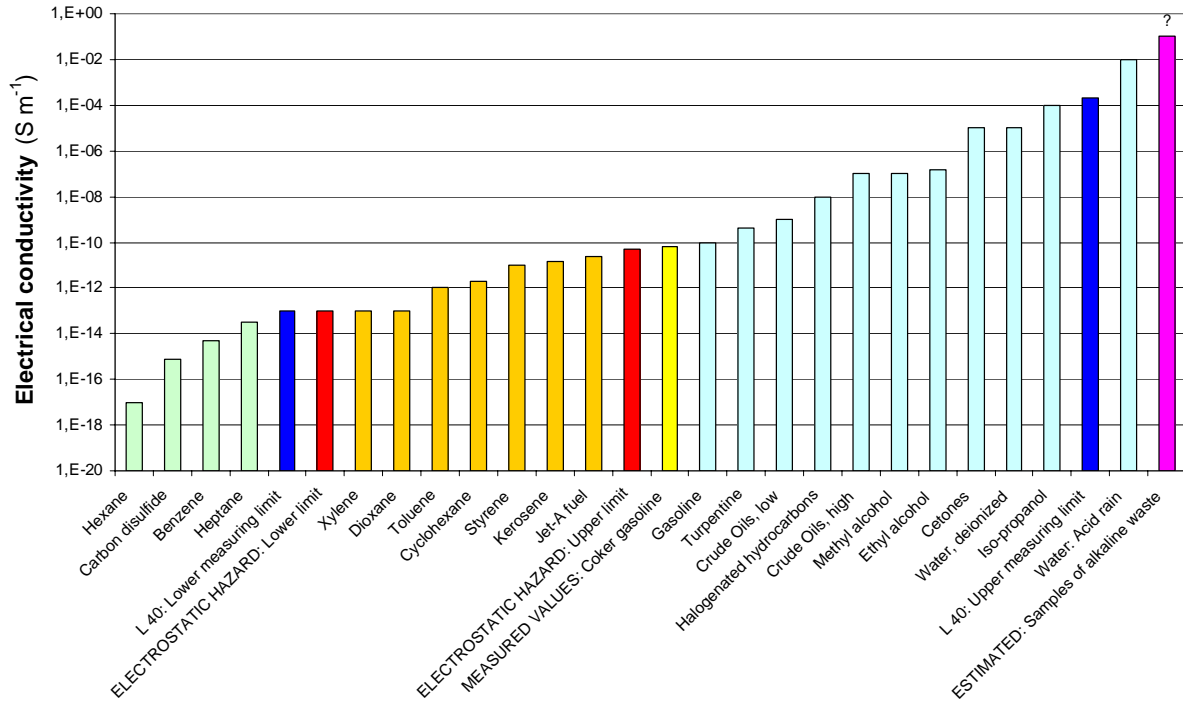
**Figure 6-1** The liquid conductivity meter, Model L40 from Wolfson Electrostatics, with the bottle of calibration fluid (*n*-heptane) and 3 samples of alkaline waste (left); close-up of the measuring cell (right).

**Table 6-1** Results from measurements of the electrical conductivity in six liquid samples: three samples of coker gasoline (measured 11<sup>th</sup> September 2007 by T. Skjold), and three samples of alkaline waste (measured 15<sup>th</sup> July 2007 by T. Skjold and B. Reiersen). Samples provided by the Norwegian Police, ref. 0723.11705c (2007).

Sample	Description	Conductivity (S m <sup>-1</sup> )
Coker gasoline	1 Coker gasoline marked 'M/T Puze 7005 Batch-CC'	$(68 \pm 3) \cdot 10^{-12}$
	2 Coker gasoline marked 'M/T Afrodite 7006 Batch-AA'	$(64 \pm 3) \cdot 10^{-12}$
	3 Coker gasoline marked 'M/T Puze 7005 Batch-DD'	$(67 \pm 3) \cdot 10^{-12}$
Alkaline waste	4 Mixture of 80 ml pure water and 20 ml alkaline waste from tank T3.	$> 2 \cdot 10^{-4}$
	5 Mixture of 80 ml wastewater from tank T61 and 20 ml alkaline waste from tank T3.	$> 2 \cdot 10^{-4}$
	6 Mixture of 60 ml pure water, 15 ml alkaline waste from tank T3, and 3 ml 35 % HCl.	$> 2 \cdot 10^{-4}$

