

Journal of Hazardous Materials A81 (2001) 209-222



www.elsevier.nl/locate/jhazmat

Spill behaviour using REACTPOOL Part II. Results for accidental releases of silicon tetrachloride (SiCl₄)

T. Kapias*, R.F. Griffiths, C. Stefanidis

Department of Chemical Engineering, Environmental Technology Centre, UMIST P.O. Box 88, Manchester, M60 1QD, UK

Received 19 February 2000; received in revised form 17 July 2000; accepted 17 July 2000

Abstract

Silicon tetrachloride is a toxic, corrosive water reactive substance that is used widely in the process industries. On spillage from containment it creates liquid pools that can either boil or evaporate. The main feature of the pool behaviour is the exothermic reaction with water. There are three sources of water available for reaction: free ground water, substrate water and atmospheric moisture. Hydrogen chloride gas and *ortho*-silicic acid solid (or silica gel) are produced by the hydrolysis reaction. The purpose of this paper is to describe the dangers involved in cases of accidental releases of silicon tetrachloride, to report its properties, referring to toxicity data, major accidents and mitigation tests. It also describes pool behaviour using REACTPOOL [1]. Model results indicate that the pool behaviour is governed mainly by the amount of water available for reaction. Surface roughness and wind speed also have a significant effect on the results. Results are compared with those for other water reactive chemicals in Part III of this series of papers [3]. The generated cloud will initially contain silicon tetrachloride and hydrogen chloride with numerous processes taking place.

Although silicon tetrachloride has been involved in many major hazard incidents, there are no experimental data relevant to the modelling requirements. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Spill behaviour; REACTPOOL; Silicon tetrachloride

1. Introduction

The silicon industry has undergone immense development since World War II. SiCl₄ is one of the most important inorganic silicon compounds. It is the only chlorosilane

^{*} Corresponding author. Present address. Georgiou Seferi 34, Neapoli, 56728 Thessaloniki, Greece.

Tel.: +30-972-187950/453597.

E-mail address: kapap@otenet.gr (T. Kapias).

^{0304-3894/01/\$ –} see front matter © 2001 Elsevier Science B.V. All rights reserved. PII: S0304-3894(00)00296-X

that is neither flammable nor combustible. Even so, it is very toxic and corrosive and presents a major hazard to humans and the environment, as is recognised by its inclusion in many pieces of national and international legislation relating to industrial safety.

SiCl₄ is used and transported in its liquid phase and therefore on spillage it creates liquid pools, usually on land. Since it contains the Si–X bond it has a pronounced haloanhydride character, being highly reactive and aggressive. On escape from containment and exposure to moisture, it reacts readily, exothermically and violently with water, releasing HCl gas and *ortho*-silicic acid solid. This reaction supplies the pool with energy, raising its temperature and thus increasing the vapour evolution rates. Water is supplied to the pool from three sources; free ground water, substrate water and atmospheric moisture.

The pool usually contains only $SiCl_4$ liquid, since there would not usually be enough water to allow HCl to enter into solution. The *ortho*-silicic acid solid particles are assumed to be insoluble in liquid $SiCl_4$. In cases where the pool and other characteristics are such that insoluble settled particles are formed, the pool composition and properties will be constant. In all cases the pool will either boil or evaporate; there is no possibility of solidification.

Apart from HCl that is directly evolved from the hydrolysis reaction, SiCl₄ will also evolve in view of its high volatility. Thus, the generated cloud will initially contain SiCl₄ and HCl vapour. SiCl₄ will react with atmospheric moisture yielding HCl and *ortho*-silicic acid solid in a similar way to the liquid phase hydrolysis reaction. Overall, the behaviour of the generated cloud is expected to be very complicated because of all these phenomena. The fact that it is possible for the generated cloud to be initially denser than air adds to this complexity.

Until now, there have been no published attempts to model the release behaviour of SiCl₄. Furthermore, the only experiments that have been conducted were to test the effectiveness of some techniques for suppressing fumes generated from SiCl₄ spills.

