

WATER REACTIVE MATERIALS — INCORPORATION INTO SAFETY AND ENVIRONMENTAL RISK ASSESSMENTS

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Water reactive chemicals are generally aggressive materials that are used widely in the process industries. Common water reactive substances are sulphur trioxide, oleum, titanium tetrachloride, silicon tetrachloride, chlorosulphonic acid, chloroacetyl chloride and phosphorus trichloride.

When released to the atmosphere, water reactive materials generally react readily with any free ground water, substrate water and atmospheric water. The exact nature, kinetics and thermodynamics of these reactions govern the subsequent consequences of a release.

Consequence modelling and dispersion analysis of water reactive materials is notoriously difficult due to the uncertainties surrounding the reaction with water. Very little experimental data are available on the release behaviour of many water reactive materials. There are often discrepancies and gaps in the data available on the liquid phase hydrolysis reaction; these discrepancies can be as extreme as whether the reaction is exothermic or endothermic.

This paper will use a case study to show how the behaviour of water reactive materials has been incorporated into safety and environmental risk assessments, in particular for the purposes of the predictive aspects of COMAH Safety Reports.

KEYWORDS: COMAH, reactive, consequence, dispersion, predictive, hydrolysis.

THE REQUIREMENT TO MODEL WATER REACTIVE CHEMICALS

The COMAH Regulations 1999¹ require that operators demonstrate that they have identified potential major accident hazards and taken measures to prevent them and limit their consequences.

Schedule 4 Part 2 Para 4b also requires an “assessment of the extent and severity of the consequences of identified major accidents”. There are two reasons why information on extent and severity are required:

- For the purpose of determining the depth of risk analysis and demonstrating that the necessary measures have been taken.
- For the purpose of supplying sufficient information to enable an off-site plan to be drawn up in order to take the necessary measures in the event of a major accident.

In simple terms, the ‘extent and severity’ information is essentially who might get hurt, how badly and how many might it be? To do this, the hazard assessment of

the identified major accidents must be carried out and then a prediction of the consequences made.

The approach in the Competent Authority guidance on environmental risk assessment² mirrors the approach applied to accidents that affect human safety. However the guidance acknowledges that the depth of an environmental risk assessment may not be as great as that for a safety risk assessment, mainly because of a paucity of data available to establish whether major accidents to the environment (MATTEs) are likely, but also because there is a lack of suitable models to assess release behaviour of some substances.

COMAH environmental risk assessments require, in particular:

- Clearly defined criteria for a MATTE.
- Identification of potential MATTEs and an indication of the acceptability.
- Use of the EA guidance on risk assessment.
- Consideration of all major liquid releases and aerial releases into the environment and their effect on the environment. In particular:
 - The focus is to be on bulk tanks, pipelines and bunds.
 - A description of the consequences of a release.
 - Estimation of area affected.
 - The species, habitat or inorganic environment affected are to be identified.
 - Short term/Long Term harm is to be considered.

The COMAH Regulations apply to sites where the amount of dangerous substances held on the site exceeds the threshold quantity. Water reactive materials are listed under Schedule 1 Part 3 as those materials with risk phrases R14: “Reacts violently with water” (including R14/15) or R29: “in contact with water, liberates toxic gas”.

Therefore sites storing or processing water reactive materials at a quantity above the COMAH threshold are required to carry out the assessments as described above, including consequence assessment of these water reactive materials.

WATER REACTIVE MATERIALS — RELEASE BEHAVIOUR

On escape to the atmosphere, water reactive materials usually create liquid pools that will either boil or evaporate or even solidify³.

The spreading liquid will react with any water available. There are three sources of water available for reaction: free ground water encountered, atmospheric moisture absorbed by the liquid and water extracted from the substrate. Free ground water is usually the dominant source (70–98%) and its contribution increases with increasing ground water film thickness. Atmospheric water is usually the second most important water source (2–30%) and its contribution increases with decreasing amount of free ground water. Substrate water is usually the least significant source and its contribution increases with decreasing free ground water film thickness.

