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Accidental releases of titanium tetrachloride ($TiCl_4$) in the context of major hazards—spill behaviour using REACTPOOL

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Abstract

Titanium tetrachloride is a highly toxic and corrosive substance that is used widely in the process industries. On accidental release, it creates liquid pools that can either boil or evaporate. The main feature of the liquid pool is the reaction of titanium tetrachloride with water. There are three sources of water available for reaction: free ground water, atmospheric moisture and substrate water. Unfortunately, there is no specific study that examines the liquid phase hydrolysis reaction of titanium tetrachloride. Based on thermodynamic calculations and relevant information found on the topic, it is concluded that liquid titanium tetrachloride reacts exothermically with all three sources of water yielding hydrogen chloride gas and a solid complex of titanium oxychloride.

The purpose of this paper is to describe the spill behaviour of titanium tetrachloride reporting a number of results using the REACTPOOL model [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. A81 (2001) 1–18]. It also addresses the dangers involved in cases of accidental release of titanium tetrachloride and reports its properties, referring to toxicity data and other relevant information. The spill behaviour of titanium tetrachloride has been incorporated into REACTPOOL. Model results indicate that the pool behaviour is mainly affected by the amount of free ground water, the wind speed and surface roughness.

Although titanium tetrachloride has been involved in a number of major accidents, there are no experimental data relevant to the modelling requirements.

Keywords: $TiCl_4$; REACTPOOL; Water reactive chemicals

1. Introduction

Titanium tetrachloride is a highly aggressive material whose major hazardous potential comes from the clouds of HCl and titanium compounds created whenever this substance escapes from containment and is exposed to moisture. It is listed as a “highly toxic” chemical in various pieces of international legislation on major hazards [2,3]. The severity of some $TiCl_4$ accidents, certain animal tests and human toxicology studies also reveal its highly hazardous nature [1,4].

$TiCl_4$ is used widely in the process industries and mainly as an intermediate in the production of titanium rutile, titanium dioxide, titanium pigments, in the manufacture of iridescent glass artificial pearls, as a polymerization catalyst, and to produce smoke screens. It has been involved in a number of accidents. A survey of accidents that involved releases of water reactive chemicals that occurred in the US during the period January 1990 to November 1999, revealed that there had been 473 reported incidents involving spillages of $TiCl_4$, of which 13 involved evacuation, injuries or death [1]. The only attempt at modelling its pool behaviour has been published recently [5], and was based on the REACTPOOL modelling procedure, though much simplified. The authors adopted a simple description of the pool generated by the rupture of a heat exchanger in order to model this aspect for a particular scenario in the risk assessment of

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a titanium sponge production plant. They did not explore the model behaviour beyond this limited application. Studies involving dispersion of titanium tetrachloride seem to ignore the liquid phase hydrolysis reaction, and model the liquid source as a non-reactive evaporating pool [6]. It has been shown, however, that in cases of spills of other water reactive chemicals, this assumption is rather pragmatic and can lead to very large discrepancies as compared with more realistic modelling approaches that do include these factors [7].

The physical and thermodynamic properties of $TiCl_4$ are generally well defined in the literature. However, there are a number of discrepancies and gaps concerning its liquid phase hydrolysis reaction. In this study we have found that the literature contains only some "short statements" regarding this reaction. Based on thermodynamic calculations, estimation methods and other relevant information, it can be shown that a number of these statements could not realistically represent the liquid phase hydrolysis reaction of $TiCl_4$.

Furthermore, this study concludes that the following reaction realistically represents the liquid phase hydrolysis reaction of $TiCl_4$, in cases of accidental spills:

$$TiCl_4(l) + 3H_2O(l, v) \rightarrow TiO_2{\cdot}H_2O \cdot 3HCl(s) + HCl(g) + \Delta H \quad (1)$$

According to the exothermic reaction (1), liquid $TiCl_4$ will react with ground water, substrate water and atmospheric moisture, producing a solid complex of titanium oxychloride and hydrogen chloride gas. The pool will contain $TiCl_4$ and solid particles of the titanium oxychloride complex and will have changing composition and properties as the reaction proceeds. Hydrogen chloride gas will be directly liberated by the hydrolysis reaction. Apart from HCl, $TiCl_4$ vapour will also evolve from the pool due to its relatively high volatility. The solid complex is expected ultimately to settle onto the bottom of the pool forming a film. The generated cloud will initially contain HCl and $TiCl_4$ vapour with several complex chemical and physical interactions taking place as shown in the CMA Dispersion Model Scientific Report [6]. Although this report quotes certain correlations for the liquid phase hydrolysis reaction of $TiCl_4$, it ignores these reactions in modelling the behaviour of the liquid source (see discussion in Section 4.3).

The pool behaviour has been developed into a module and incorporated into REACTPOOL. Model results indicate that the pool behaviour is mainly affected by the amount of free ground water, the wind speed and surface roughness. Although there are no experimental results to validate the model, REACTPOOL gives useful insights into the likely pool behaviour of $TiCl_4$.

In this paper, the main uses and properties of $TiCl_4$ are reported in Section 2. Data on its toxicity and relevant accidents are quoted in Section 3. Section 4 reports all information relevant to its behaviour on reaction with water, including previous modelling attempts and concludes by identifying the most satisfactory and thermodynamically sound hydrolysis reaction of liquid $TiCl_4$. Its expected pool behaviour and the modelling approach followed in order to incorporate its behaviour into REACTPOOL, are described in Sections 5 and 6, respectively. Values of the input parameters of a number of scenarios that were carefully chosen in order to present the main aspects of the $TiCl_4$ pool behaviour, are quoted in Section 7. In Section 8, the significant effect of the amount of free ground water on the $TiCl_4$ pool behaviour is depicted. The surface roughness and the wind speed effects are shown in Sections 9 and 10, respectively. Conclusions based on the work are summarised in Section 11.