The pool behaviour of SiCl₄ is modelled using REACTPOOL [1], substantially extending some preliminary work [2]. Model results indicate that the pool behaviour is mainly affected by the amount of water available for reaction. Surface roughness and wind speed also have a significant effect on the results [3].

2. Uses and properties

SiCl₄ is a colourless, clear, mobile, fuming liquid with a suffocating odour. Its main industrial use is in the production of semiconductors and other silicon compounds. It has also been used as a warfare agent. Some of its properties are shown in Table 1 [4–6], and further details are given in Appendix A.

Silicon tetrachloride is included in various pieces of national and international legislation on major hazards. Although it is not specifically named in the list of substances covered by the European Union Seveso II Directive [7], it is included in the category of chemicals that react violently with water according to the supplementary guidelines published by the Major Hazards Accident Bureau (MHAB) [8].

Table 1 Properties of SiCl₄ [4–6]

Property	Value
Molecular weight (kg kmol ⁻¹)	169.9
Boiling point (K)	330.2
Freezing point (K)	204.3
Critical temperature (K)	507
Critical pressure (bar)	35.93
Critical volume ($cm^3 mol^{-1}$)	326
Liquid density at 25° C (kg m ⁻³)	1490
Heat of vaporisation at 25° C (kJ mol ⁻¹)	29.7
Vapour pressure at 25°C (atm)	0.311

3. Toxicity data, accidents and mitigation tests

No published tests to examine human toxicity to silicon tetrachloride could be found in the literature. From accidents that occurred it was observed that contact with liquid $SiCl_4$ may cause severe burns to the skin and the eye. Exposure to the vapour is irritating to the eyes, skin and throat, and can be fatal. Prolonged exposure to small concentrations may result in pulmonary oedema [9–12].

Animal toxicity data are very limited. The oral LC50 in rats was about 8000 ppm for 4 h exposure. A 500 mg quantity applied for 24 h on the skin of rabbits caused severe erythema to slight eschar (injuries in depth) formation. A 20 mg quantity applied for 24 h on the rabbits eyes caused effects varying from beet redness to injuries in depth [9,11].

In cases of accidental spills the generated cloud will contain HCl as well as SiCl₄; the HCl is highly toxic and corrosive. It should be noted though that SiCl₄ is reported to be much more toxic than HCl [5]. HCl is generally irritant to the eyes and respiratory tract. A concentration of 35 ppm usually causes irritation of the throat after short exposure. Concentrations of 50–100 ppm are tolerable for 1 h. More severe exposures result in pulmonary oedema and often laryngeal spasm. Concentrations of 1000–000 ppm are extremely dangerous even for brief exposures [9].

Occupational exposure standards have been set for SiCl₄ in the USA as follows: Emergency Response Planning Guidelines (ERPG) [13]: ERPG(1) = 0.75 ppm (no more than mild, transient effects) for up to 1 h exposure; ERPG(2) = 5 ppm (without serious, adverse effects) for up to 1 h exposure; ERPG(3) = 37 ppm (not life threatening) up to 1 h exposure.

A number of accidents have occurred involving spillages of SiCl₄. A survey of accidents that involved spills of water reactive chemicals showed that there is about one accident per year involving SiCl₄ in the USA. About half of the reported spillages of SiCl₄ involved evacuations and/or injuries and/or deaths [1].

One of the largest and most disruptive accidents occurred in 1974 at the Bulk Terminals storage facility in Chicago, IL. This incident in noteworthy for several reasons including the quantity of material involved (3300 m^3) , the location (a large metropolitan area), the duration (leakage for 8 days, emissions for 20 days), and the nature of the chemical. "Within hours one ruptured tank affected the lives of tens of thousands of Chicagoans. As the escaping SiCl₄ reacted with the moisture-laden air, an enormous, breathtaking, eye watering,

nausea-inducing acid cloud spewed forth. At times the acid cloud was measured from 8 to 16 km long as it moved across the city, disrupting traffic, work and normal living activities" [14]. One fatality, 300 injuries and more than 2000 evacuations were the result of this severe accident [14–16].