The generated pool will usually have changing properties and composition. Depending on the hydrolysis reaction, the pool may be a mixture of two or even more liquids. Solid products may also be formed by the reaction (e.g. SiCl₄ spills) and could either

solute into the liquid or settle onto the bottom of the pool forming a film⁴. Reaction with water occurs continuously.

Overall, the pool behaviour is complicated and strongly affected by the liquid phase hydrolysis reaction.

The hazardous nature of water reactive materials is mainly associated with the generated toxic cloud. This toxic cloud is mainly composed of the toxic acid gas (e.g. H₂SO₄, HCl, HF) that is generated by the hydrolysis reaction and the water reactive chemical vapour being evolved by the pool^{4-6,8}. The toxic cloud could initially be denser than air, containing two or even more species. The water reactive chemical reacts with any atmospheric moisture in the vapour phase, yielding gas(es) and possibly other products (e.g. aerosols). Usually after some distance downwind, allowing adequate dilution with air, will the cloud becomes passive. Generally the cloud behaviour is complicated and strongly affected by the vapour phase hydrolysis reaction.

MODELLING THE RELEASE BEHAVIOUR OF WATER REACTIVE MATERIALS

Until recently, the release behaviour of water reactive materials was modelled in a rather simplistic way. Reaction with water either in the liquid, in the vapour, or even in both phases was ignored. In other words water reactive substances were modelled as being non-reactive. Furthermore, phenomena like boiling, solidification, properties and composition change were ignored in the liquid phase. In the vapour phase it was often assumed that the cloud will be passive and will merely contain the toxic gas generated by the vapour phase hydrolysis reaction from its onset. In other words, it was assumed that there is enough atmospheric moisture above the pool for complete and instantaneous reaction of the vapour evolved.

It has been shown that ignoring the phenomena associated with the liquid and vapour phase reactions with water could lead to serious errors⁶. Therefore a new approach to modelling such materials was developed.

REACTPOOL is a model that describes the pool behaviour of water reactive materials. It was initially developed at the Environmental Technology Centre of the Chemical Engineering Department at UMIST, Manchester. Its initial scope was to describe the pool behaviour of sulphur trioxide and oleum releases. Apart from the pool model, a cloud dispersion model was also developed for sulphur trioxide and oleum releases⁶. The project was sponsored by the Health and Safety Executive (HSE).

This model has been further developed in an inclusive form in order to include other water reactive materials. Chemicals already incorporated into the model are:

- Sulphur trioxide
- Oleum of all strengths
- Chlorosulphonic acid
- Silicon tetrachloride
- Phosphorus trichloride

- Phosphorus oxychloride
- Acetyl chloride
- Chloroacetyl chloride
- Titanium tetrachloride

A detailed description of the modelling procedure followed in REACTPOOL can be found elsewhere³⁻¹⁰.

The model consists of the core code, which is identical for all water reactive chemicals and a number of different modules for each water reactive substance that contain mathematical descriptions of all necessary properties. It should be noted that new chemicals are continuously added. The unique feature of REACTPOOL is that it mathematically describes and calculates all pool features mentioned earlier. The model has been used in a number of different applications regarding hazard analysis of water reactive chemicals and is widely published in various pieces of literature. Running the model for a number of different substances and scenarios has shown that the pool behaviour of these chemicals is mainly affected by the amount of water available for reaction. Parameters such as the wind speed and surface roughness also impose a relatively strong effect on the model results.

CASE STUDY — CONSEQUENCE ASSESSMENT FOR TITANIUM TETRACHLORIDE (TiCl₄)

Huntsman Tioxide's Greatham site is a Top Tier COMAH site by virtue of the dangerous substances stored and processed. Huntsman Tioxide were therefore required by the Competent Authority to produce a COMAH Safety Report as described earlier.

The ICON plants at the Greatham site process titanium ore, coke, chlorine and oxygen to produce titanium dioxide slurry, which is then processed further to produce the finished pigment product. Titanium tetrachloride is produced as an intermediate in this process. A titanium tetrachloride tank farm exists to provide buffer storage for the ICON plants and also to store a proportion of the titanium tetrachloride for export from the site via a tanker loading facility.