Figure 6-2 illustrates typical values of electrical conductivity for various liquids, including the measured results for the samples summarised in Table 6-1. The results for the samples of alkaline waste show that the electrical conductivity is higher than the upper limit of the measuring range for the conductivity meter, and hence significantly higher than conductivities normally associated with electrostatic ignition hazards. The measured conductivity of the coker gasoline samples (represented by the yellow column in Figure 6-2) is just above the upper limit of hazardous conductivities (the red column in the centre). It is possible that the conductivity of coker gasoline was somewhat reduced when polar components like mercaptans were transferred to the sodium hydroxide solution during the treatment at Vest Tank. Hence, it is not straightforward to predict whether the conductivity of 'cleaned' coker gasoline would fall within the hazardous area, i.e. between the two red columns in Figure 6-2. The likelihood of generating hazardous levels of electrostatic charge on the liquid surface inside tank T3 is nevertheless very small. Most of the liquid in the tank had very high conductivity, and there was no splash filling of liquid into the tank. Hence, it is not straightforward to envisage how efficient charge separation could take place in this system.

Based on the properties of the liquids in the system, and the procedures used for adding hydrochloric acid to the alkaline waste, it seems highly unlikely that electrostatic discharges may have ignited the explosive atmosphere inside tank T3 on 24<sup>th</sup> May 2007.



**Figure 6-2** Characteristic and measured values of electrical conductivities for various liquids. The liquids represented by the light-green columns on the left normally have too low conductivities to accumulate hazardous levels of electrostatic charge; however, a small amount of impurities can significantly influence the conductivity. The two red columns represent the lower and upper limits of hazardous conductivities, and the intervening orange columns represent liquids that may accumulate hazardous levels of electrostatic charge. The liquids represented by the light-blue columns on the right generally have too high conductivities to accumulate hazardous levels of electrostatic charge. The measured conductivities for the three samples of coker gasoline are represented by the yellow column ( $66 \pm 5 \text{ pS m}^{-1}$ ), and estimated conductivities for the three samples of alkaline waste are represented by the pink column (significantly above  $0.2 \text{ mS m}^{-1}$ ). The measuring range of the liquid conductivity meter, Model L40 from Wolfson Electrostatics Ltd., lies between the two dark-blue columns in the diagram.

### 6.1.2 Self-ignition in the activated carbon canister

Air filters with activated carbon are frequently used to limit the release of malodorous gases from the process industry. Adsorption of organic vapours on the surface of activated carbon granules may however generate sufficient heat to cause self-ignition in the filter medium (EPA, 1997e; Zerbonia *et al.*, 2001; Kletz, 2003). This hazard is most relevant for organic compounds like ketones, aldehydes, certain organic acids (e.g. propionic acid and butyric acid), and sulphur containing compounds like mercaptans.

Figure 1-4 shows where the air filter from tank T3 landed in the terrain after the explosion on 24<sup>th</sup> May 2007: about 90 meters from its original position of the roof of the tank. Figure 3-1 illustrates the position of the filter on the roof of the tank prior to the accident, and Figure 6-3 shows various views of the filter in the position the investigators found it during the first on-site inspection on 31<sup>st</sup> May 2007. When a literature study (Chapter 2) indicated that self-ignition in this process unit could have triggered the accident, the pictures from the first inspection were re-examined, and one of them revealed an ash like substance among the activated carbon granules (the upper left picture in Figure 6-6). This discovery led to the second on-site inspection on 18<sup>th</sup> June 2007, where the primary focus was to examine the air filter for indications of self-ignition in the filter medium. The following were present

during the second inspection: T. Skjold and K. van Wingerden (both GexCon), and I. Holmås (Police Chief Superintendent at Masfjorden Police Station). The air filter was found in the same position as before, and nothing indicated that it had been moved or opened since the first inspection on 31<sup>st</sup> May 2007.