This accident was the first major spill of reactive chlorides and it has served to draw attention to the hazards of this class of chemicals. The inability to control the leak and the vapours released prompted serious consideration of the available spill technology not only for SiCl₄ but for all water reactive chemicals. It was clear that direct application of water was not only ineffective; it worsened the situation [17].

In 1981, in San Francisco, USA, a spill of SiCl₄ at a chemical plant caused the evacuation of several thousands of people from an industrial park; 28 persons sought medical attention. Medical examination of the affected people gave some indication of the effects of SiCl₄ fumes on humans. Most of the affected individuals suffered only transient eye and upper airway irritation. Six of the plant employees were later referred for detailed evaluation of possible lung injury, but no definite evidence of SiCl₄ induced pulmonary disfunction was found. Five of these workers also experienced recurrent headaches and two complained of pedal dysesthesias (numbness or loss of mobility) after the accident. Although the temporal relationship between the exposure and onset of these symptoms is notable, no definite causal relationship could be established [12].

In 1998, in Moses Lake, Washington, 30,000 pounds of chemicals were released forming a cloud of hydrogen, silicon tetrachloride and trichlorosilane that drifted 3 miles north of the plant. A warning telling residents within 1 mile of the plant to stay indoors was lifted within a day. The gas cloud was contained an hour after the blast. Plant emergency workers used water to suppress and convert it into hydrochloric acid and a sand-like material (fume silica). Six workers were injured in this incident and two of them died after some days [18].

In recent years, some work has been carried on mitigation techniques for spills of SiCl₄. Overall, it has been shown that application of water-based foams is an effective technique for mitigating spills of most water reactive chemicals including SiCl₄. To be effective the foam must be applied in a certain way so that a blanket is formed over the total spill surface. Although the use of foam was recommended during the Chicago spill, it was only given a cursory test. Aqueous foams contain water and this reacts with the spill in the same way as free water, though more slowly. Although the reaction violence may be less than with a direct water application, a large dense cloud is formed. There will be little visible change in this cloud until a blanket of foam covers the total spill surface. According to Hiltz [17], failure of the foam to be effective in the Chicago spill can be attributed to one or more of three factors; insufficient time allowed to develop a full blanket, an application rate too slow for the spill size, or a foam not sufficiently resistant to the character of the spilled liquid.

Field tests have been carried out by MSA and Wah Chang Division of Teledyne [17]. Both crude SiCl₄ (containing measurable quantities of free chlorine and phosgene) and commercial grade SiCl₄ were tested. Two different types of water-based foams were applied; a high water retention foam and an ammoniated foam system. Based upon visual observation, the low expansion foam was most effective in reducing the vapour release rate. However, it required the longest time to cover the spill area and it is extremely difficulty to spread. The high expansion foam showed a degree of control almost equal to the low expansion

foam and spreading was easier. The ammoniated foam was least effective; development of the foam blanket took longer and after it was complete the apparent vapour release rate was greater than for straight foam. Generally, it was shown that for large impounded areas, high expansion foams could be employed to reduce the vapour hazards. For small localised spills the lower expansion foam may be a better choice. Overall, these tests showed that application of foams can be an effective mitigation technique for spills of SiCl₄.

In May 1990, Silicones Environmental Health and Safety Council (SEHSC) and DOE tested the effectiveness of aqueous foams in extinguishing chlorosilane fires and in vapour suppression. Trichlorosilane, HSiCl₃ (highly flammable) and SiCl₄ were examined. A total of 13 tests were conducted, 7 with HSiCl₃ and 6 with SiCl₄ [19].