TiCl₄ is used widely in the process industries and has been involved in a number of accidents. A survey of accidents that involved releases of water reactive chemicals that occurred in the US within January 1990 and November 1999, revealed that there have been 473 reported incidents involving spillages of TiCl₄, out of which 13 involved evacuation, injuries or death³.

The Chemical Hazards (Hazard Information and Packaging for Supply) Regulations 2002 (CHIP 3) provide details of the properties of titanium tetrachloride. These are summarised in Table 1.

It can be seen that titanium tetrachloride is described by the risk phrase R14 "Reacts violently with water".

Titanium tetrachloride is a highly aggressive material, it hydrolyses rapidly in air to form a dense white cloud containing titanium dioxide (TiO₂), oxychloride/hydroxide particulates and hydrogen chloride (HCl), gas. The particulates do not segregate from the

Table 1. Classification of titanium tetrachloride

Material	CAS No.	CHIP 3 Risk Phrases	CHIP 3 Category — Description
Titanium tetrachloride	7550-45-0	R14 C: R34	Reacts violently with water Causes burns

gases and form a dense white cloud. The cloud mixture is highly irritating and corrosive to the mucous membranes (including the upper respiratory tract), the skin and the eyes.

Titanium tetrachloride is enlisted as a “highly toxic” chemical in various pieces of international legislation on major hazards^{11,12}. The severity of some TiCl₄ accidents, certain animal tests and human toxicology studies also reveal its highly hazardous nature^{3,13}.

Extensive research of published toxicology studies has been carried out, these studies suggest that titanium tetrachloride vapours are more ‘toxic’ than pure HCl. The increased toxicity is largely because HCl alone is very soluble and will dissolve in the upper respiratory tract and may not fully penetrate the lungs. However HCl, in association with titanium oxychloride particles, is likely to be less soluble and thus penetrate deeper into the lungs, causing increased damage.

PREVIOUS MODELLING OF TITANIUM TETRACHLORIDE

The behaviour of liquid titanium tetrachloride releases has previously been modelled by Huntsman Tioxide using the Chemical Manufacturers Association (CMA) titanium tetrachloride dispersion modelling tool.

The CMA pool evaporation model¹⁵ predicts the evaporation of liquid titanium tetrachloride from either a standing pool or a leak from tanks and pipework. The evaporated titanium tetrachloride vapour then reacts with atmospheric moisture producing HCl gas as it disperses downwind. As the CMA plume model accounts for the vapour reactions it is therefore appropriate for modelling vapour releases. However, when modelling liquid releases there are a number of disadvantages with this approach:

- The CMA pool model does not take into account HCl gas evolved from the hydrolysis reaction with groundwater or substrate water. Hence, the amount of free HCl evolved from the surface of the pool and available for dispersion will be underestimated.
- For liquid releases of titanium tetrachloride, the evaporation rate predicted by the CMA pool model will be underestimated as the model ignores the exothermic reaction that takes place when titanium tetrachloride reacts with available groundwater and substrate water. The heat generated by the exothermic reaction could cause the pool to boil and hence increase the amount of titanium tetrachloride vapour evolved.

In conclusion, by ignoring the liquid phase hydrolysis reaction, the CMA pool model underestimates the amount of both titanium tetrachloride vapour and hydrogen chloride available for dispersion. This in turn could lead to both an underestimate of the severity of a release and a high degree of uncertainty in the predicted results.

The only attempt on modelling its pool behaviour has been published recently and was based on the REACTPOOL modelling procedure¹⁴. However, it is a simple description of the pool generated by the rupture of a heat exchanger of a specific titanium sponge production plant.

