

## Chemical Incident Investigation, Millennium Inorganic Chemicals (MIC), Stallingborough UK, 2010

Stephen Graham<sup>1</sup>, Jonathan Buston<sup>1</sup>, Brian Fotheringham<sup>2</sup> and Stephen Hargreaves<sup>2</sup>

<sup>1</sup>Health and Safety Executive, Harpur Hill, Buxton SK17 9JN

<sup>2</sup>Health and Safety Executive, Redgrave Court, Merton Road, Bootle L20 7HS

On 5th March 2010, reaction vessel D650 at the Millennium Inorganic Chemical works at Stallingborough suffered a catastrophic failure, releasing its contents both over the ground below and an operator present there. A large dense white cloud of corrosive and toxic gas was created.

The process being run on site was designed to manufacture titanium tetrachloride, used in the manufacture of high purity titanium dioxide, a major component of paints and pigments.

Key to explaining the incident was understanding the possible causes of the catastrophic rupture of vessel D650, which suffered a rapid temperature and pressure increase prior to failure. Although it was deemed inevitable that this was caused by the reaction between a significant amount of titanium tetrachloride and water, two scenarios were proposed:

1. An extremely large slug of liquid titanium tetrachloride entered vessel D650, reacting instantaneously.  
or
2. A far greater than normal accumulation of unreacted constituents (including titanium tetrachloride) occurred over time, which was then allowed/induced to react at a later point in time.

The catastrophic rupture of vessel D650 occurred immediately after the changeover of a recirculation pump to a reserve pump. Given the timing of the incident relative to this changeover, it seems likely that a substantial amount of titanium tetrachloride was already present within vessel D650 but separated in such a manner as to have avoided reaction. The starting of the reserve pump restarted effective mixing/contact between the accumulated titanium tetrachloride and aqueous hydrochloric acid solution, resulting in the violent reaction observed.

### Incident Summary

On 5th March 2010, vessel D650 at the Millennium Inorganic Chemical (MIC) works at Stallingborough suffered a catastrophic failure, releasing its contents both over the ground below and an operator present there. A large dense white cloud of corrosive and toxic gas was created. The process being run on site was designed to manufacture titanium tetrachloride (TiCl<sub>4</sub>), used in the manufacture of high purity titanium dioxide (TiO<sub>2</sub>), a major component of paints and pigments.

TiCl<sub>4</sub> is a liquid, boiling at 135°C, which reacts vigorously with water. The products of this reaction include (depending on the conditions of the reaction) a range of titanium oxychloride species, (formed as a particulate smoke), hydrogen chloride gas and TiO<sub>2</sub>. TiCl<sub>4</sub> is itself a toxic substance named under the COMAH regulations. Hydrogen chloride is also a toxic gas, with workplace exposure limited in the UK to 5 ppm (over a 15 min. period). It has an "IDLH" (Immediately Dangerous to Life and Health) limit of 50 ppm. The titanium oxychloride species that are present are also known to be toxic. Although no specific toxicity data is available for these compounds, it is likely that particulate oxychloride species present a greater degree of hazard than just hydrogen chloride, due to the ability of the fine particles to penetrate deeper into the respiratory tract before hydrolysis is complete.

The part of the process where this incident took place, Unit 600, has the role of removing trace titanium tetrachloride from the waste gas stream before the gas stream is emitted to the atmosphere.

In normal operation, the TiCl<sub>4</sub> produced by the manufacturing process (within a chlorinator where chlorine gas is combined with titanium ore and coke at >1000°C) is initially a gas at high temperature and is cooled and condensed to a liquid by passing through a series of condensers. Any remaining gas then passes into a series of vessels in Unit 600. Vessel D650 is the first vessel in that part of the plant. The primary purpose is to remove the reactive components within the gas flow (predominantly TiCl<sub>4</sub>), allowing hydrogen chloride gas to pass onto the downstream vessels D651 and D652 for harvesting. The removal of the TiCl<sub>4</sub> is achieved by contact with water by both a Venturi mixer on the inlet and two spray heads through which the liquid content of the vessel is recirculated. The recirculation is powered by one of two pumps (G650A or G650B). As TiCl<sub>4</sub> is consumed HCl is formed by the reaction and the contents of the vessel become more dense and viscous, and need to be thinned by the gradual removal of the liquors and addition of fresh water.

The plant was being prepared for production just prior to the incident and was in 'start up' on the evening of 4th March 2010. No new TiCl<sub>4</sub> was actually being produced. However, despite this, the design of the plant meant that TiCl<sub>4</sub> vapour would still have been present as part of the gas flow into the vessel where the catastrophic rupture occurred. The chlorinator had been warmed up on the evening of 3rd March, but cooling water had been lost on the plant and some condensers were no longer working. This meant that the gas stream was hotter than normal. Change orders were produced to allow this warm up to take place with hotter than normal gas streams.

In the days and hours leading up to the incident, plant operators had observed a number of problems with vessel D650:

- A blockage of a sampling line
- Pressure ‘bouncing’
- A higher temperature within vessel D650 than normal with temperature spikes of up to 50°C
- A ‘thicker’ (less runny) mixture

The higher temperatures and thicker contents at this time should have been an indication to the operators of higher than usual levels of liquid  $\text{TiCl}_4$  entering the vessel due to less efficient removal by condensation caused by the loss of cooling water and condensers. Prior to the incident, Pump G650A, recirculating the scrubbing liquid in vessel D650 had been stopped for at least 32 min. to allow a sampling port to be cleaned. G650A had been switched back on, but since there was no direct indication or measurement of whether G650A was functioning (rather than merely turned on), no one could be certain that the sprays were working and the contents were recirculating.

Immediately prior to the incident, fumes were observed coming from G650A. An operator went to investigate. G650A was stopped to allow swap over to pump G650B (On standby duty).