A manual on chlorosilane emergency response guidelines was published in 1998 [20]. According to this manual, small spills should be handled with dry absorbent materials or covered with medium expansion foam. Large spills should be contained by the use of dikes and should be covered with any medium expansion aqueous film-forming foam. Initial application of foam will release significant amounts of corrosive vapours and water spray may be used downwind to suppress the corrosive vapour cloud. In all cases direct application of water should be avoided. This manual also provides information on safe transfer procedures, foam application, requirements of personal protective equipment and decontamination of personnel and equipment.

4. Reaction with water

The hydrolysis reaction of SiCl₄ takes place almost instantaneously and very energetically. Most of the available work on the liquid phase reaction with water was carried out more than 40 years ago. Even so, it provides useful information. Andrianov [21] reports in detail the hydrolysis reaction with water and other media. Overall, the reaction of SiCl₄ with water can be represented by the following equation:

$$SiCl_4 + 4H_2O \rightarrow [Si(OH)_4] + 4HCl$$
⁽¹⁾

The *ortho*-silicic acid [Si(OH)₄] is a solid product, but according to Mendeleyev ([22], see also Part II) it does not remain in that form; it loses part of its water with extraordinary ease. In other words, the hydrate formed does not contain as much water as would correspond to Si(OH)₄. This process of water loss is referred to as condensation. The gel is usually in the hydrate form $n\text{SiO}_2 \cdot m\text{H}_2\text{O}$, with m < n. The loss of water proceeds until *n* becomes much greater than *m*. The final product is known as silica gel, which has a complex polymeric structure. The main factor determining the number of free hydroxyl groups in the end reaction product, when the hydrolysis is run under ordinary conditions, is the reaction temperature contain a smaller number of free OH groups. The silica gel obtained under ambient conditions gradually undergoes condensation in air; its molecular weight increases, whilst the number of free OH groups and the amount of absorbed water decreases. Generally, the reaction of SiCl₄ and water cannot be represented by a single formula. It is recommended that the aggregate of the processes of hydrolysis and condensation of the hydrolysis products should be represented by reaction (1) [21,22]. In the vapour phase, the hydrolysis reaction with atmospheric moisture proceeds in a way similar to reaction (1). Generally, the SiCl₄ hydrolysis reaction with moist air is very similar to that for titanium tetrachloride. Most of the work in this field has been carried out in recent years.

El-Shall [23] investigated the vapour phase nucleation of SiCl₄ using an upward thermal diffusion chamber. Revised results, using the same experimental set-up but more precise calculations and equipment calibrations, have been published by Wimpfheimer et al. [24]. Experimentally calculated values of critical supersaturation at different temperatures at the onset of homogeneous nucleation have been reported in both references.

Bautista and Atkins [25] examined the competition between oxidation and hydrolysis of SiCl₄ in a diffusion flame burner during manufacture of optical fibre preform. In the low-temperature region of the flame, hydrolysis was the main route of conversion of SiCl₄, while oxidation was dominant in the high temperature region.

Okuyama et al. [26] have studied the aerosol formation by rapid nucleation during the preparation of silica thin films from SiCl₄ and oxygen gas by a chemical vapour deposition process. A vapour nucleation and diffusion model was used to describe and simulate the process.

5. Pool behaviour and incorporation into REACTPOOL - model results

For a spill on land, the main feature of the pool is the exothermic reaction of SiCl₄ with water. If there is excess water, HCl is produced in its liquid aqueous form. However, it is unlikely that there will be excess water, unless there is an external supply (e.g. by addition of aqueous-based foams for mitigation). Therefore, in most cases reaction with water will proceed under SiCl₄ excess conditions with HCl gas being directly produced and evolved to the atmosphere. The heat of reaction (1) in these cases was calculated to be around -4050 kJ kg^{-1} water.

Whilst the pool is spreading it encounters free ground water and substrate water, and also absorbs atmospheric moisture. After spreading has ceased water will be supplied only from the substrate and the atmosphere.