INCORPORATION OF TITANIUM TETRACHLORIDE INTO REACTPOOL

TiCl₄ physical and thermodynamic properties are generally well defined in the literature. However, there are a number of discrepancies and gaps on its liquid phase hydrolysis reaction. It has been found that the literature contains only some “short statements” regarding this reaction. There is no published study that specifically examines the reaction of liquid TiCl₄ with liquid water and/or atmospheric moisture under any conditions. There are a number of different “simple statements” that describe these reactions.

The following were found in different pieces of literature:

- a. TiCl₄ is soluble in cold water and decomposes in hot water¹⁶.
- b. TiCl₄ reacts exothermically with water forming TiO₂ and HCl gas^{17–20}.
- c. Under TiCl₄ excess conditions, TiCl₄ readily hydrolyses forming titanium oxychloride and HCl gas⁸.
- d. TiCl₄ reacts exothermically with water forming complex solid particles and hydrogen chloride gas¹⁵.

All references agree at certain points: the liquid phase hydrolysis reaction of TiCl₄ is highly exothermic, violent and occurs almost instantaneously.

The only experimental work found on the topic, was published in 2000 by the Office of Hazardous Materials Safety, which is within the United States Department of Transportation’s Research and Special Programs Administration¹⁶. 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 TiCl₄) have been conducted. Two methods have been 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 fivefold molar excess. In both methods the amount of the evolved gas was measured.

Hydrolysis reaction of TiCl₄ is described according to statement b. 0,19 g (1 mmol) of TiCl₄ 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.

Table 2. Experimental results

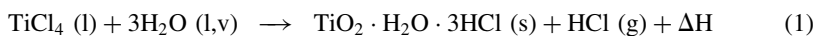
Time (min)	Mass of HCl (g) evolved	
	Method A	Method B
1	0.023	0.023
5	0.039	0.0114
10	0.039	0.091
20	0.039	0.091

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

- The theoretical yield of the reaction was measured to be equal to 27%. This result was based on the stoichiometry of reaction 2.1, “one molecule of TiCl_4 produces 4 molecules of HCl gas”. In other words, it was noted that “one molecule of TiCl_4 produces about 1 molecule of HCl gas”.
- The reaction of liquid TiCl_4 with water produces solid particles of a titanium compound.

Based on thermodynamic calculations, estimation methods and any other relevant information, it was shown that a number of these statements could not realistically represent the liquid phase hydrolysis reaction of TiCl_4 .

Based on the conducted investigation, on the only piece of relevant experimental information and on certain indications found in the literature, the liquid phase hydrolysis reaction is described according to the following:



According to the above reaction, liquid TiCl_4 will react with ground water and atmospheric moisture producing a solid complex of “titanium oxychloride” and hydrogen chloride gas. It is concluded that the above reaction is a realistic representation under TiCl_4 excess conditions, expected to be encountered in cases of accidental spills. Furthermore, it is compatible with the findings and conclusions observed in the only experimental work found on the topic. It should be noted that the conducted investigation has shown that the reaction of TiCl_4 with water depends on the amount of water available for reaction. It is believed that under water excess conditions, the solid complex will further hydrolyse, possibly yielding titanium dioxide and HCl.

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 possibility of solidification is extremely low (m.p. $\text{TiCl}_4 = 250 \text{ K}$). As the pool spreads, TiCl_4 will continuously react with any free ground water according

to reaction 1. It will also absorb atmospheric moisture. 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. 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 Figure 1.

The hydrolysis reaction and properties of all substances involved have been parameterized for incorporation into REACTPOOL.

The REACTPOOL — TiCl_4 model was run for a number of different spill scenarios. Model results indicated the following:

- The pool behaviour is governed by the amount of water available for reaction. Pool temperature, TiCl_4 vapour evolution rate, HCl gas and solid particles generation rate generally increase with increasing amount of water available for reaction. Pool radius decreases with increasing amount of water available for reaction.
- Free ground water is the main source of water, followed by the atmospheric moisture.
- Wind speed is also an important parameter affecting the pool behaviour. TiCl_4 vapour evolution rate increases with increasing values of wind speed. The solid particles generation rate increases with decreasing values of wind speed.
- The pool usually boils during the first spill stages, even under average values of the amount of free ground water. The boiling period increases with increasing values of the amount of free ground water and decreasing values of wind speed.
- There is almost no possibility of solidification.