Immediately after G650B started operation, the vessel suffered a catastrophic failure, causing the manway (24” diameter) at the bottom of the vessel to break off and be propelled away. Vessel D650 also suffered severe damage at the top, when it was forced, by the force of the internal reaction, upwards into the supporting steel superstructure surrounding the vessel. The contents of the vessel were released, and the liquid components drained down onto the area where the pumps were situated. The operator was subsequently rescued from this area which was described as being covered in a thick black bubbling covering, 12-18” deep with the consistency of “porridge”. The operator and areas surrounding the ruptured vessel structure were engulfed in a large, dense white fume cloud of HCl causing severe distress to those in it. Fumes continued to be emitted for some time as the contents reacted with water in the atmosphere, on the ground and the superstructure.

## Chemical Investigation

The nature of the incident which caused catastrophic failure of vessel D650 appeared to be consistent with rapid or instantaneous reaction of a substantial quantity of  $\text{TiCl}_4$  with water (whether as water, or as part of aqueous hydrochloric acid solution). Accordingly, several lines of experimental investigation were pursued to determine the likely cause of the failure and to determine credible scenarios that may have led to the incident occurring.

## Foam formations

It had previously been observed [Buston, 2011; Cruse, 2011] that if  $\text{TiCl}_4$  reacts with water, when there is more  $\text{TiCl}_4$  present than water, a yellow foam/crust is generally formed. Experiments were performed to investigate whether similar semi-solid foam or crust formation was observed when adding  $\text{TiCl}_4$  to aqueous hydrochloric acid. Experiments were performed from test tube (*ca.* 1 cm diameter) up to 1 litre reactor scale.  $\text{TiCl}_4$  addition was carried out either as a continuous trickle, or as a larger single portion or portions (‘slugs’). In all the experiments performed, a crust/sponge like foam was formed by addition of  $\text{TiCl}_4$  to the aqueous hydrochloric acid. In most, but not all, experiments this was a contiguous layer over the whole surface of the reaction vessel, allowing the subsequent build-up/accumulation of a layer of liquid  $\text{TiCl}_4$  above this crust (Figure 1).

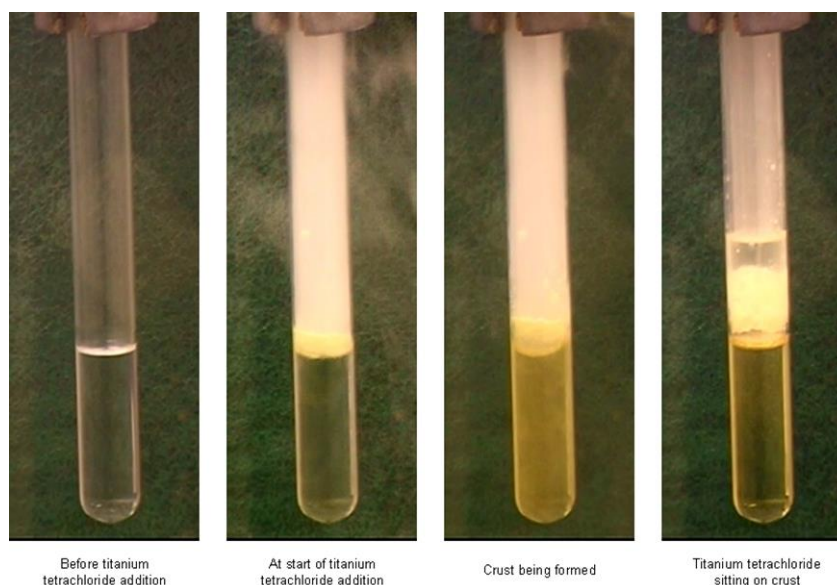


Figure 1. Representative example showing formation of crust when adding  $\text{TiCl}_4$  to aqueous hydrochloric acid

Subsequent addition of water to the reaction mixture containing the described foam/crust led to an extremely violent reaction, characterised by very rapid temperature rises and the evolution of large quantities of smoke/gas (Figure 2).

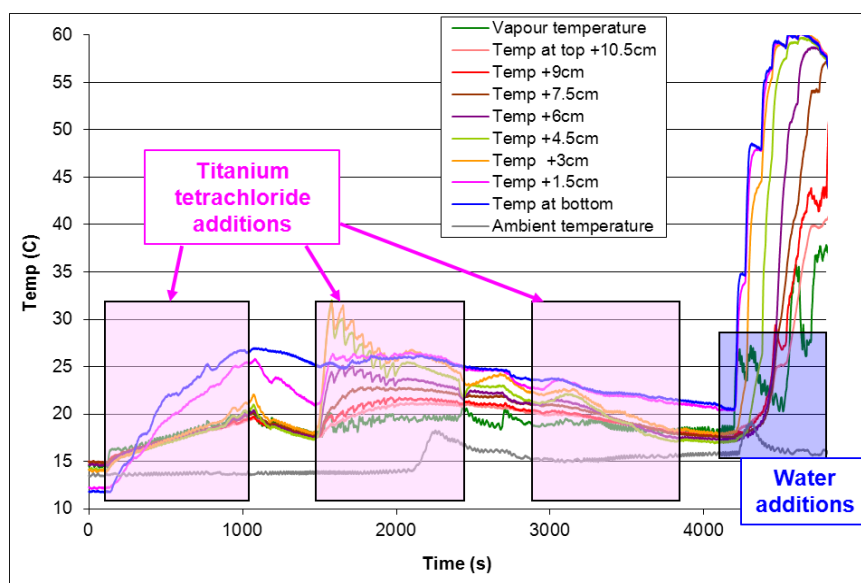


Figure 2. Representative example showing temperature changes when adding  $\text{TiCl}_4$  to aqueous hydrochloric acid and subsequent addition of water

In experiments where portions of  $\text{TiCl}_4$  were added rapidly onto an aqueous phase of hydrochloric acid previously treated with  $\text{TiCl}_4$ , substantial foams were formed. Subsequent addition of water through a spray nozzle onto these foams once again resulted in vigorous reactions, with substantial and rapid temperature rises being observed. An example of the foam formation is shown (Figure 3).