Table 1
Properties of $TiCl_4$ [4,9–18]

Molecular weight (kg kmol^{-1})	189.69
Boiling point (K)	136 °C
Freezing point (K)	−25 °C
Specific gravity at 20 °C	1.72
Specific heat of liquid at 25 °C	37.53 cal mol^{-1} °C^{-1}
Critical temperature (K)	358 °C
Liquid viscosity (cP) at 25 °C	0.73
Liquid heat capacity (kJ kg^{-1} °C^{-1}) at 25 °C	0.14509
Heat of formation of liquid (kJ mol^{-1}) at 25 °C	−804.2
Heat of fusion (kJ kg^{-1})	52.5

2. Main uses and properties

$TiCl_4$ is a colourless to light yellow watery liquid with a sharp, pungent odour that is produced by the chlorination process of titanium compounds. It is used as a starting and/or intermediate material for the production of a variety of organic and inorganic titanium compounds such as titanium pigments. In the United States, more than 1.5 million tons of $TiCl_4$ were produced in 1990 [8].

Some of its properties are summarized in Table 1.

3. Toxicity and accidents

$TiCl_4$ is generally ranked as one of the compounds that are most hazardous (worst 10%) to human health. It is described as more hazardous than most chemicals in 8 out of 8 ranking systems [19].

A detailed report on the "Toxicological Profile of Titanium Tetrachloride" was published in 1997 by the U.S. Department of Health and Human Services, Public Health Services, Agency for Toxic Substances and Disease Registry [4]. This report contains useful information and data on $TiCl_4$ human and animal toxicity. The toxic effect of $TiCl_4$ is strongly associated with its exothermic and vigorous reaction upon contact with water.

Overall, $TiCl_4$ is highly hazardous to humans. Human toxicity surveys and past accidents suggest that:

- it causes severe burns to eyes and the skin. Swallowing the liquid will cause burns of mucous membranes, esophagus and stomach;
- $TiCl_4$ fumes may be fatal if inhaled; it may cause lung damage.

A worker has died after having accidentally splashed his whole body with $TiCl_4$, from the complications of severe pulmonary injury caused by inhalation of $TiCl_4$ fumes [20].

A survey of occupational exposure of 209 workers to titanium tetrachloride and dioxide particulates was conducted [21,22]. Results suggest that pulmonary impairment may be caused by exposure to $TiCl_4$. It was difficult however to determine the precise cause of these pulmonary abnormalities.

A few epidemiological studies have examined cancer mortality in workers employed in industries using $TiCl_4$. No association between $TiCl_4$ exposure and lung cancer mortality could be found in a study that examined 969 male workers exposed to $TiCl_4$ concentrations within the range 0.5 and 3 mg/m^3, for periods up to more than 5 years [23,24]. The authors state, however, that the results of this study should not be interpreted as definitive.

Findings in animals support the observations made in humans [4]. In a study that compared the effects of $TiCl_4$ and HCl in mice, after acute inhalation exposure, it was concluded that an active component in both cases was hydrochloric acid [25]. The results showed that 9 of 15 mice exposed to $TiCl_4$, and 1 of 15 mice exposed to HCl, died.

Based on toxicity tests conducted on rats [26–28], the U.S. Department of Health and Human Services has calculated the following values of Minimal Risk Levels (MRL) for $TiCl_4$ [4]:

- 0.01 mg/m^3 for intermediate inhalation exposure (15–364 days) to hydrolysis products of $TiCl_4$;
- 0.0001 mg/m^3 for chronic inhalation exposure (365 days or more) to hydrolysis products of $TiCl_4$;

where MRL is an estimate of daily human exposure to a dose of a chemical that is likely to be without an appreciable risk of adverse non-cancerous effects over a specified duration of exposure.

Non-human toxicity values are reported as follows:

- LC50 mouse inhalation = 100 mg/(m^3 2 h) [29];
- LC50 rat inhalation (head-only) = 460 mg/(m^3 4 h) [4];
- LC50 rat inhalation (head-only) = 108000 mg/(m^3 2 min) [4];

where LC50 stands for the lethal concentration of the chemical in the air that kills 50% of the test animals in a given time (usually 4 h).

In a survey of water reactive chemical accidents reported in the U.S. during the period January 1990 to November 1999, $TiCl_4$ is at the top of the list amongst a number of water reactive substances [1]. About half of the 889 accidents reported involved spillage of $TiCl_4$. Unfortunately, no detailed report of any of the accidents that involved spills of $TiCl_4$ could be found.

4. Reaction with water—previous modelling attempts

Unfortunately, the liquid phase hydrolysis reaction of $TiCl_4$ is not well established in the literature. Only very limited theoretical or experimental data could be found on the topic. The only relevant experimental work found was published in 2000 by the Office of Hazardous Materials Safety, part of the United States Department of Transportation's Research and Special Programs Administration [30]. The experimental programme was conducted to support an empirical basis for the amount of toxic-by-inhalation (TIH) gas emitted upon the reaction of a substance with water. A series of 42 small-scale experiments involving 21 water reactive substances (including $TiCl_4$) were conducted. Two methods were used. In Method A, stoichiometric amounts of water and water reactive chemical were mixed; in Method B the water reactive material was added to the water, which was present in five-fold molar excess. In both methods the amount of evolved gas was measured.

The hydrolysis reaction of $TiCl_4$ is described in [30] according to reaction (2):

$$TiCl_4(l) + 2H_2O \rightarrow TiO_2(s) + 4HCl(g) + \Delta H \qquad (2)$$

0.19 g (1 mmol) of $TiCl_4$ was used for the two experiments.

The main observations during these experiments were: "In Method A, the injected water was immediately covered with a white crust of titanium dioxide. Only 27% of the predicted theoretical yield of HCl occurred. In Method B, it appeared that in addition, some HCl that initially escaped as a gas dissolved in the excess water. The yield peaked at 16% of maximum after 1 min and dropped to 6% within 10 min. In the free atmosphere, a smaller fraction of the HCl produced would dissolve in the excess water as a result of advection".

Experimental results are given in Table 2.