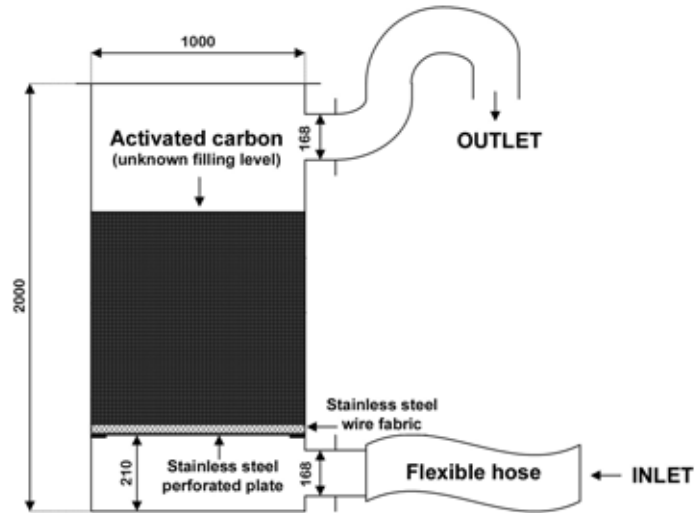


**Figure 6-3** The air filter from tank T3: position in the terrain (above), inlet with the remains of the flexible pipe (lower left), the lid on top of the filter (lower centre), and the outlet from the filter (lower right).

### Description of the air filter

Figure 6-4 shows a principle drawing of the air filter. The filter vessel, or canister, was shaped like a cylinder, with height 2 meters and diameter 1 meter (total internal volume 0.79 m<sup>3</sup>). Figure 3-1 indicates the original position of the filter along the railing on the roof of tank T3. A six-inch flexible hose connected the tank to the inlet of the canister. Air and vapours would enter in the bottom of the canister, and pass through the filter medium before exiting the upper part of the canister through a swan-neck.

The filter medium was activated carbon granules of type 'AIRPEL 10' from Tøssebro AS, specially prepared for purifying air (e.g. high adsorption capacity). A perforated plate of stainless steel and several layers of stainless steel wire fabric supported the granules. Two screws held the flanged lid on the canister in place (the rest of the screws were missing), and the lid had been somewhat deformed in the explosion (Figure 6-3). The exact level of filling in the filter prior to the accident is unknown, but both witness statements and the examination of the filter suggest that the top layer of activated carbon granules was close to the lower edge of the outlet pipe (see Figure 6-4).



**Figure 6-4** Principle drawing illustrating a vertical cross-section of the air filter (drawing by K. van Wingerden; dimensions in millimetres).

### Examination of the air filter

The air filter was opened and examined during the second on-site inspection on 18<sup>th</sup> July 2007. Figure 6-5 shows the perforated stainless steel plate that had supported the filter medium. The plate was clearly deformed, presumably upon impact when the canister landed in the terrain. A layer of soot covered about half of the surface on the upper side of the plate (facing the filter medium). Removing the soot revealed areas of where the surface of the stainless steel plate had undergone discolouration characteristic of heat tinting (shades of yellow, brown, purple, and blue).

Figure 6-6 shows the whitish ash-like material found amongst the activated carbon granules. Although the content of the canister obviously had been somewhat stirred during the accident, it was apparent that most of the ash like material originated from the activated carbon granules near the bottom of the canister. Furthermore, large portions of the stainless steel wire fabric from the bottom of the canister had undergone the same type of discolouration as seen on the perforated plate (Figure 6-6). Figures 6-6 and 6-7 show granules of activated carbon from the canister that apparently have undergone combustion reactions, and a significant portion of these granules were found in between the stainless steel wire fabric. According to an employee at Vest Tank, the air filter had been installed in November 2006, but the filter medium had been replaced 1-2 days prior to the accident (i.e. shortly before the process of adding hydrochloric acid was initiated).