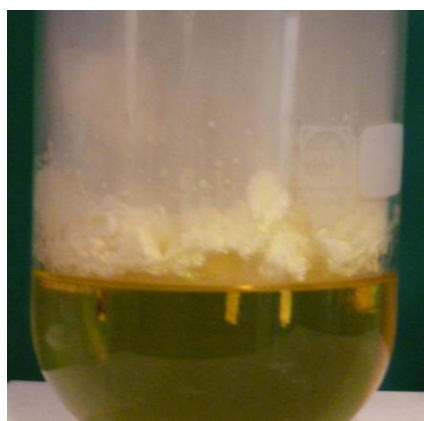


Figure 3. Foam formation in 1 litre vessel –  $\text{TiCl}_4$  added in portions to aqueous hydrochloric acid previously treated with  $\text{TiCl}_4$

### Implications of foam formation

Given that, under normal conditions, a controlled reaction between water/aqueous hydrochloric acid and  $\text{TiCl}_4$  was regularly taking place within D650, and that  $\text{TiCl}_4$ , aqueous hydrochloric acid and the products from the reaction between them are the only constituents that could reasonably be expected to be present within the vessel D650, two likely scenarios that could produce the massive forces that would lead to a catastrophic rupture of the vessel were proposed:

- In the first scenario, an extremely large slug of liquid titanium tetrachloride found its way into vessel D650, overwhelmed whatever scrubbing capacity that may have been operating at the time, and reacted instantaneously.
- In the second scenario, a far greater than normal accumulation of these unreacted constituents ( $\text{TiCl}_4$ ) occurred over time, which was then allowed/induced to react at a later point in time.

In considering the first scenario, a slug of  $\text{TiCl}_4$  that would rupture vessel D650 would most likely need to be larger than any of those which it had already survived, *if* the vessel was operating in a consistent fashion throughout. Furthermore, it did not appear that any specific operation or action was taken on the plant that would have induced the slug of  $\text{TiCl}_4$  to pass into vessel D650 and react at the time that it did. It would therefore have been an unfortunate and unlikely coincidence that the operator was tending to a fuming pump under the vessel D650 at the exact time that it ruptured.

In the second scenario, an accumulation of unreacted 'reactive titanium species' has occurred. In order for this build up to take place two factors are necessary:

- No or little circulation of the contents
- Separation of the constituents to prevent them mixing and reacting normally

It was determined (using data from the site instrumentation) that there was at least one period of time when no circulation was taking place (when the pump was stopped to clear the blockage). In addition, just before the time of the incident, fume was seen to be emitted from one pump, resulting in the operator performing a changeover to the standby pump. It is not possible to show that in the intervening period prior to the incident that effectual, or indeed any, circulation of the contents of D650 was occurring, even if the control system showed the pump was supplied with power.

Throughout this time the gases were kept on. The violent reactions taking place within D650 which prompted investigation by the site operators, the observed temperature and pressure spikes as well as higher Twaddle density readings/blockages of the sampling line, all indicate that larger than normal amounts of liquid  $\text{TiCl}_4$  were entering the vessel D650 prior to the incident. This leads us to believe that, if the recirculation from the top of the vessel D650 was not properly functioning, a significant accumulation of reactive  $\text{TiCl}_4$  could occur.

Lack of effective circulation could have led to a condition within vessel D650 where the aqueous scrubbing media (a mixture of water, hydrochloric acid, and the products from reacting  $\text{TiCl}_4$  with water) present within the vessel settled at the bottom, while  $\text{TiCl}_4$  vapour or liquid continued to be carried over into D650. The lack of circulation could have led to the formation of a crust of partly reacted titanium species when the  $\text{TiCl}_4$  reacted with the aqueous scrubbing mixture. Our experiments have demonstrated that such an accumulation could be as a localised foam/crust of partially reacted material, with liquid/gaseous titanium tetrachloride contained within the pores of such a foam, or, in the extreme case of a contiguous crust being formed over most or all the surface of the scrubbing liquor, as a layer of liquid  $\text{TiCl}_4$  sitting on top of that crust, separated from the layer of the aqueous scrubbing mixture below the crust. This is shown schematically in Figure 4.

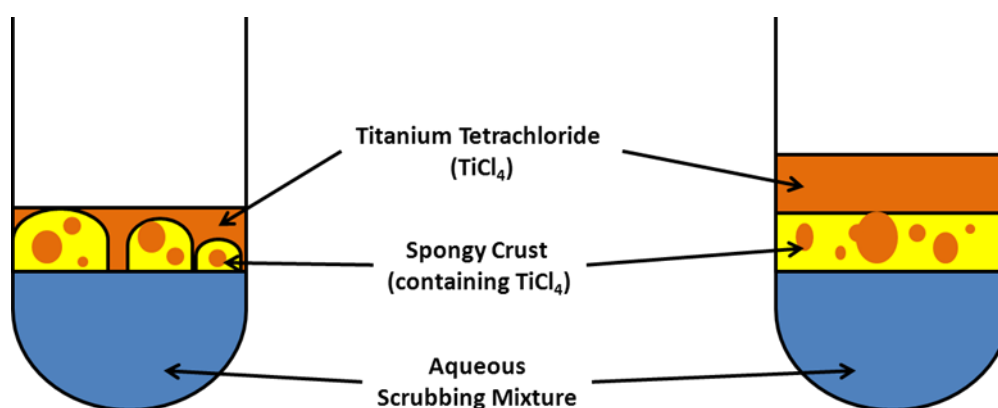


Figure 4. Possible reservoirs separating  $\text{TiCl}_4$  and aqueous scrubbing mixture

Once the switch-over to pump G650B was made, the contents were disturbed, breaking the crust, spraying water (water was often used for priming the pump when first started) and/or aqueous hydrochloric acid down upon the reactive layer and causing an extremely rapid and violent reaction of any accumulated reactive titanium species. This would rapidly produce heat, and gas in the form of hydrogen chloride vapour, most probably containing titanium oxychloride fume/smoke, which, if not able to escape quickly enough through designed routes, would cause a pressure rise enough to rupture vessel D650.