It should be noted that the scope of these experiments was simple. Looking at the findings, one can draw the following conclusions:

(a) The theoretical yield of the reaction was measured to be equal to 27%. Based on the stoichiometry of the adopted reaction (2), "one molecule of $TiCl_4$ produces 4 molecules of HCl gas", it was observed that one

Table 2
Experimental results [30]

Time (min)	Mass of HCl (g) evolved	
	Method A	Method B
1	0.023	0.023
5	0.039	0.0114
10	0.039	0.091
20	0.039	0.091

molecule of $TiCl_4$ produces about 1 molecule of HCl gas ($4 \times 27\% \approx 1$).

(b) The reaction of liquid $TiCl_4$ with water produces solid particles of a titanium compound (as shown in Section 4.1 this compound cannot be TiO_2).

Although there is no published study that specifically examines the reaction of liquid $TiCl_4$ with water under any conditions, there are a number of different "simple statements" that describe this reaction. Some of these "simple statements" are controversial.

The following such statements were found in different pieces of literature:

- $TiCl_4$ is soluble in cold water and decomposes in hot water [31].
- $TiCl_4$ reacts exothermically with water forming TiO_2 and HCl gas [10–12,30].
- Under $TiCl_4$ excess conditions, $TiCl_4$ readily hydrolyses forming titanium oxychloride and HCl gas [6].
- $TiCl_4$ reacts exothermically with water forming complex solid particles and hydrogen chloride gas [15].

Most references agree on certain points: the liquid phase hydrolysis reaction of $TiCl_4$ is highly exothermic, violent and occurs almost instantaneously. The above statements are examined in detail in Sections 4.1–4.4.

4.1. *$TiCl_4$ is soluble in cold water and decomposes in hot water*

It is suggested that liquid $TiCl_4$ does not react with cold water, but is soluble in it. On the other hand, it is said to decompose in hot water [31]. It should be noted that most references disagree with this statement, but instead concur that $TiCl_4$ reacts with water vigorously and exothermically, irrespective of the water temperature.

Additionally, animal tests and past accidents show that liquid $TiCl_4$ causes severe burns to human and animal skin. This hazardous characteristic of $TiCl_4$ is associated with its reaction with any moisture present on the skin and surrounding atmosphere, producing HCl, which is highly corrosive [4].

Moreover, the experimental conditions of the tests described above in [30] showed that, at 25 °C, liquid $TiCl_4$ undergoes hydrolysis.

Conclusion: Based on the above, it is concluded that statement 4.1 is unrealistic.

4.2. *$TiCl_4$ reacts exothermically with water forming TiO_2 and HCl gas*

It is also suggested [6,10–12] that the liquid phase hydrolysis reaction proceeds according to the following:

$$TiCl_4(l) + 2H_2O(l) \rightarrow TiO_2(s) + 4HCl(g) + \Delta H \quad (2.1)$$

$$TiCl_4(l) + 2H_2O(v) \rightarrow TiO_2(s) + 4HCl(g) + \Delta H \quad (2.2)$$

Thermodynamic calculations at different temperatures for reactions (2.1) and (2.2) were conducted, in order to examine whether these reactions are spontaneous, and to calculate the generated heats.

It is shown (Table 3) that in all temperature ranges to be expected in cases of accidental spills, both reactions are spontaneous ($\Delta G < 0$). However, reaction with liquid water (reaction (2.1)) is endothermic ($\Delta H > 0$), while reaction with atmospheric moisture (reaction (2.2)) is exothermic ($\Delta H < 0$).

Conclusion: Based on the widely accepted exothermic nature of the hydrolysis reaction of $TiCl_4$, it is concluded that reaction of liquid $TiCl_4$ with free ground water will not occur according to reaction (2.1).

4.3. *Under $TiCl_4$ excess conditions, $TiCl_4$ readily hydrolyses forming liquid titanium oxychloride and HCl gas*

According to [6], the reaction between $TiCl_4$ and H_2O is a Lewis-acid Lewis-base reaction, and the products depend on the relative concentrations of $TiCl_4$ and H_2O:

Table 3
Calculation of ΔH and ΔG of reactions (2.1) and (2.2)

T (K)	*H*					ΔH		ΔG	
	$TiCl_4$(l)	H_2O(l)	H_2O(v)	TiO_2(s)	HCl(g)	Reaction (2.1)	Reaction (2.2)	Reaction (2.1)	Reaction (2.2)
298	−804.2	−285.8	−241.8	−944.8	−92.3	61.83	−26.2	−59	−76.2
300	−803.4	−285.7	−241.8	−944.7	−92.3	61.6	−26.2	−59.8	−76.5
320	−801	−284.2	−241.1	−943.5	−91.7	59.1	−27	−67.8	−79.8
340	−798.1	−282.7	−240.4	−942.4	−91.1	56.7	−27.8	−75.6	−83.1
360	−795.2	−281.2	−239.7	−941.2	−90.5	54.3	−28.5	−83.4	−86.3
380	−792.2	−279.6	−239.1	−939.9	−89.9	51.9	−29.3	−90.9	−89.5
400	−789.3	−278.1	−238.4	−938.7	−89.3	49.5	−30	−98.3	−92.7
420	−786.4	−276.6	−237.7	−937.4	−88.8	47.1	−30.7	−105.7	−95.8
440	−783.5	−275	−237	−936.1	−88.2	44.7	−31.3	−112.9	−98.9
460	−780.6	−273.4	−236.6	−934.8	−87.6	42.2	−32	−120.1	−101.9
480	−777.6	−271.8	−235.6	−933.5	−87	39.7	−32.7	−127.1	−105
500	−774.7	−270.1	−234.9	−932.1	−86.4	37.2	−33.3	−134	−108

All energy values are given in kJ/mol.