Apart from HCl, SiCl₄ will also evolve to the atmosphere in view of its high volatility. The energy produced by the reaction with water increases the pool temperature and the vapour evolution rate. The *ortho*-silicic acid solid will also be generated from the hydrolysis reaction. These solid particles may exist in various forms of silica gel since *ortho*-silicic acid undergoes condensation, as discussed in Section 4. As reported by Andrianov [21], it is impossible to predict the exact formula of this gel and therefore it is assumed here that no condensation takes place.

The pool behaviour of SiCl₄ has been incorporated into REACTPOOL [1]. All the properties of reactants and products involved have been parameterised as functions of temperatures and are listed in Appendix A. The *ortho*-silicic acid is soluble only in very hot acids and hydrogen fluoride. It has been assumed that Si(OH)₄ particles are insoluble in the liquid and settle onto the bottom of the pool forming a film that resists conduction of heat from the ground. The sensitivity of the model to the assumption that solid particles settle rather

Table 2 Values of the release scenario input parameters

Spill rate (kg s ⁻¹) for 600 s	16
Maximum duration of release to the atmosphere (s)	1800
Maximum pool radius (m)	50
Type of substrate	Concrete
Free water film thickness on the ground, w_g (m)	0.0005, 0.0015, 0.003, 0.005
Surface roughness length ^a , z_0 (m)	0.1, 0.01, 0.001, 0.0001
Wind speed at 10 m, U_{10} (m s ⁻¹)	5, 2, 10
Air and release temperature (K)	288
Atmospheric radiation factor	0.84
Cloud cover factor	7
Relative humidity (%)	70
Location	North England, UK (latitude = 54° , longitude = 2°)
Time and day	09.00 h and 298 (25 October)
Time step used in the calculations (s)	0.01

^a The corresponding values for h_{\min} are 1 cm, 8.5 mm, 7 mm, 5 mm, respectively.

than remain suspended has been examined and it was found that model results are generally not sensitive (see Section 6).

Critical aspects of the pool behaviour of SiCl₄ have been revealed by the use of REACT-POOL. Overall, the pool behaviour is strongly affected by the amount of water available for reaction. The main water source is usually the free ground water. In all cases investigation of the reaction with water occurred under conditions of excess SiCl₄. The surface roughness and the wind speed also have a strong effect on the results. The rest of the input parameters have weaker effects. As shown in Fig. 5, SiCl₄ pools usually boil for a considerable portion of the spreading period.

A large number of release scenarios was examined. The values of the release scenario input parameters are shown in Table 2. The effects of significant parameters on the pool characteristics are described in Part III of this series of papers, where a comparison with the pool behaviour of other water reactive chemicals is also presented [3].

Figs. 1–8 show the results for the above scenarios. These show the behaviour of the main pool properties and vapour evolution rates. The detailed commentary on these results is given in the comparative discussion in Part III of this series of papers [3].

5.1. Solid particles of ortho-silicic acid — model sensitivity to the assumption that solid particles settle onto the bottom of the pool

Model results indicate that relatively small quantities of solid particles will be formed. Even under very high water availability ($w_g = 0.005 \text{ m}$), the mass of solids produced (about 520 kg) is about 5.5% of the total amount of liquid spilled (9600 kg). It is believed that these particles are insoluble and it has been assumed that they settle onto the bottom of the pool. Their only influence on the pool behaviour is that they form a film that alters conduction of heat from the ground. In the previous sections it was shown that in most cases



Fig. 1. Percentage supply of the three water sources to the total amount of water provided for reaction with SiCl₄ for spills of 16 kg s⁻¹ for 600 s ($z_0 = 0.1$ m, $U_{10} = 5$ m s⁻¹).

the generated pool evaporates for the majority of the release duration (even when $w_g = 0.005 \text{ m}$, it evaporates for 1380 s which represents about 76% of the total release duration). In an evaporating pool, there will not be adequate turbulence and mixing in the liquid to keep the particles suspended. Therefore, the assumption that particles of *ortho*-silicic acid will settle is the most likely condition. Even so, model sensitivity to this assumption has been checked and it was shown that even in cases where the solid particles constitute a relatively high percentage of the total mass of the pool (i.e. for $w_g = 0.005 \text{ m}$), they affect the results only weakly. Table 3 shows that results will change less than 5% in almost all cases.