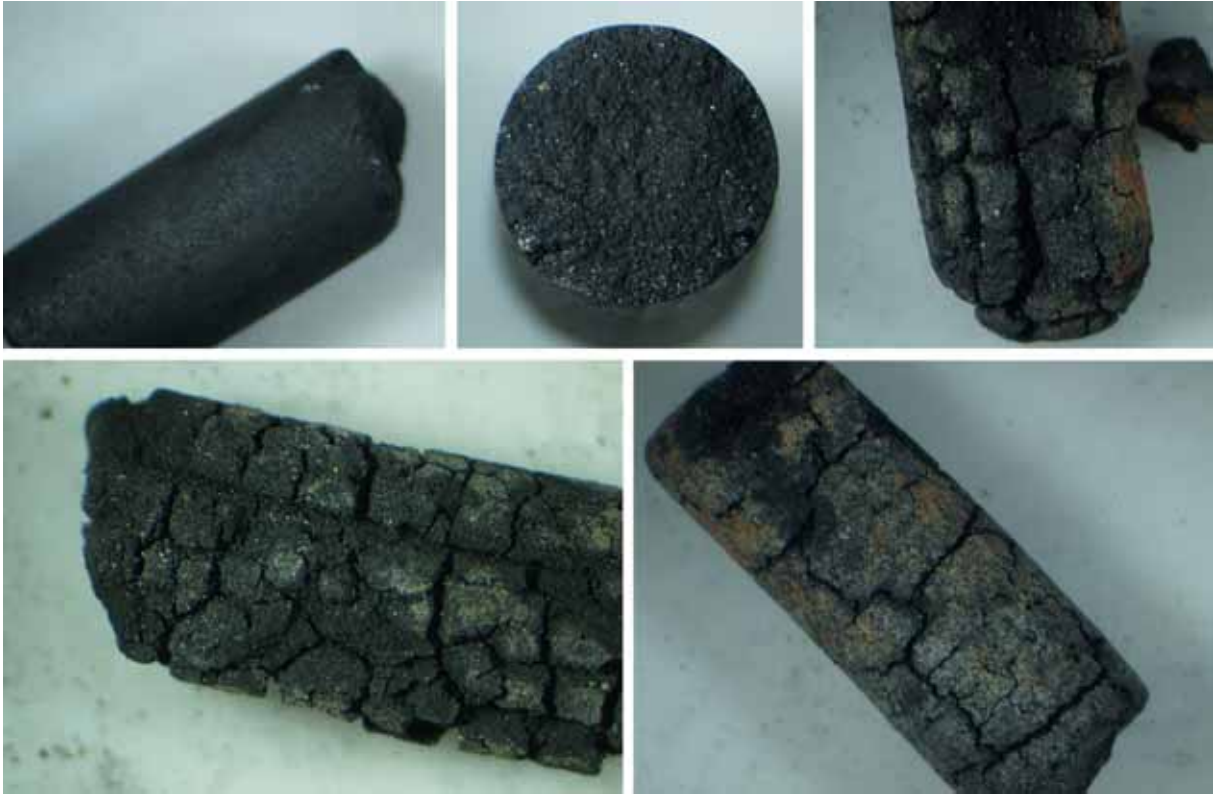


**Figure 6-5** The perforated stainless steel plate from the bottom of the air filter: the plate viewed through the inlet to the canister (upper left); the plate removed from the canister, with a deposit of soot covering about half the surface area (upper centre); holes in the plate at old spot welds, presumably formed during deformation of the plate upon impact of the canister (upper right); the plate before (left middle) and after (right middle) removing the soot deposit; discolouration of the surface of the stainless steel plate, characteristic of heat tinting (lower left and lower right). Photos by T. Skjold.





**Figure 6-6** Filter medium, ash like material, and stainless steel wire fabric from the air filter: activated carbon granules poured from the canister, with a pinch of ash-like material (upper left – photo taken by Ø. Larsen during the first on-site inspection on 31<sup>st</sup> May 2007). Close-up of the ash-like material beside the canister (upper right); activated carbon granules with ash like material near the inlet to the canister (middle left); stainless steel wire fabric with evident discolouration (middle right); close-up of stainless steel wire fabric with whitish ash like material (lower left); close-up of activated carbon granules between layers of stainless steel wire fabric (lower right); photos taken by T. Skjold during the second on-site inspection on 18<sup>th</sup> July 2007.