Table 4
Available properties of liquid $TiOCl_2$ [32,33]

Property	Value [32]	Value [33]
Molecular weight	134	134
Physical state	Liquid	Liquid
Melting point (°C)	<10	n/a
Boiling point (°C)	105–112	59
Vapour pressure (mmHg) (25 °C)	94	147

- $TiCl_4$ is in excess:

$$TiCl_4(l) + H_2O(l) \rightarrow TiOCl_2(l) + 2HCl(g) \quad (3.1)$$

$$TiCl_4(l) + H_2O(v) \rightarrow TiOCl_2(l) + 2HCl(g) \quad (3.2)$$

- H_2O is in excess:

$$TiCl_4(l) + 4H_2O(l) \rightarrow Ti(OH)_4(aq) + 4HCl(g) \quad (4)$$

$$TiCl_4(l) + 4H_2O(v) \rightarrow Ti(OH)_4(s) + 4HCl(g) \quad (5)$$

It is also reported [6] that under normal operating conditions, the reaction of $TiCl_4$ with H_2O will not produce solids. Additionally, titanium oxychloride produced by reactions (3.1) and (3.2) is soluble in $TiCl_4$.

In cases of accidental spills, it is expected that in most cases $TiCl_4$ will be in excess and according to [6] the reaction of $TiCl_4$ with water will proceed according to reactions (3.1) and (3.2).

In order to describe and investigate these reactions, the properties of $TiOCl_2$ should be defined. An extensive survey was conducted. Unfortunately, very limited information could be found on liquid $TiOCl_2$ (Table 4). Different estimation methods were used in order to define the properties of $TiOCl_2$ liquid. Results of this procedure are presented in Table 5. It should be noted that most methods quoted in Table 5 are based on energy bonds and group contributions. For each of the calculated properties (Table 5) the most appropriate method was chosen.

Thermodynamic calculations at different temperatures for reactions (3.1) and (3.2) were conducted, in order to calculate the generated heats (Table 6).

Conclusion: As shown in Table 6, both reactions (3.1) and (3.2) are endothermic ($\Delta H > 0$) and could not realistically represent the expected hydrolysis reaction of $TiCl_4$ in cases of accidental spills. It should be noted that in order for reaction (3.1) to be exothermic, the value of the heat of formation of liquid $TiOCl_2$ would need to be above 900 kJ/mol (such high values are extremely rare for liquid compounds).

4.4. *$TiCl_4$ reacts exothermically with water forming complex solid particles and hydrogen chloride gas*

It is stated that liquid $TiCl_4$ reacts with water (either liquid ground water or atmospheric moisture) in an exothermic, violent reaction forming a complex solid of "titanium oxychloride" and HCl gas [15].

4.4.1. *Derivation of an appropriate set of hydrolysis reactions*

Hydrolysis of $TiCl_4$ is reported to produce a solid complex of the type $Ti(OH)_nCl_x$ [15]. A similar solid was identified by research conducted by member companies of the CMA Titanium Dioxide Panel during 1992 [6]. This research showed that the vapour phase hydrolysis reaction of $TiCl_4$ (vapour $TiCl_4$ reacting with atmospheric moisture) produces solids which are consistent with the formula $TiO_{1.6}Cl_{0.8}{\cdot}4H_2O$. They have used the following correlation in order to represent the vapour phase hydrolysis reaction of $TiCl_4$:

$$TiCl_4(v) + 6H_2O(v) \rightarrow TiO_2{\cdot}0.8HCl \cdot 4H_2O(s) + 3.2HCl(g) \quad (6)$$

Table 5
Calculated properties of liquid $TiOCl_2$

Property	Calculated value	Method
Molecular weight	134	
Melting point (°C)	0	Assumption based on [32]
Boiling point (°C)	83.5	Based on vapour pressure value quoted in [32]
Heat of vaporisation (25 °C) (kJ/mol)	32.3	Fedors [34]
Heat of formation (25 °C) (kJ/mol)	−648	Benson [34]
Critical temperature (°C)	303.7	Ambrose [34]
Critical pressure (Pa)	4.6×10^6	Ambrose [34]
Critical volume (m^3/kmol)	0.298	Ambrose [34]

Table 6
Calculation of ΔH of reactions (3.1) and (3.2) [34]

T (K)	*H*					ΔH	
	$TiCl_4$(l)	H_2O(l)	H_2O(v)	$TiOCl_2$(l)	HCl(g)	Reaction (3.1)	Reaction (3.2)
298	−804.2	−285.8	−241.8	−648	−92.3	258	29
300	−803.4	−285.7	−241.8	−648	−92.3	258	29
400	−789.3	−278.1	−2384	−643	−89.3	247	24

All energy values are given in kJ/mol.

Table 7
Calculation of ΔH of reactions (1.1) and (1.2)

T (K)	H					ΔH	
	$TiCl_4$(l)	H_2O(l)	H_2O(v)	Ti complex(l)	HCl(g)	Reaction (1.1)	Reaction (1.2)
298	−804.2	−285.8	−241.8	−1740	−92.3	−169	−301
300	−803.4	−285.7	−241.8	−1740	−92.3	−170	−302
400	−789.3	−278.1	−2384	−1737	−89.3	−201	−333

All energy values are given in kJ/mol.

Based on the above, it was judged that a similar interaction could occur during the liquid phase hydrolysis reaction of $TiCl_4$. A theoretical investigation was conducted in order to check the thermodynamic feasibility of different alternatives. The criteria used to determine and evaluate different possibilities were:

- The chemical type of the solid produced will either be $Ti(OH)_nCl_x$ or $TiO_2{\cdot}n HCl{\cdot}x H_2O$.
- The hydrolysis reaction should be spontaneous ($\Delta G < 0$) and exothermic ($\Delta H < 0$).
- If possible, the reaction should be consistent with the experimental finding that one molecule of $TiCl_4$ produces one molecule of HCl gas [30].
- In cases of accidental spills, H_2O will be the limited compound ($TiCl_4$ will be in excess).

A number of different possibilities were identified and evaluated. Detailed presentation of the calculation procedure of all identified scenarios is judged to be beyond the scope of this paper. Finally, the reaction that best fitted the above four criteria is reaction (1):

$$TiCl_4(l) + 3H_2O(l) \rightarrow TiO_2{\cdot}H_2O \cdot 3HCl(s) + HCl(g) + \Delta H \quad (1.1)$$

$$TiCl_4(l) + 3H_2O(v) \rightarrow TiO_2{\cdot}H_2O \cdot 3HCl(s) + HCl(g) + \Delta H \quad (1.2)$$

The calculated heats of reaction are given in Table 7.