Fig. 2. Effect of w_g on the total amount of vapour evolved and solids produced for the total release duration ($t_{s2} = 1800 \text{ s}$) ($z_0 = 0.1 \text{ m}$, $U_{10} = 5 \text{ m s}^{-1}$).



Fig. 3. Effect of w_g on the vapour evolution rates for the spreading period ($z_0 = 0.1 \text{ m}, U_{10} = 5 \text{ m s}^{-1}$).

6. Behaviour of the generated cloud

Clouds generated from accidental spills of SiCl₄ will initially contain SiCl₄ vapour and HCl gas. SiCl₄ vapour will continuously react with the atmospheric moisture yielding HCl gas and solid particles, which will gradually deposit on the ground. HCl gas may also interact with the atmospheric moisture yielding aerosols. It is unlikely that there is enough atmospheric moisture in the airflow above the pool for complete and instantaneous reaction of SiCl₄ to HCl, in view of the initially large amounts of SiCl₄ vapour present in the cloud. The cloud behaviour will resemble the behaviour of a SO₃/oleum cloud [27]. It is expected that the SiCl₄/HCl cloud will initially be denser than air and only after some distance downwind, allowing adequate dilution with air, will it become passive and chemically



Fig. 4. Effect of w_g on the vapour evolution rates for the after spreading period ($z_0 = 0.1 \text{ m}, U_{10} = 5 \text{ m s}^{-1}$).



Fig. 5. Pool temperature profiles for different values of w_g ($z_0 = 0.1 \text{ m}$, $U_{10} = 5 \text{ m s}^{-1}$).

inactive, containing only HCl. Some portion of the aerosols will be deposited on the ground due to gravitational settling and other deposition effects.

7. Discussion, conclusions, further investigation

Silicon tetrachloride is a highly toxic material that can severely harm humans and the environment and can cause fatalities, as shown from past incidents. When accidentally spilled it creates liquid pools, the main feature of which is the exothermic reaction with water.



Fig. 6. Pool radius profiles for different values of w_g ($z_0 = 0.1 \text{ m}$, $U_{10} = 5 \text{ m s}^{-1}$).



Fig. 7. Effect of z_0 on the total amount of vapour evolved and solids produced for the total release duration ($t_{s2} = 1800 \text{ s}$) ($w_g = 0.0015 \text{ m}$, $U_{10} = 5 \text{ m s}^{-1}$).



Fig. 8. Effect of U_{10} on the total amount of vapour evolved and solids produced for the total release duration ($t_{s2} = 1800$ s) ($w_g = 0.0015$ m, $z_0 = 0.1$ m).

Table 3

Sensitivity of the model to the assumption that the solid particles settle onto the bottom of the pool

Solid particles settle onto the bottom of the	Solid particles are suspended in the liquid medium
pool, $w_{\rm g} = 0.005 {\rm m}$	affecting the pool properties, $w_{\rm g} = 0.005 \mathrm{m}$
SiCl ₄ evolved for the total release	SiCl ₄ evolved for the total release
duration = 7763.4 kg	duration = $80.83.6 \text{ kg} (+3.9\%)$
HCl evolved for the total release	HCl evolved for the total release
duration = 784.3 kg	duration = $819.7 \text{kg} (+4.5\%)$
Amount of solids produced $= 516.3 \text{ kg}$	Amount of solids produced = $537 \text{ kg} (+4\%)$

In respect of its toxicity very limited data are available. More investigation is required in this field in order to draw firmer conclusions.