**Figure 6-7** Pictures of activated carbon granules taken through a microscope: granules without visible signs of combustion reactions (upper left and centre), and three single granules with evident signs of combustion reactions (upper right and below); photos by T. Skjold, 15<sup>th</sup> August 2007.

## Discussion

The findings from the previous sections show that glowing combustion took place in the filter medium inside the air filter on top of tank T3. This does not exclude the possibility that other ignition sources may also have been present inside the tank on 24<sup>th</sup> May 2007. However, the glowing granules of activated carbon, or a metal surface heated by the smouldering nest, could definitely have ignited a flammable mixture that entered the filter through the flexible tube that connected it to the tank.

In a small laboratory experiment (Figure 6-8), excessive heating of activated carbon granules with an open flame did not result in self-sustained combustion reactions. It is therefore very unlikely that the explosion itself ignited the activated carbon inside the canister. The glowing combustion reactions terminated most likely shortly after the explosion, partly due to stirring of the filter medium, but primarily because the flow of flammable gas through the canister ceased. Zerbonia *et al.* (2001) points out that adsorption of water and organic vapours on the surface of the particles releases most of the heat, but exothermal oxidation or polymerization reactions may also contribute. Eventually, the surface temperature becomes sufficiently high to cause self-ignition of the activated carbon. Activated carbon that has adsorbed a significant amount of combustible vapours are likely to burn more readily than pure activated carbon, and a steady flow of flammable (or near-flammable) mixture may sustain combustion reactions on the surface of the granules.

Several witnesses noticed an outflow of white smoke or steam from the air filter prior to the accident. These observations support a scenario in which glowing combustion in the lower part of the air filter initiated the explosion in tank T3. According to the discussion in section 5.1, the addition of hydrochloric acid to the alkaline solution in T3 would increase the temperature in the solution, and at

the same time reduce the solubility of mercaptanic sulphur compounds in the solution. This led most likely to evaporation and gas production inside the tank, and hence a steady flow of moist air and vapours through the air filter. The initial temperature of the filter medium was presumably lower than the temperature in the solution, and hence the temperature of the flowing vapours, resulting in condensation of water on the filter medium. The local heat release following the self-ignition and subsequent smouldering combustion inside the filter would later cause evaporation of condensed liquids, and possibly produce smoke. From the statement by *Witness C* (Table 3-1), it appears the glowing combustion reactions started some time between 6 am and 8 am in the morning.

Self-ignition in the filter medium can explain the significant delay from the onset of adding hydrochloric acid to the tank the previous evening, to the explosion on the morning of 24<sup>th</sup> May 2007. The fuel concentration in the mixture that entered the filter may have been below the lower flammability limit (LFL) up to the time of the explosion. Alternatively, the origin of the smouldering nest may initially have been too remote from the perforated bottom plate inside the filter either to heat the plate directly, or to allow a flame to propagate from the glowing particles to the flammable mixture at the inlet section of the filter. The simulation results presented in section 5.1 suggest that the concentration of flammable gas in the free volume inside the tank most likely decreased with the height above the liquid surface. Hence, the fuel concentration in the mixture entering the air filter would most likely increase over time, and once ignition occurred inside the canister, the flame could propagate back to the tank through the flexible pipe.

After ignition in the inlet section of the filter, the flame front presumably accelerated through the pipe, partly due to more optimal fuel/air concentrations upstream of the filter, but primarily due to expansion of combustion products inside the filter. Expansion generated flow of unreacted mixture inside the pipe resulted in turbulent flow conditions, and hence significantly increased rates of combustion. It is not straightforward to predict whether the flexible pipe ruptured before or after the flame reached the tank, but the flame nevertheless entered into the tank. Due to the limited area of the available vent openings, i.e. the two six-inch openings on top of the tank, thermal expansion of combustion products inside the tank increased the overpressure until the tank eventually ruptured. Witness observations, describing a loud hissing sound immediately prior to the first explosion (see Table 3-1), suggest that the tank ruptures after about 1-2 seconds. Both the strength of the tank, and the rate of volumetric heat release inside the tank, determined the time it took for the tank to rupture. Apparently, the base/wall weld yielded first, and the upper part of the tank lifted off and landed in the corner of the tank farm, besides tank T4. It is likely that the upper part of tank T3 inflicted some damage to tank T4, and that combustion of flammable liquids from T4 contributed to the rapid escalation of the subsequent fire scenario in the tank farm (see Figure 1-4 and Figure 1-5).