It should be noted that the heat of formation of the solid complex was estimated according to [6]. The rest of the properties of the solid complex, necessary for incorporation into REACTPOOL were taken as being equal to the ones of TiO_2.

Conclusion: Based on thermodynamic calculations and a number of crieteria, it is concluded that reaction of liquid $TiCl_4$ with free ground water will occur according to reactions (1.1) and (1.2).

4.5. Previous modelling attempt

The only work on modelling pools of $TiCl_4$ has been published very recently by Roy et al. [5]. The general approach is based on the REACTPOOL procedure and was conducted within the context of a quantitative risk assessment for accidental release of $TiCl_4$ in a titanium sponge plant. Roy et al. describe the liquid phase hydrolysis reaction by the following [5]:

$$TiCl_4 + H_2O \rightarrow TiOCl_2 + 2HCl, \text{ when } TiCl_4 \text{ is in excess} \quad (7)$$

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl_{(aq)}, \text{ when water is in excess} \quad (8)$$

Reaction (7) is identical to reactions (3.1) and (3.2). As shown in Section 4.3 these reactions could not realistically represent the $TiCl_4$ liquid phase hydrolysis reaction. In the single case presented by Roy et al., water was in excess and they have used reaction (8) for their calculations. No further information on reaction (8) is quoted.

Their modelling work was limited to describing a single case of a heat exchanger rupture of a specific $TiCl_4$ plant. It is not a general approach to modelling the behaviour of pools of $TiCl_4$. In cases of accidental spills it is expected that in most cases $TiCl_4$ will be in excess and reaction (7) could not realistically represent these cases.

5. Pool behaviour—modelling approach

When released to the atmosphere, liquid $TiCl_4$ will create a pool that will either boil or evaporate, depending on the amount of water available for reaction and other parameters. The probability of solidification is extremely low (m.p.,$TiCl_4 = 250$ K). As the pool spreads, $TiCl_4$ will continuously react with any free ground water and substrate water according to reaction (1.1). It will also absorb atmospheric moisture reacting with it according to reaction (1.2). A complex solid of "titanium oxychloride" will be produced by the overall hydrolysis process. These solid particles are assumed to settle onto the bottom of the pool, forming a film that alters the conduction of heat from the ground. The pool will contain only one liquid, $TiCl_4$, and its properties will be constant. Apart from HCl gas (directly produced by the reactions), $TiCl_4$ will also evolve due to its relatively high volatility. The overall pool behaviour is depicted in Fig. 1 and is similar to that of other water reactive chemicals [1,35–40].

6. Incorporation into REACTPOOL

REACTPOOL is a model describing the source behaviour of water reactive chemicals. It consists of the core code and a

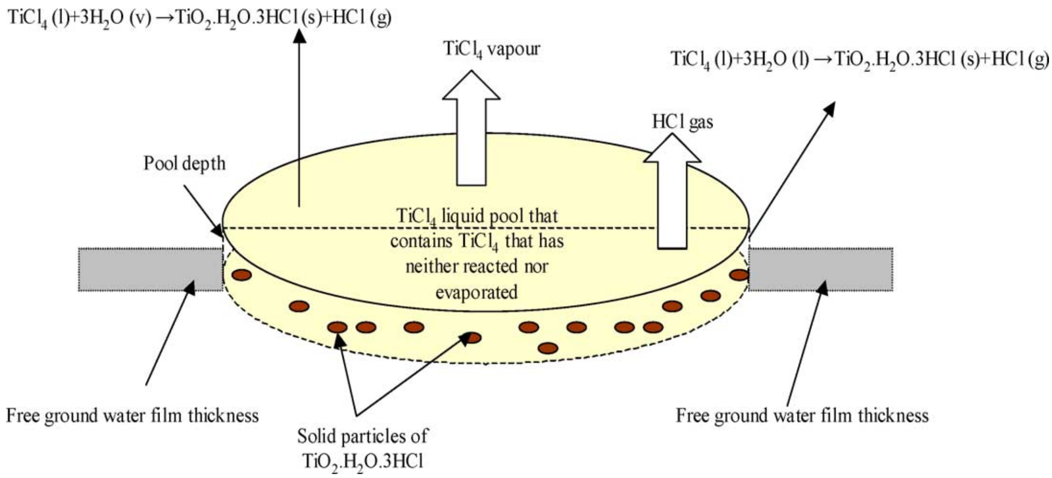

Fig. 1. $TiCl_4$ pool behaviour.

number of modules. The core code consists of mathematical descriptions of pool spreading, mass and energy balances, pool evaporation, boiling and solidification, hydrolysis reaction kinetics and thermodynamics. It is identical for all water reactive chemicals. Detailed description of the REACTPOOL code can be found elsewhere [1,35–40]. A separate module is developed for each water reactive substance incorporated into the model. The following water reactive chemicals are already incorporated into REACTPOOL:

- sulphur trioxide (SO_3);
- oleums of all strengths;
- chlorosulphonic acid (HSO_3Cl or CSA);
- silicon tetrachloride ($SiCl_4$);
- phosphorus trichloride (PCl_3);
- phosphorus oxychloride ($POCl_3$);
- acetyl chloride (CH_3COCl);
- chloroacetyl chloride (CH_2COCl_2);
- titanium tetrachloride ($TiCl_4$).

Other water reactive chemicals could readily be incorporated by developing their properties module. In order to develop the $TiCl_4$ module, all its properties, and the properties of the products on reaction with water have been parameterised as functions of temperature.