#### Fume generation when passing gas flow over $\text{TiCl}_4$

A key feature of the incident was the generation of a large dense white cloud. In an effort to replicate the condition of the plant post-incident, an experiment was performed to demonstrate the effect of venting to atmosphere a process gas stream which had passed through pipework containing  $\text{TiCl}_4$ . A length of glass pipework was assembled, the initial horizontal section of which was filled with  $\text{TiCl}_4$ . When a dry, non-reactive, gas (nitrogen) was passed over the liquid, white fumes were observed at the end of the pipework due to gaseous  $\text{TiCl}_4$  becoming entrained in the gas stream and reacting atmospheric moisture (Figure 5).



Figure 5. Fumes leaving pipework

### Implications of fume generation

When the pipework feeding into unit 600 was dismantled post-incident, a significant quantity (up to 7,000 kg) of  $\text{TiCl}_4$  was found to be present. With the process gas flow running, a quantity of  $\text{TiCl}_4$  would have been entrained within, and been transported by the flow. Therefore, it would seem likely that a substantial quantity of liquid  $\text{TiCl}_4$  may have been pushed through the pipework and into vessel D650. Any  $\text{TiCl}_4$  entrained in the gas stream would contribute to the temperature rises and the continuing thickening of the scrubber solution observed within vessel D650 in the run up to the incident. In addition, once vessel D650 had ruptured, this entrained titanium tetrachloride contained in the process and purge gases would have reacted with atmospheric moisture to create a smoke cloud that would have continued to grow (as well as being moved and dissipated by the wind) for as long as there was any gas flow. This would have contributed to the smoke cloud observed by witnesses to the incident.

### Heats of reaction and rates of gas evolution

A number of experiments were performed to investigate the amount of heat generated when  $\text{TiCl}_4$  reacts with water, aqueous hydrochloric acid, or the product of previously reacting hydrochloric acid with  $\text{TiCl}_4$ . These experiments are analogous to those described in the literature [Buston, 2011; Cruse, 2011; Brown, 2000] between  $\text{TiCl}_4$  and water, but are here extended to other aqueous substrates. Details of these experiments are shown in Table 1.

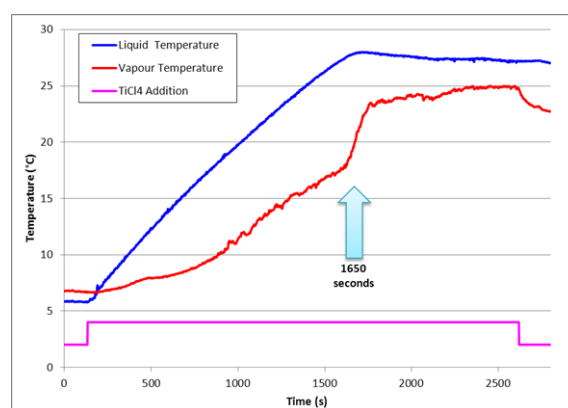
Substrate	Water	36% Aqueous hydrochloric acid	{ 36% Aqueous hydrochloric acid previously reacted with titanium tetrachloride }
Concentration (%w/w)	-	35.5% HCl	41.2% HCl 6.2% titanium
Density ( $\text{g}/\text{cm}^3$ )	1	1.18	1.35
Density ( $^{\circ}\text{Tw}$ )	1	36	70
Volume used (ml)	250	250	250
Mass used (g)	250	296	333
Heat capacity $\text{J}/\text{g}^{\circ}\text{C}$ (average over temperature range observed: from literature)	4.18	2.10	Unknown
Rate of temperature increase with titanium tetrachloride addition at 1 ml/min ( $^{\circ}\text{C}/\text{min}$ )	1.738	0.894	0.799



Power measured in temperature gain in reaction (J/s)	30.3	9.3	Depends on knowing the heat capacity
Approximate $\Phi$ Factor (measure of the efficiency of Dewar system)	1.27	1.55	---
Power released in temperature gain in reaction (J/s) (compensated for $\Phi$ Factor)	38.5	14.4	---

Table 1: Comparison of Heats Generated

This data shows that the reaction of  $\text{TiCl}_4$  with water generates more heat than the analogous reaction with aqueous hydrochloric acid. It can reasonably be expected that the reaction with {hydrochloric acid previously reacted with  $\text{TiCl}_4$  would be similar to, or less heat producing than that with aqueous hydrochloric acid. A similar experiment was performed in which a much larger quantity of  $\text{TiCl}_4$  was added, at the same rate and in the same system, to aqueous hydrochloric acid. A graph of the temperatures seen in this experiment is shown (Figure 8).