**Figure 6-8** Granules of activated carbon: attempts at igniting activated carbon granules with an open flame did not result in self-sustained combustion reactions (photo by R. Abiven, 12<sup>th</sup> September 2007).

### 6.1.3 Other potential ignition sources inside tank T3

Apart from the discussion in section 6.1.2 that clearly identifies self-ignition in the air filter as a likely ignition source, there is no available information pointing towards other plausible ignition sources inside tank T3 at the time of the accident. On the contrary, all available background material suggests that:

- There was no electrical equipment inside the tank.
- The level gauge did not represent any ignition hazard.
- There was no movable mechanical equipment inside the tank.
- The heating coils in the bottom of the tank were not in use.
- There was no hot work going on inside or near the tank farm.
- There were no processes that normally would produce significant build-up of electrostatic charge inside the tank to cause ignition by electrostatic discharges (section 6.1.2).

Hence, all the available evidence suggests that the only plausible ignition sources inside the tank originated from self-ignition inside the air filter.

## 6.2 Potential ignition sources outside tank T3

The simulation results presented in section 5.3 suggest that rapid dilution of potential releases of flammable mixture from openings in tank T3 would prevent the formation of significant volumes of explosive atmosphere outside the tank. With the hinged lid closed, active ignition sources near the inlet side of the filter (see section 6.1.2) would presumably ignite any explosive mixture entering the filter from the tank, thereby preventing it from escaping to the outside. However, should an explosive atmosphere nevertheless ignite outside the tank, the bed of activated carbon inside the filter would most likely serve the purpose of a flame arrester, preventing the flame from propagating through the filter and into the tank. Witness observations of flames outside the tank prior to the first explosion may partly be due to the difference between the speed of sound and the speed of light, since these witnesses stood some distance away from Tank farm II. It is also likely that T3 started rupturing at the base/wall weld facing M/T Karen Knutsen, since the upper part of the tank flew towards T4 (see Figure 1-2), and this could explain how Witness X could observe flames between the bund of Tank farm II and tank T3 prior to the first explosion.

There is no available information indicating that ignition occurred outside the tank, and both witness statements and other sources exclude several of the most common ignition sources:

- Lightning is one of the most common ignition sources in tank explosions, but there are no observations of such phenomena in the relevant area on the particular day.
- There are no witness statements suggesting that hot work, smoking, or similar activities were going on inside or near the tank farm.
- There is no evidence that electrical or mechanical equipment could cause ignition in areas where explosive atmospheres were likely to occur (see section 5.3).
- There were no vehicles inside the tank farm.

Hence, it is highly unlikely that ignition of an explosive atmosphere outside the tank initiates the course of events on 24<sup>th</sup> May 2007.

## 7 Conclusions

### 7.1 Main conclusions

The following are the main conclusions from the investigation carried out by GexCon into the direct causes of the accident that took place at Sløvåg on 24<sup>th</sup> May 2007:

- From the chemical composition of the liquid solution inside tank T3, as well as descriptions of the course of events by relevant witnesses (primarily the fact that the tank suddenly exploded), it is highly unlikely that it was a *physical explosion* that caused the accident.
- Descriptions of the cause of events by relevant witnesses, as well as the fact that an accident scenario involving a physical explosion seems highly unlikely, strongly suggest that the accident was a result of a *chemical explosion* that occurred when a flammable mixture was ignited inside either the air filter connected to the tank, or the tank itself.
- The chemical composition of the solution in the tank (i.e. an alkaline solution with precipitated waste from the treatment of coker gasoline), as well as the ongoing process (i.e. the adding of hydrochloric acid to an alkaline solution), suggest that a *flammable mixture* formed as combustible gases/vapours released from the solution mixed with the air inside the tank. Furthermore, several factors point towards mercaptans as the predominant constituent in the fuel:
  - o The relatively high initial content of mercaptans in the coker gasoline that was treated,
  - o The likely composition of the solid precipitants formed during the process of reducing the content of mercaptans in coker gasoline with sodium hydroxide, and
  - o The process of treating the waste from the cleaning process with hydrochloric acid that was taking place up to the time of the accident.