7. Model results—input parameters

REACTPOOL was run for a large number of different release scenarios of $TiCl_4$. It was shown that the $TiCl_4$ pool behaviour is mainly affected by the free ground water film thickness, the surface roughness and wind speed. Results of representative release scenarios that show the effects of the above mentioned parameters are described in detail in Sections 8–10, respectively. The values of the input parameters for the release scenarios are shown in Table 8. It should be noted that other parameters, such as the air and release temperatures, the atmospheric humidity and the type

Table 8
Release scenarios input parameters presented in Section 8

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, z_o (m)	0.0001, 0.001, 0.01, 0.1
Wind speed at 10 m, U_{10} (m)	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

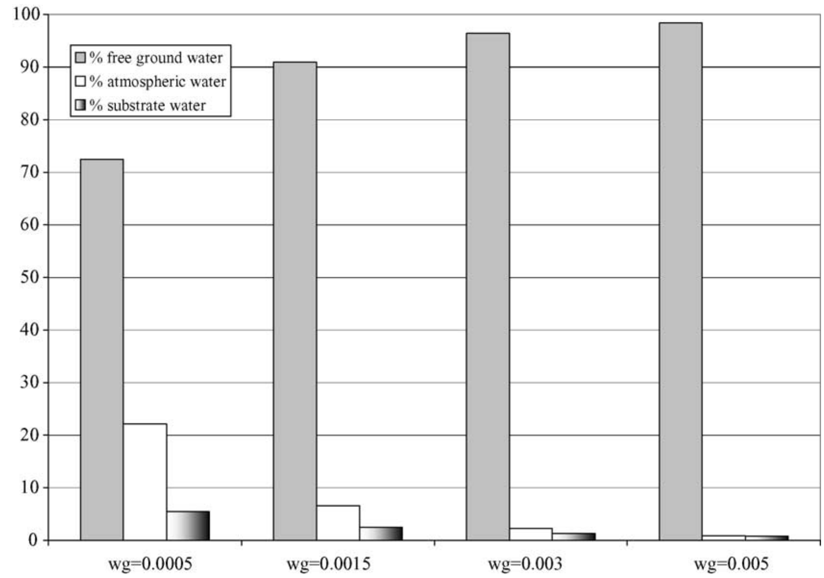

Fig. 2. Effect of w_g on the percentage of contribution of all three water sources to the total amount of water available for reaction.

of substrate also have a relatively strong effect on the pool behaviour.

8. Model results—free ground water film thickness effect

Results for four different release scenarios are presented in order to show the free ground water film thickness effect ($w_g = 0.0005$ m, 0.0015 m, 0.003 m and 0.005 m). In all four scenarios the values of surface roughness length and wind speed are assumed to be the same ($z_o = 0.1$ m and $U_{10} = 5\ \mathrm{m\,s^{-1}}$). The rest of the input parameters are assumed to be equal to the values quoted in Table 8.

Overall the value of free ground water has a very strong effect on the pool behaviour. For the scenarios presented in this section, free ground water is the main source of water (73–90% of the total water amount), as shown in Fig. 2. It should be noted that in the period after spreading has ceased, atmospheric and substrate water are the only sources of water available for reaction. Atmospheric water is more significant than substrate water in the scenarios described in this section (1–22% and 0.5–5%, respectively). The value of pool radius increases with decreasing values of w_g, as shown in Fig. 3. In

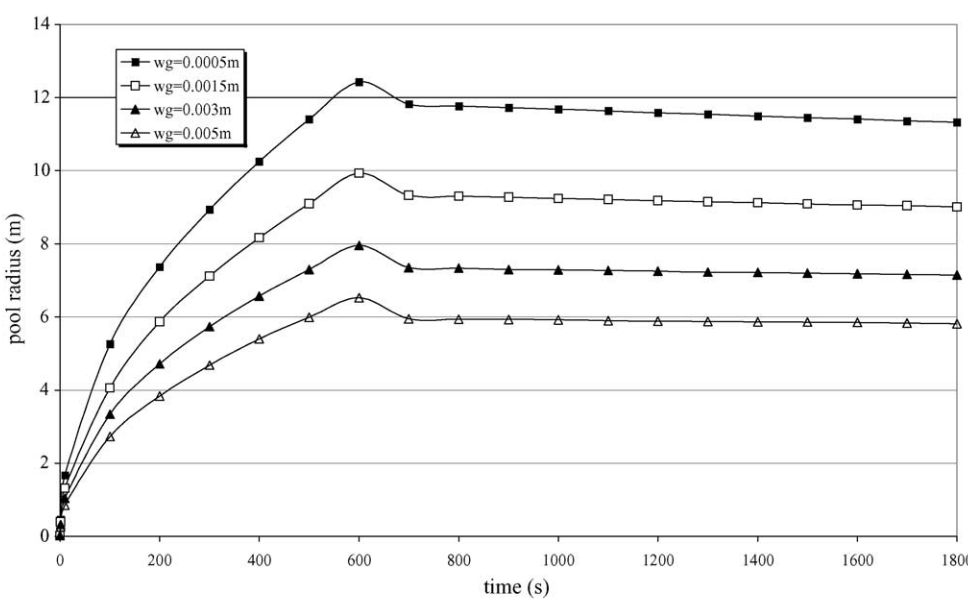

Fig. 3. Effect of w_g on the pool radius profile.

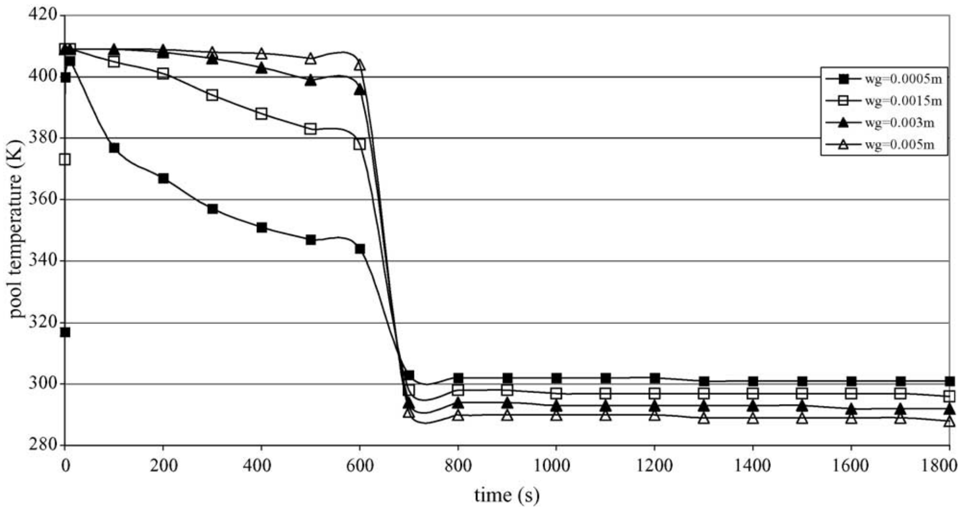

Fig. 4. Effect of w_g on the pool temperature profile.

the spill period, the pool temperature increases with increasing values of w_g, and so does the boiling period, which usually lasts for about 100 s from the start of the spill (Fig. 4). The amount of $TiCl_4$ evolved to the atmosphere increases with increasing w_g (Fig. 5), and so does the amount of HCl gas directly evolved by the hydrolysis reaction (Fig. 6). The amount of oxychloride solids deposited onto the bottom of the pool also increases with increasing values of w_g (Fig. 7).