A literature survey revealed no published attempts to model the pool or cloud behaviour. An extensive investigation of any relevant data sources was conducted in support of this study. Certain data (e.g. on interactions with substrate compounds, absorptivity of atmospheric moisture) are either not available or not well defined. Sufficient information was found to permit worthwhile use of REACTPOOL.

Although a number of accidents involving spills of SiCl₄ have occurred, no experiments have been conducted on the release behaviour. Further improvement and validation of the model depends on the availability of these data.

Further investigation should be focused on describing and modelling the behaviour of the cloud generated from accidental spills of SiCl₄. The behaviour of such a cloud resembles the behaviour of clouds generated from SO₃ and oleum spills.

Acknowledgements

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

Appendix A

Various sources were used to identify the properties of SiCl₄ and Si(OH)₄ [4–6,28]. Properties of liquid SiCl₄:

- molecular weight, $MW = 169.9 \text{ g mol}^{-1}$;
- boiling point, bp = 330.2 K;
- freezing point, fp = 204.3 K;
- liquid density, ρ (kg m⁻³):

$$\rho = 521.16 \times 0.26416^{(-1 - (T/507))^{0.2815}}$$

• heat capacity, C_p (kJ kg⁻¹ K⁻¹):

$$C_p = 1.00164 - 1.00214 \times 10^{-3}T - 2.40288 \times 10^{-6}T^2 + 1.08366 \times 10^{-8}T^3;$$

• viscosity, μ (cP):

$$\log \mu = 14.917 - \frac{1635.3}{T} - 4.2676 \times 10^{-2}T + 3.3228 \times 10^{-5}T^{2};$$

• thermal conductivity, k (kW m⁻¹ K⁻¹):

$$k = 0.0151 \times 10^{-3} - 8.0951 \times 10^{-8}T - 2.9387 \times 10^{-10}T^{2};$$

• vapour pressure, *P* (atm):

$$\log P = 25.5694 - \frac{2391.1}{T} - 7.3965 \log T - 9.3193 \times 10^{-10} T + 2.7569 \times 10^{-6} T^2;$$

• heat of vaporisation, H (kJ kg⁻¹):

$$H = 254.44 \left(1 - \frac{T}{507} \right)^{0.383};$$

- Schmidt number, Sc (estimated according to [28]) = 1.974;
- critical temperature, $T_c = 507 \text{ K}$;
- critical volume, $V_c = 326 \text{ cm}^3 \text{ mol}^{-1}$;
- latent heat of fusion, $H_s = 45.069 \,\text{kJ}\,\text{kg}^{-1}$.

Properties of Si(OH)₄:

- molecular weight, $MW = 96.1 \text{ g mol}^{-1}$;
- density at 25°C, ρ (kg m⁻³) = 2185 (varies from 2150 to 2220);
- heat capacity, C_p (kJ kg K⁻¹):

$$C_p = 0.04124 + 2.75 \times 10^{-3}T - 0.161 \times 10^{-5}T^2$$

• thermal conductivity, $k (kW m^{-1} K^{-1}) = 0.00133$ (for SiO₂ particles).