The addition of hydrochloric acid presumably lowered the pH value in the solution, thereby reducing the solubility of mercaptans and related compounds. However, it is also likely that vapours from volatile hydrocarbons, floating on top of the aqueous solution, contributed to the formation of the explosive mixture.

- Results from simulations with the CFD code FLACS do not support scenarios that involve the formation of significant volumes of flammable mixture outside the tank. It is therefore highly unlikely that an ignition source outside the tank, or outside the air filter, initiated the accident.
- Results from measurements of the electric conductivity of relevant liquid samples, and descriptions by witnesses of the process of adding hydrochloric acid to the tank, indicate that it is unlikely that the source of ignition was electrostatic discharges inside the tank.
- Examination of the air filter from tank T3 strongly suggests that adsorption of sulphur containing hydrocarbons on the surface of activated carbon granules led to *self-ignition*, and subsequent smouldering combustion, in the filter media. Furthermore, it is highly likely that either glowing particles, or a hot metal surface near the inlet section of the filter, ignited the flammable mixture inside the filter; the flame then propagated into the tank through the flexible pipe. A literature study revealed descriptions of previous accidents involving self-ignition in beds of activated carbon granules inside air filters used for removing malodorous sulphur containing hydrocarbons like mercaptans.

The authors emphasize that these conclusions are based on, and consequently limited by, the information and documentation available at the time of issuing this report.

## 7.2 Course of events

On 24<sup>th</sup> May 2007, storage tank T3 exploded at the Sløvåg industrial area, in the municipality Gulen, in the county council district of 'Sogn og Fjordane', on the west coast of Norway. This section presents a brief summary of a plausible course of events that follows from the main conclusions summarized in section 7.1.

From October 2006 to March 2007, the company Vest Tank had periodically treated shiploads of a petroleum product called coker gasoline in order to reduce the content of malodorous sulphur containing components, especially mercaptans (thiols). The essential chemical principle behind this process was the high solubility of mercaptans in alkaline solutions of sodium hydroxide and water (caustic soda), compared to the solubility in coker gasoline. The cleaning process took place in two atmospheric storage tanks, T3 and T4, and resulted in the precipitation of solid waste that over time accumulated in the bottom of the tanks. The amount of dissolved or precipitated waste eventually reached a level where it was no longer possible to treat further tank loads of coker gasoline.

The purpose of the process that went on when the accident took place was to dissolve the precipitated waste in tank T3, and at the same time reduce the pH value in the alkaline solution, by adding hydrochloric acid. Vest Tank had tested this process in small-scale experiments, and the first large-scale process started in the afternoon on Wednesday 23<sup>rd</sup> May 2007.

The addition of hydrochloric acid to the alkaline solution in tank T3 resulted in significantly reduced solubility of mercaptans, and to a displacement of other chemical equilibriums in the solution. It is also likely that coker gasoline and/or similar chemical compounds separated from the alkaline solution and formed a thin surface layer of flammable liquid that vaporized and mixed with the air inside the tank. This release of mercaptans and flammable vapours led to the formation of a flammable mixture. It is likely that the flammable mixture initially was limited to an area immediately above the liquid surface, but as more gases or vapours were released from the solution, the extent of the flammable mixture gradually increased until it covered the entire free volume of the tank, and eventually also the air filter on top of the tank.

To limit the release of malodorous sulphur containing components, the tank was equipped with an air filter with activated carbon. Adsorption of mercaptans and other hydrocarbons by the filter medium resulted in self-ignition in the activated carbon granules. Around 10 am on Thursday 24<sup>th</sup> May, glowing particles of activated carbon, or a hot metal surface, in the lower part of the air filter, ignited the flammable mixture from the tank. The flame then propagated through the flexible hose connecting the tank and the filter, and the tank exploded.

The first explosion in tank T3 escalated rapidly to additional explosions in other tanks, and a fire that involved the entire tank farm, as well as an office building and three tank trucks parked nearby.