Overall, the pool behaviour of TiCl_4 is similar to other water reactive chemicals^{4,7–9}. It should be noted that further experimental work would be necessary to define the exact kinetics and thermodynamics of the TiCl_4 liquid phase hydrolysis reaction under different conditions.

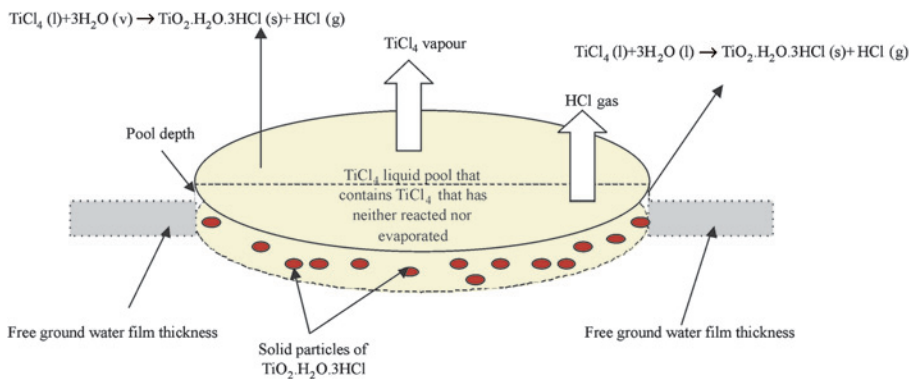


Figure 1. TiCl_4 pool behaviour

CONSEQUENCE ASSESSMENT FOR TITANIUM TETRACHLORIDE

There are three distinct elements to modelling a release of titanium tetrachloride; firstly the discharge, then the reaction with water and finally the subsequent dispersion of the products of the water reaction.

The initial discharge of titanium tetrachloride releases was modelled using DNV's PHAST 6.21. PHAST considers the physical and chemical properties of the hazardous substances stored and processed and their responses when released at defined operating temperatures and pressures. Given the process conditions, the type of failure and the physical properties of titanium tetrachloride, PHAST calculates the release rate, release duration and pool size (for liquid releases only) for each event.

REACTPOOL was used to predict the generation of the products of the reaction with water (hydrogen chloride vapour, titanium tetrachloride vapour and other species).

To model the dispersion of the materials generated from the reaction with water, the titanium tetrachloride dispersion modelling system developed by the Chemical Manufacturers Association (CMA) was used.

The modelling approach used at each stage of this predictive assessment is summarized in Table 3.

The CMA Jet Plume (JP) model was used to calculate the downwind dispersion of the titanium tetrachloride and hydrogen chloride mixture, reacting the titanium tetrachloride with atmospheric water as the plume disperses downwind. The output from the CMA JP model gives the distance and cloud footprint to specified concentrations of interest for titanium tetrachloride vapour and hydrogen chloride gas.

The use of CMA JP model was considered to be more appropriate for the modelling the vapour phase reaction of titanium tetrachloride with atmospheric moisture because it gives more pessimistic results. For this reason it was used to model both titanium tetrachloride vapour release scenarios and the vapour released from the surface of a pool (following use of the REACTPOOL model).

Using the above methodology allowed the consequences of a release of titanium tetrachloride to be assessed and the severity of such releases estimated in terms of the number of fatalities, major and minor injuries. This information was then used with the frequency of the releases within the COMAH predictive assessment to calculate the individual and societal risk for the installation.

ENVIRONMENTAL ASSESSMENT FOR TITANIUM TETRACHLORIDE

A similar approach was taken to the environmental risk assessment.

Table 3. Summary of models used

	Discharge	Pool reaction	Dispersion
Titanium tetrachloride liquid	PHAST	REACTPOOL	CMA Jet Plume
Titanium tetrachloride vapour	PHAST	N/A	CMA Jet Plume

The objective of the environmental risk assessment for the Greatham site was to determine the potential for major accidents to the environment (MATTEs) at a number of the sensitive receptors close to the site.