Figure 8. Temperature rises in Dewar experiment adding  $\text{TiCl}_4$  to aqueous hydrochloric acid

These temperature traces show that there comes a point in this experiment (after approximately 1650 seconds) where continued addition of  $\text{TiCl}_4$  does not predominantly result in heat being generated and the liquid warming up. However, a stream of white fume from the vent pipe was seen, commencing at about the same time, which increased in intensity as the experiment continued. If the reaction maintains the same pathway, i.e. the  $\text{TiCl}_4$  is reacting with the water within the aqueous hydrochloric acid to form similar products, then one would expect the same energy to be released from the chemical bonds involved in this reaction, whether the water originates from aqueous hydrochloric acid or pure water. As a result, we would expect that the energy released from these changes in chemical bonds is being dissipated by a means other than heating up the reaction mixture and its immediate surroundings. The most obvious means for consuming this energy is by the vapourisation of hydrogen chloride from solution to gas (energy is consumed in this process). This would imply that more hydrogen chloride gas is generated at this stage in the process. This appears to be a reasonable assumption since there is a maximum amount of a gas that can be dissolved in any given solvent (with this generally diminishing as the temperature is increased). Thus, hydrogen chloride produced in the reaction of  $\text{TiCl}_4$  with hydrochloric acid will not be able to be dissolved in the reaction medium as readily as in the corresponding reaction of  $\text{TiCl}_4$  with water. In addition, the reaction of  $\text{TiCl}_4$  with aqueous hydrochloric acid will consume some of the water within the aqueous hydrochloric acid, thus making it more concentrated and even less able to dissolve further hydrogen chloride gas.

In order to test this hypothesis, a set of experiments were performed to measure the amount of gas being produced as  $\text{TiCl}_4$  reacted with water, aqueous hydrochloric acid or {aqueous hydrochloric acid previously reacted with titanium tetrachloride}. An inert gas (nitrogen) flow was applied to the experimental set-up which enabled the gas stream to be collected in traps containing clean water. Where  $\text{TiCl}_4$  was added to a large excess of water, no significant weight gain was observed in any of the traps. Nor, when sampled, were any found to be significantly acidic. The temperature in the reaction vessel rose steadily during the addition of  $\text{TiCl}_4$ , reaching a peak of  $54^\circ\text{C}$ . This is consistent with all the energy released during the reaction being used to heat the reaction mixture, leaving the hydrogen chloride in solution.

However, when titanium tetrachloride was similarly added to a large excess of aqueous hydrochloric acid, a smaller temperature rise (to  $25^\circ\text{C}$ ) was observed. In contrast, appreciable quantities of acidic gas were trapped. Indeed, temperature rise was observed to plateau, after which the quantity of acidic gas evolved continued to increase (Figure 9).

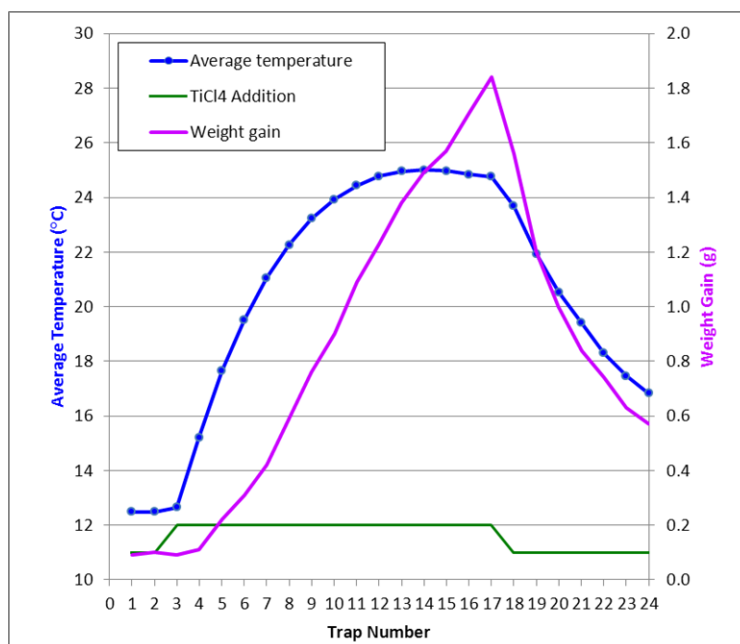


Figure 9. Temperature rises and gas evolved adding  $\text{TiCl}_4$  to aqueous hydrochloric acid

In a similar manner, titanium tetrachloride was reacted with titanium oxychloride solution (the product from allowing  $\text{TiCl}_4$  to react with hydrochloric acid). Continuing the trend observed above, lower temperature rises ( $8^\circ\text{C}$ ), and higher evolved gas quantities were seen. A direct comparison of these three experiments is shown in Figure 10. This clearly shows the related trends of smaller temperature rises and greater hydrogen chloride gas evolution when  $\text{TiCl}_4$  is added to aqueous hydrochloric acid and {aqueous hydrochloric acid previously reacted with  $\text{TiCl}_4$ }, as compared to when it is reacted with water.