9. Model results—surface roughness effect

Results for four different release scenarios are presented in order to show the surface roughness length effect (z_o = 0.0001 m, 0.001 m, 0.01 m and 0.1 m). In all these scenarios the values of w_g and wind speed are assumed to be the same (w_g = 0.0015 m and $U_{10} = 5\,m\,s^{-1}$). The rest of the input parameters are set equal to the values quoted in Table 8.

Overall the value of the surface roughness length could have a strong effect on the pool behaviour. Results for the scenarios presented in this section are shown in Table 9. Free ground water is the main source of water (69–90%), followed by the atmospheric moisture (7–29%) and concrete water (about 2%). Pool radius is not highly affected by z_o, although there is a trend that shows that pool radius increases with increasing z_o. In cases that z_o takes values within the range 0.0001–0.01 m, it is shown that the pool temperature, the total average $TiCl_4$ and HCl evolution rates and the total oxychloride solids production rates remain almost unchanged. However, when z_o = 0.1 m, the pool temperature, the total average $TiCl_4$ and HCl evolution rates and the total oxychloride solids production rates decrease. In other words, for z_o within the range 0.01–0.1 m, there is a critical point at which

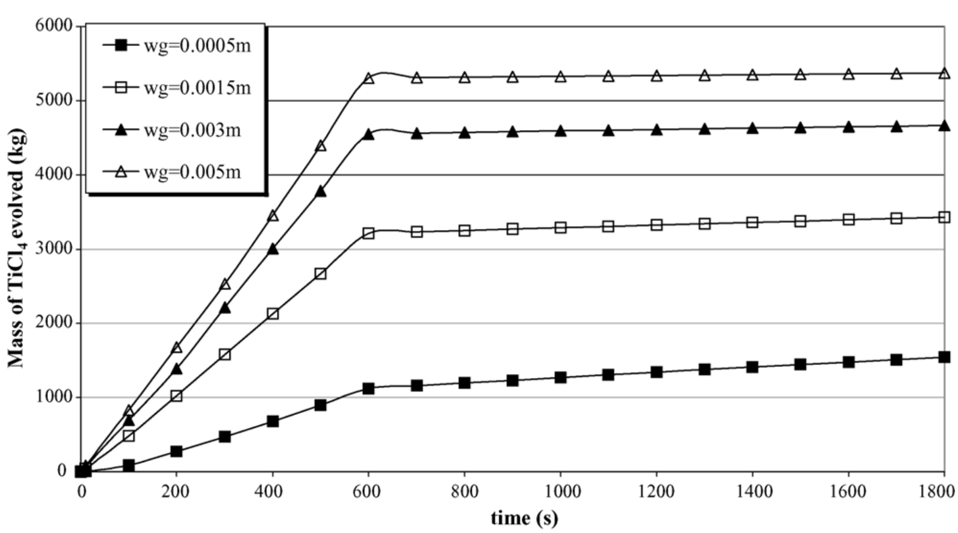

Fig. 5. Effect of w_g on the amount of $TiCl_4$ evolved.

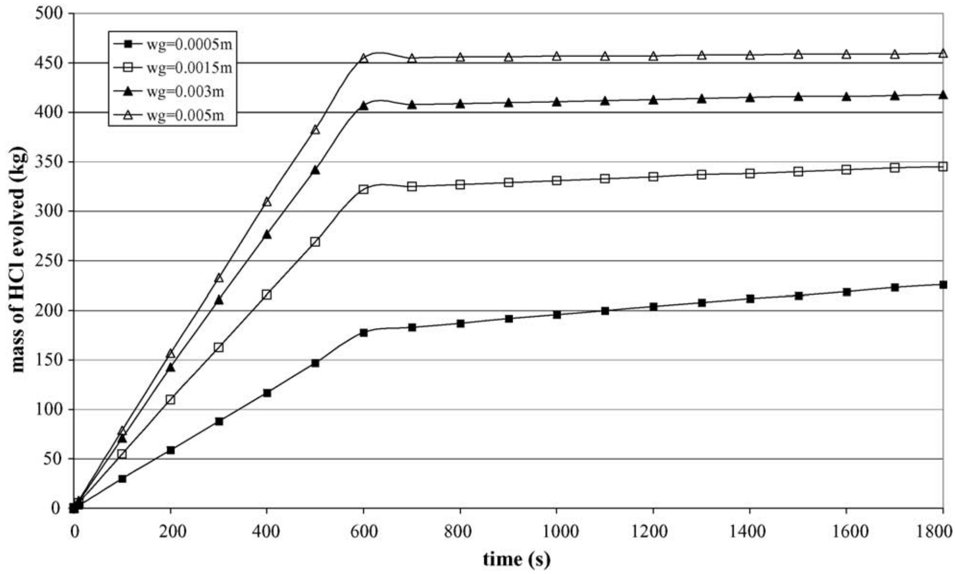

Fig. 6. Effect of w_g on the amount of HCl evolved.

the behaviour of the pool changes. The effect of the surface roughness length (z_o) on the pool behaviour is quite complicated as there are many interrelated phenomena involved. The surface roughness length is the parameter that determines the value of the minimum layer thickness h_{min} and therefore strongly affects the pool radius and the surface area of evolution. One could expect higher values of z_o to be associated with higher values of h_{min} and therefore smaller pool radius and surface areas and lower vapour evolution rates. It should be noted however that there are many interrelated variables involving the surface roughness length; namely the friction velocity u^*, the evaporation flux from the pool surface, and the flux of atmospheric moisture being absorbed by the pool. In the scenarios presented here, there is a regime of values of z_o ranging from 0.0001 m to 0.01 m, where the expected effect of higher values of z_o resulting in lower values of pool radius and vapour evolution rates is being balanced by the effect of z_o on other parameters such as the friction velocity and the amount of atmospheric moisture available for reaction. There is a critical point of z_o within the range 0.01 and 0.1 m where the complicated effect of z_o on the evaporation flux and the atmospheric moisture flux, cannot balance its expected effect on the pool behaviour.