The environmental impact was assessed using a combination of PHAST, REACTPOOL and ADMS modelling. The source term was calculated using PHAST, the generation of products of the reaction with water was estimated using REACTPOOL. For the purposes of this environmental risk assessment, the reaction with atmospheric water is assumed to occur instantaneously, with each molecule of titanium tetrachloride vapour forming 3.2 molecules of HCl. The HCl formed in the vapour reaction is in addition to the HCl released directly from the surface of the pool as a result of the liquid reaction.

Finally, the ground level concentrations of hydrogen chloride were predicted using the proprietary dispersion model, ADMS (Atmospheric Dispersion Modelling System), version 3.1.7. ADMS models a wide range of buoyant and passive releases to atmosphere either individually or in combination. The rate of wet deposition was also modelled using the ADMS deposition module to assess the potential impact of hydrogen chloride washed out in rainfall. In this assessment it was assumed that titanium tetrachloride is fully reacted to HCl by the time it is deposited.

The impact of the ground level concentrations of HCl on the environment and the effect of the wet deposition was then assessed and this information was used with the frequency of the releases within the COMAH Environmental Risk Assessment to understand the potential for MATTEs from the installation.

REACTPOOL MODEL LIMITATIONS

The procedure of incorporating a number of different water reactive substances into REACTPOOL could be quite difficult. Water reactive substances are used widely in the process industries and have been involved in numerous accidents as revealed in a survey conducted for accidents that took place in the USA during the previous decade³.

It should be noted that most data found on water reactive chemicals are mainly theoretical. Unfortunately, there is almost no experimental data on their release behaviour.

The REACTPOOL model averages the evolution of titanium tetrachloride and hydrogen chloride vapour over a 1 hour period regardless of the rate of spillage of liquid titanium tetrachloride. In reality, the generation of vapour from the pool would be a dynamic process, with maximum vapour generation occurring at the beginning as the pool initially spreads rapidly over the ground reacting with standing and substrate water.

Although the rate at which titanium oxychloride particles are formed within the pool is modelled by REACTPOOL, no estimate has been made for the amount of solid oxychloride particles transferred from the reacting pool into the evolved vapour plume.

The exact temperature of the vaporised titanium tetrachloride and hydrogen chloride generated from the REACTPOOL model is uncertain. The vapour temperature of the release will influence the initial buoyancy of the plume. This will cause variation in the ground level concentrations experienced close to the source. Over longer distances (beyond 100 m), temperature has less influence on ground level concentrations.

CONCLUSIONS

REACTPOOL is considered to have a number of advantages over the CMA pool evaporation model, as the behaviour of liquid releases of titanium tetrachloride can be quantified. REACTPOOL has established:

- The nature of the hydrolysis reaction of liquid titanium tetrachloride with free ground water, substrate water and atmospheric water.
- The thermal behaviour of the liquid pool including whether the pool is predicted to boil. The heat available has then been used to determine the enhanced titanium tetrachloride evolution rate from the liquid pool.
- The behaviour of the pool radius with time.
- The mass evolution rate of titanium tetrachloride vapour.
- The mass evolution rate of hydrogen chloride gas from the hydrolysis reaction.

The assumptions that the REACTPOOL model makes include:

- During the initial spill there may be a time where the reaction rate is high and hence the evolution of titanium tetrachloride and hydrogen chloride is high. Titanium tetrachloride and hydrogen chloride evolution rates have been ‘averaged’ over the reaction period that is taken to be a maximum of 1 hour.

There is no estimate made for the amount of particulates entrained in the evolved titanium tetrachloride and hydrogen chloride plume although some entrainment is expected.

Despite these assumptions the REACTPOOL model is believed to more closely resemble the spill behaviour and liquid hydrolysis of titanium tetrachloride, than the CMA pool evaporation model and the results have been successfully incorporated into a number of predictive assessments for COMAH Safety Reports.

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