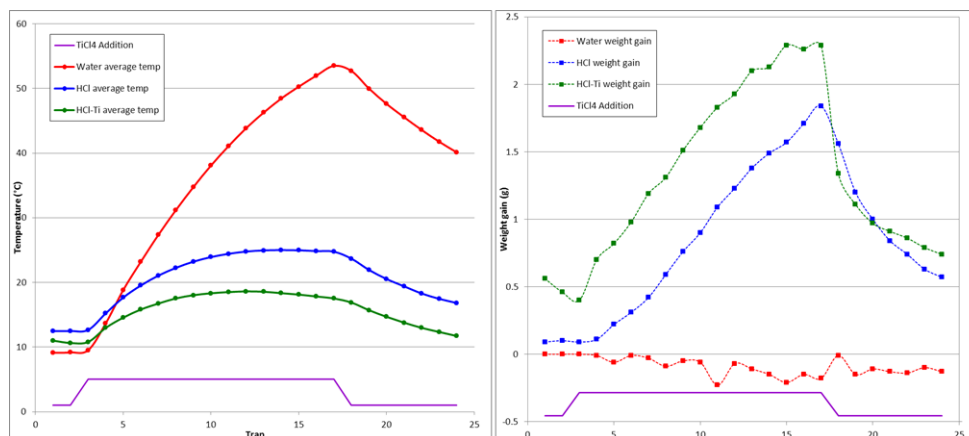


Figure 10. Comparison of temperature rises and gas evolution

### Implications of heat of reaction /rate of gas evolution studies

The smaller temperature rises observed when  $\text{TiCl}_4$  reacts with aqueous hydrochloric acid compared to when  $\text{TiCl}_4$  reacts with water can be explained by the correspondingly greater gas evolution. Thus, the energy released by the reaction is being used to liberate a larger quantity of hydrogen chloride gas. Accordingly, it is the case that addition of  $\text{TiCl}_4$  to aqueous hydrochloric acid will produce less temperature rise, but generate more acidic hydrogen chloride gas than addition of  $\text{TiCl}_4$  to water.

During the incident investigation, it was noted that, in the 48 h. leading to the rupture of vessel D650, a number of notable temperature 'spikes' occurred within vessel D650. The most likely cause of these are slugs of liquid  $\text{TiCl}_4$  passing through into the vessel from the pipework leading up to D650 and reacting with aqueous hydrochloric acid, producing both heat and hydrogen chloride gas. It has already been shown that it is highly likely that substantial quantities of liquid titanium tetrachloride were present in the pipework.

The experimental results reported above, most notably in Table 1, were used to provide an approximate calculation indicative of the quantity of  $\text{TiCl}_4$  that would need to pass into vessel D650 to produce the observed temperature spikes.

Taking one of the observed temperature spikes from the site process instrumentation, a 50°C temperature rise observed at 21:25 on 4th March 2010 (Figure 11), it was calculated that in the order of 1 tonne of  $TiCl_4$  would need to be added to vessel D650 to produce the observed temperature rise.

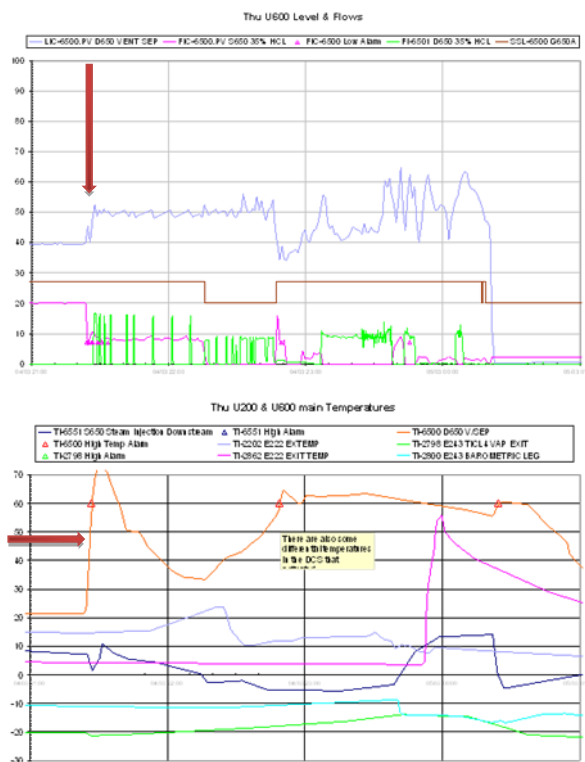


Figure 11. Excerpts from process instrumentation to Vessel D650 showing level increase (top) and 50°C temperature rise (bottom)

**Determination of magnitude and rate of pressure increase**

A number of experiments were performed to investigate both the magnitude and rate of the pressure rise when  $TiCl_4$  and an aqueous system were mixed. A closed system was used equipped with a pressure transducer. Each experiment was performed by placing a measured quantity (2-40 ml) of  $TiCl_4$  into the glass vessel. The aqueous reagent, either tap water or 36% aqueous hydrochloric acid solution, was placed into the pipe reservoir above the valve and the system sealed. Once data collection had commenced, the valve was opened and a rapid, pressure generating reaction occurred, forcing all of the aqueous added reagent down into the glass vessel. A typical trace of pressure against time is shown (Figure 13).

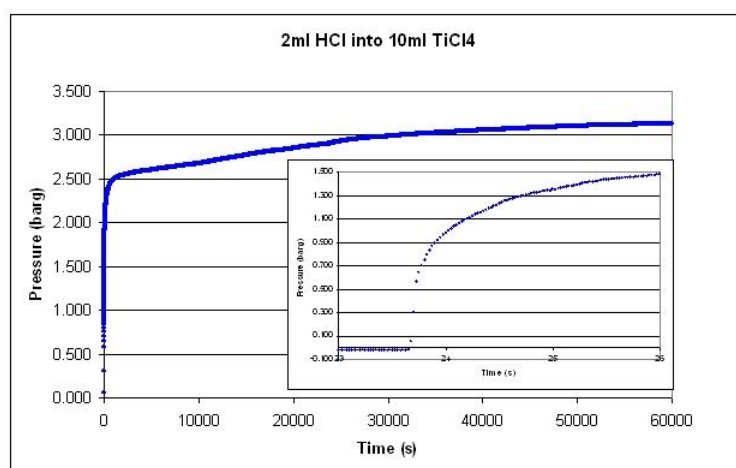


Figure 13. Typical Pressure-time trace

From this it can be seen that there is a very rapid initial pressure rise (for this example, about 0.4 s. to increase by 1 bar). After the initial pressure rise, the pressure continued to climb slowly for some hours. This is most probably related to a combination of: firstly an equalisation of pressure across all the pores of the foam and the reaction vessel, and secondly the release of reagents held up within the pores of the foam for further reaction. Several repeat experiments were run for each



ratio of reagents (eg. 2 ml HCl with 10 ml  $\text{TiCl}_4$ ) investigated. Some variation within each set of results was observed (Figure 15), arising from the non-homogeneous nature of the reaction mixture. However, all consistently demonstrated a very rapid pressure rise, followed by a more protracted pressure increase at a much lower rate.