10. Model results—wind speed effect

Results for three different release scenarios are presented in order to show the wind speed effect ($U_{10} = 2\ \mathrm{m\,s^{-1}}$, $5\ \mathrm{m\,s^{-1}}$ and $10\ \mathrm{m\,s^{-1}}$). In all these three scenarios the values of w_g and z_o are assumed to be the same ($w_g = 0.0015$ m and $z_o = 0.1$ m). The rest of the input parameters are set equal to the values

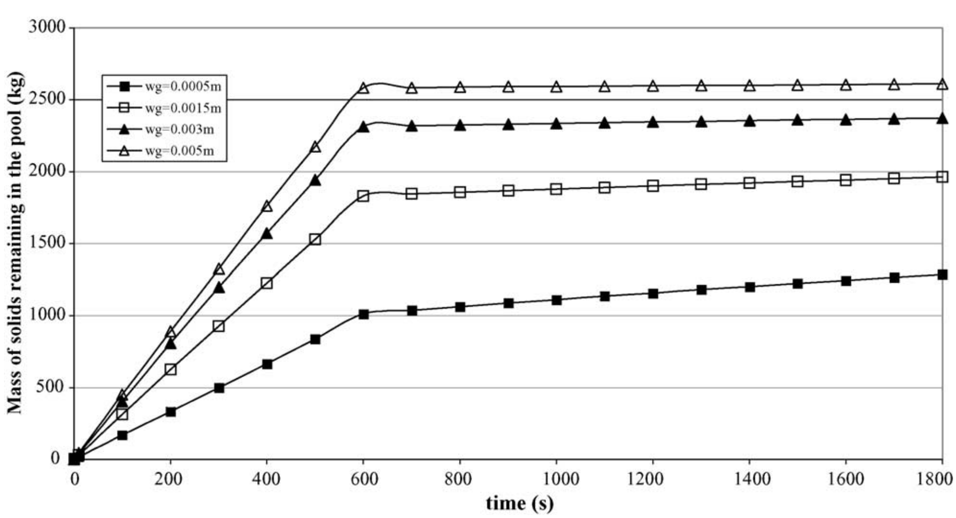

Fig. 7. Effect of w_g on the amount of the oxychloride solid produced.

Table 9
Surface roughness effect

	z_o (m)			
	0.0001	0.001	0.01	0.1
Water budget (%)				
Free ground water	69.5	69.4	69.1	90.9
Atmospheric water	28.5	28.6	28.9	6.6
Concrete water	2	2	2	2.5
Average pool radius (m)	7.95	7.88	8.17	8.12
Average pool temperature (K)	360	361	362	331
Total average $TiCl_4$ evolution rate ($kg\,s^{-1}$)	3.01	3.01	2.98	1.91
Total average HCl evolution rate ($kg\,s^{-1}$)	0.31	0.31	0.30	0.19
Total average oxychloride solid production rate ($kg\,s^{-1}$)	1.77	1.76	1.71	1.09

Table 10
Wind speed effect

	U_{10} ($m\,s^{-1}$)		
	2	5	10
Water budget (%)			
Free ground water	94.5	90.9	86.2
Atmospheric water	2.9	6.6	11.6
Concrete water	2.6	2.5	2.2
Average pool radius (m)	8.34	8.12	7.89
Average pool temperature (K)	331	331	331
Total average $TiCl_4$ evolution rate ($kg\,s^{-1}$)	1.69	1.91	2.14
Total average HCl evolution rate ($kg\,s^{-1}$)	0.19	0.19	0.20
Total average oxychloride solid production rate ($kg\,s^{-1}$)	1.10	1.10	1.10

quoted in Table 8. The former increases with decreasing values of wind speed while the latter increases with increasing values of wind speed.

Overall the value of the wind speed has a relatively strong effect on the pool behaviour. As shown in Table 10, the main pool features affected by the wind speed are the pool radius and the total average $TiCl_4$ evolution rate. The rest of the main pool features remain almost unchanged with changing values of wind speed.

11. Conclusions and discussion

$TiCl_4$ is a highly toxic, water reactive fuming material that can severely harm humans and the environment. When accidentally spilled it creates liquid pools that can either boil or evaporate.

In respect of its toxicity, human and animal studies and past accidents reveal its severity and aggressiveness. Although $TiCl_4$ is used widely in the process industries and has been involved in numerous accidents, very limited data are available on its liquid phase hydrolysis reaction. A systematic approach based on the available data revealed that there are a number of gaps and unrealistic assumptions regarding its reaction with water in the liquid phase. Based on thermodynamic calculations, a possible realistic formula was adopted in order to describe its hydrolysis reaction in cases of accidental spills. $TiCl_4$ pool behaviour was successfully incorporated into REACTPOOL. Model results reveal crucial aspects of the pool behaviour, which is strongly affected by the amount of free ground water. Surface roughness could also have a strong effect on the model results. Other parameters such as the wind speed, release temperature, atmospheric humidity could also have a significant effect. As already stated, there are no detailed reports on $TiCl_4$ accidents available in the literature, in order to incorporate a real case into the new REACTPOOL-module and present its findings. It should be noted that the hydrolysis reaction adopted in REACTPOOL is compatible with the findings of the only relevant experiments found. These experiments however were of very small scale. Further experiments are necessary in order to improve and validate the modelling procedure and results.

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