References

- T. Kapias, R.F. Griffiths, C. Stefanidis, REACTPOOL: a code implementing a new multi-compound pool model that accounts for chemical reactions and changing composition for spills of water reactive chemicals, J. Hazard. Mater. 81 (2000) 1–18.
- [2] T. Kapias, R.F. Griffiths, Proceedings of the International Conference and Workshop on Modeling the Consequences of Accidental Releases of Hazardous Materials, San Francisco, USA, 1999, pp. 133–144.
- [3] T. Kapias, R.F. Griffiths, Spill behaviour using REACTPOOL. Part III. Results for accidental releases of phosphorus trichloride and oxychloride (PCl₃, POCl₃), and general discussion, J. Hazard. Mater. 81 (2001) 223–249.
- [4] Kirk-Othmer's Encyclopedia of Chemical Technology, Sulfuric Acid and Sulfur Trioxide, 3rd Edition, Vol. 22, Wiley, New York, 1983.
- [5] Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, 1987.
- [6] G.L. Yaws (Ed.), Chemical Properties Handbook, McGraw Hill, New York, 1999.
- [7] Seveso II Directive, On the control of major-accident hazards involving dangerous substances, 96/082/EC, 1996.
- [8] Major Accident Hazards Bureau (MAHB), Guidance notes for implementing Seveso II Substances database, Joint Research Centre, European Commission, available from: http://mahbsrv.jrc.it.
- [9] R.J. Lewis (Ed.), Sax's Dangerous Properties of Industrial Materials, 9th Edition, 1996.
- [10] W.M. Grant, Toxicology of the Eye, 3rd Edition, Thomas, Springfield, IL, 1986, p. 889.
- [11] The Merck Index, 10th Edition, NJ, 1983, p. 1221.
- [12] K.W. Kaiser, et al., J. Occup. Med. 26 (1) (1984) 33-36.
- [13] American Industrial Hygiene Association, The AIHA 1999 Emergency Response Planning Guidelines and Workplace Environmental Exposure Level Guides Handbook, American Industrial Hygiene Association, Fairfax, VA, 1999.

- [14] W.C. Hoyle, Bulk terminals: silicon tetrachloride incident, in: G.F. Bennett, S. Feates, L. Wilder (Eds.), Hazardous Materials Spills Handbook, McGraw-Hill, New York, 1982.
- [15] EPA Accidental Release Information Program (ARIP) Database, available from: http://www.epa.gov/ceppo/ acc-his.html.
- [16] APELL: List of Selected Accidents Involving Hazardous Substances (1970–1989), United Nations Environment Programme, Division of Technology, Industry and Ergonomics, available from: http://www.unepie.org/apell/accident.html.
- [17] R.M. Hiltz, Mitigation of the vapor hazard from silicon tetrachloride using water-based foams, J. Hazard. Mater. 5 (1982) 169–175.
- [18] Moses Lake explosion injures 6, Associated Press, 1998.
- [19] WRI spill test database, available from: http://wri.uwyo.edu/Projects/STFDB/SHC/SEHSC.htm.
- [20] J.T. Higgins, W.E. Hubbs, R.A. Kayser, P. Kremer, S.W McMahan, L. Patrick, M. Strong, Chlorosilane Emergency Response Guidelines, ASTM Manual Series: MNL33, 1998.
- [21] K.A. Andrianov, Organic Silicon Compounds, State Scientific Technical Publishing House for Chemical Literature, Moscow, 1955.
- [22] D.I. Mendeleyev, Principles of Chemistry, 1st Edition, 1871.
- [23] M.S. El-Shall, Chem. Phys. Lett. 143 (1988) 381.
- [24] T. Wimpfheimer, M.A. Chowdhury, M.S. El-Shall, Vapor-phase nucleation of silicon tetrachloride: revised results, J. Phys. Chem. 97 (1993) 3930–3931.
- [25] J.R. Bautista, R.M. Atkins, The formation and deposition of SiO₂ aerosols in optical fiber manufacturing torches, J. Aerosol Sci. 22 (1991) 667.
- [26] K. Okuyama, D. Huang, J.H. Seinfeld, N. Tani, Y. Kousaka, Aerosol formation by rapid nucleation during the preparation of silica (SiO₂) thin films from silicon tetrachloride (SiCl₄) and oxygen (O₂) gases by chemical vapour deposition (CVD) process, Chem. Eng. Sci. 46 (7) (1991) 1545–1560.
- [27] T. Kapias, R.F. Griffiths, Dispersion and thermodynamics of clouds generated from spills of SO₃ and oleum, J. Hazard. Mater. A67 (1999) 9–40.
- [28] A.H.P. Skelland, Diffusional Mass Transfer, Wiley/Interscience, New York, 1974.