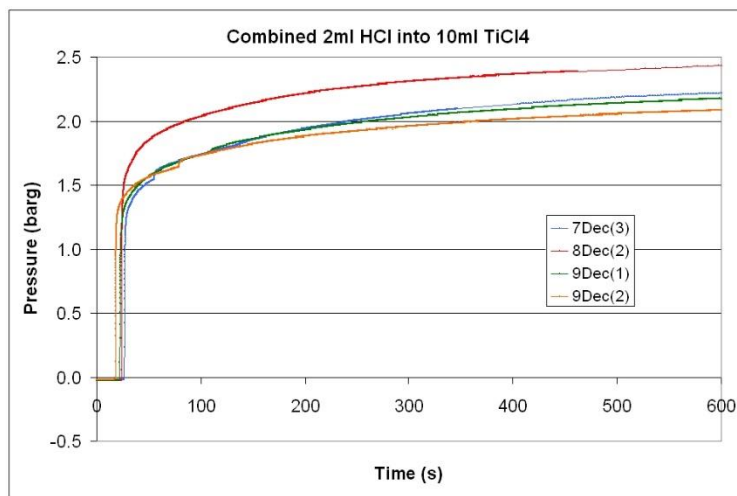


Figure 15. Variability in rates of pressure change

There are two possible sources of gas generation in this reaction; hydrogen chloride will be generated from the reaction between  $\text{TiCl}_4$  and water (the aqueous hydrochloric acid contains about 65% by weight of water). In addition, the water that was consumed by this reaction is no longer present to dissolve the hydrogen chloride from the hydrochloric acid. This can therefore be liberated as a gas and further contribute to the pressure rise. In order to examine the contributions of these two effects, further experiments were performed adding water (rather than hydrochloric acid) to  $\text{TiCl}_4$ . 1.5 ml of water was used. This is approximately the amount of water present in 2 ml of 35% aqueous hydrochloric acid. A comparison of the pressure change seen with adding 1.5 ml water (against the average from adding 2 ml hydrochloric acid) can be seen (Figure 17).

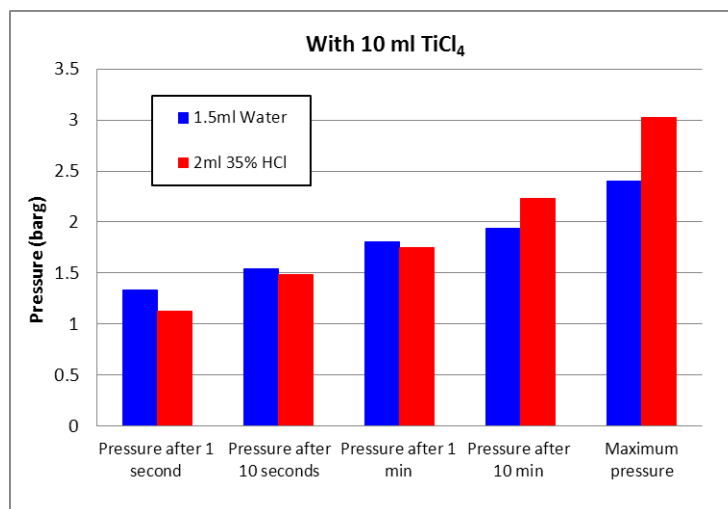


Figure 17. Comparison of pressure gains

It was observed that there was a marginal difference in the initial rates of pressure formation, with the water reacting marginally quicker than the aqueous hydrochloric acid. The final pressure reached is approximately 0.6 bar greater when hydrochloric acid is used. This demonstrates that, for this ratio of reagents, the hydrogen chloride gas dissolved in the hydrochloric acid contributes to the final pressure (and therefore the amount of toxic gas released).

### Implications of results obtained studying magnitude and rate of pressure increase

A rapid and pressure generating reaction occurs between  $\text{TiCl}_4$  and aqueous hydrochloric acid, even at room temperature, forming a sticky/foamy solid material. This is followed by a second phase of pressure increase related to the breakdown of the foam and equalisation of the internal pressure across the vessel, which takes place over a time period of several hours. The pressure rises measured in this work can be regarded as occurring at approximately constant temperature since the mass of the reaction vessel (approximately 800 g without lid) and therefore heat capacity of the vessel is very much greater than that of the contents. When considering these results scaled up to vessel D650, the heat loss to the vessel fabric or surroundings (within the timescale of the incident) would be almost negligible (a near adiabatic system). As a result, the gas generated would be at a higher temperature. The key point being made is that the experimental-scale pressure rises observed in this work most likely underestimate any pressures increases that would be observed within a larger reactor vessel.

## Representative reactions in bottles

In order to understand more clearly the effect of the reaction between  $\text{TiCl}_4$  and an aqueous system in a vessel with a limited venting capacity, a number of experiments have been carried out using 500 ml plastic drinks bottles. These bottles were chosen since they were transparent and had approximately the same ratio of cross-sectional area to aperture area as vessel D650. In the first experiment, the bottle was prepared for reaction by introducing  $\text{TiCl}_4$  (89 ml, 154 g). Water was then added through the top, although only about 45 ml was added before the addition pipe was ejected by force of the reaction. Two thermocouples measured the temperature inside the bottle; one within the liquid saw a rapid temperature rise from  $15^\circ\text{C}$  to  $32^\circ\text{C}$  within 2 s., the other, located approximately 5 cm above the surface of the liquid rose from  $15^\circ\text{C}$  to  $56^\circ\text{C}$  in the same timescale, and peaked at  $60^\circ\text{C}$ . During the course of this reaction, a sticky yellow material filled the bottle (Figure 18a), a significant quantity of which was ejected and impacted on the roof of the glove box some 50 cm above the bottle opening (Figure 18b).