## 7.3 Recommendations

A relatively thorough risk analysis is generally required for documenting adequate levels of safety for industrial processes involving potentially explosive atmospheres. A risk analysis for the type of process that took place at Sløvåg would typically document both the potential hazards, and the effect of implementing various measures of risk reduction. The hazard identification process should typically include a thorough description of the chemical reactions involved in removing mercaptans from coker gasoline by adding sodium hydroxide solution, the chemical composition of the solid precipitants, and the effect of adding hydrochloric acid to the waste from the cleaning process. The evaluation of risk reducing measures should primarily focus on preventing explosions, but measures aimed at mitigating the effects of potential explosions should also be included.

Examples of risk-reducing measures that could be applicable to the kind of process that took place at Vest Tank prior to the accident on 24<sup>th</sup> May 2007 include:

- There should be at least one flame arrester between the tank and the activated carbon canister.
- An appropriate sensor could monitor the temperature in the filter media, an alarm could indicate the possible onset of self-ignition and/or glowing combustion, and the same system could trigger an automatic suppression system.
- The activated carbon canister should be installed in a position where it could easily be replaced in the event of self-ignition in the filter medium, and not on top of the tank. Harrel *et al.* (1978), EPA (1997e), and Zerbonia *et al.* (2001) describe further recommendations concerning the installation and use of activated carbon canisters.
- It would be highly desirable from a risk reduction point of view if the treatment of the solid waste could take place in smaller vessels, thereby minimizing the volume of the potentially explosive atmosphere above the liquid surface.
- A higher design pressure for the vessel, and the possibility of pressure relief through properly dimensioned vent openings, would have reduced the risk associated with potential explosions considerably.
- There should be limited access for personnel to areas near the process vessels during this type of processing; remote methods, such as sensors or surveillance cameras, represent a safe way of monitoring potentially hazardous processes.

The authors hope that the information gathered in this report will contribute to improved safety in the process industries.

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## Chemical symbols

C <sub>2</sub> H <sub>5</sub> SH	Ethanethiol (ethyl mercaptan)
CH <sub>3</sub> SH	Methanethiol (methyl mercaptan)
HCl	Hydrogen chloride (hydrochloric acid)
H <sub>2</sub> O	Hydrogen oxide (water)
H <sub>2</sub> S	Hydrogen sulfide
Mercaptans	From Latin ' <i>mercurius captans</i> ', traditional name for <i>thiols</i> (Ringnes, 1996)
NaOH	Sodium hydroxide (lye, caustic soda)
R	Portion of a molecule, other than a given functional group
ROH	General chemical formula for alcohols (e.g. ethanol, C <sub>2</sub> H <sub>5</sub> OH)
RSH	General chemical formula for thiols (e.g. ethanethiol, C <sub>2</sub> H <sub>5</sub> SH)
Thiols	Chemical compounds that contain the functional group –SH

## Abbreviations

AS	'Aksjeselskap', or <i>Limited Company</i> (Ltd.) in the UK, and <i>Incorporated</i> (Inc.) in the US
CFD	<i>Computational Fluid Dynamics</i>
CMR	<i>Christian Michelsen Research AS</i>
DSB	'Direktoratet for Samfunnssikkerhet og Beredskap', or <i>Directorate for Civil Protection and Emergency Planning</i>
EPA	<i>The United States Environmental Protection Agency</i>
FLACS	<i>FLame ACceleration Simulator</i> (CFD software from GexCon AS)
ID	Inner diameter
Kripos	'Den nasjonale enhet for bekjempelse av organisert og annen alvorlig kriminalitet', or <i>The National Criminal Investigation Service</i> (NCIS) in Norway; previously 'Kriminalpolitisenralen', or the <i>National Bureau of Crime Investigation</i> (NBCI)
LFL	<i>Lower Flammability Limit</i>
MIE	<i>Minimum Ignition Energy</i>
NGU	'Norges Geologiske Undersøkelse', or <i>Geological Survey of Norway</i>
SFT	'Statens Forurensningstilsyn', or <i>The Norwegian Pollution Control Authority</i>
TT	Height of tank
UFL	<i>Upper Flammability Limit</i>