Figure 18. Result of adding water to  $\text{TiCl}_4$  in a bottle

Additional tests of this nature were performed, each of which produced similar results, with temperatures up to  $100^\circ\text{C}$  observed at the lip of the bottle. It was found that considerable effort was required to break up the initially formed crust. On breaking through the crust, further reaction was observed (Figure XX).

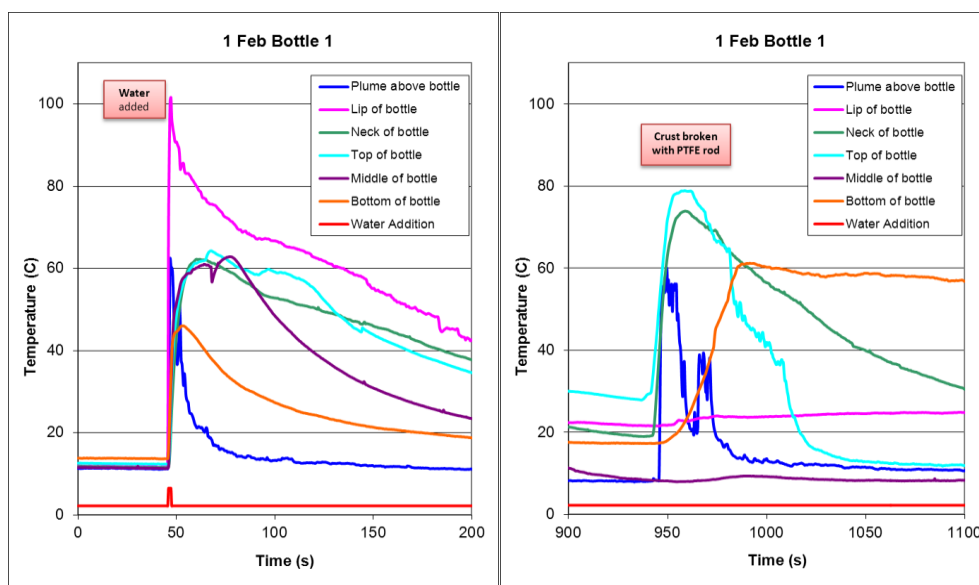


Figure 19. Temperatures seen in experiment adding water to  $\text{TiCl}_4$  in bottle

## Implications of Bottle Experiments

All of the 'bottle' experiments performed demonstrate the extreme reactivity of  $\text{TiCl}_4$  with water. This reactivity rapidly generates heat and hot gases and forms a non-homogeneous solid which can act to separate portions of the reaction mass from each other. Sticky solid materials have been observed to be ejected vigorously from the bottle; this would have the potential to reduce the bore, or in extreme cases, completely close the normal outlet flow route of a vessel. Accordingly, the experiment results presented here suggest that some degree of obstruction of the vessel outlet is likely.

## Conclusions

Initial experiments investigating foam formation have shown the effect of adding  $\text{TiCl}_4$  to water and aqueous hydrochloric acid. In all cases, a non-homogeneous crust or foam (often sticky) of partially reacted titanium species was formed, which could lead to the separation of a distinct layer of  $\text{TiCl}_4$ . Adding water to this led to an extremely violent reaction, generating heat, white fume and hydrogen chloride gas.

Passing an inert gas-flow over  $\text{TiCl}_4$  within a pipeline demonstrated that the flow of a non-reactive gas over a pipe partially filled with liquid  $\text{TiCl}_4$  will lead to the entrainment of titanium tetrachloride vapour within that gas stream. When this  $\text{TiCl}_4$  vapour comes into contact with moist air, it will react, forming dense white fumes.

Measurement of the heat and gas generated when  $\text{TiCl}_4$  reacts in a controlled manner with water, aqueous hydrochloric acid, or aqueous hydrochloric acid pre-reacted with  $\text{TiCl}_4$  has shown that the observed temperature rise decreases, and the gas generation rate increases when hydrochloric acid is reacted rather than water. Thus, with hydrochloric acid aqueous systems the chemical energy liberated from the reaction is channelled into vapourising hydrogen chloride rather than heating the reaction mixture. These results have been used to estimate the size of a slug of  $\text{TiCl}_4$  which is likely to have been responsible for a specific sharp temperature rise observed in vessel D650 some hours prior to the rupture of the vessel.

Investigation of the magnitude and rates of the pressure increase observed when  $\text{TiCl}_4$  reacts with water and aqueous hydrochloric acid has demonstrated that extremely rapid initial pressure rises are produced, as the mixture forms a non-homogeneous foam. A continuing but slower pressure rise is subsequently observed.

Finally, 'bottle' experiments continued to demonstrate the non-homogeneous products formed by the reaction of  $\text{TiCl}_4$  with water, and how considerable 'splatter' can be produced during this violent reaction. This splatter could reduce the effective venting capacity of any vessel it was produced in.

Given the rapid temperature and pressure increase within Vessel D650 at the time of the rupture, it seems most likely that this was caused by the reaction between a significant amount of  $\text{TiCl}_4$  and water (whether as pure water, or a component of the scrubbing mixture in the vessel). Two possible scenarios which could lead to a large amount of  $\text{TiCl}_4$  reacting instantaneously within the vessel have been proposed:

- In the first scenario, an extremely large slug of liquid  $\text{TiCl}_4$  found its way into vessel D650, overwhelming whatever scrubbing capacity that may have been operating at the time and reacted instantaneously. This would correspond to a very large slug of material.
- In the second scenario, a far greater than normal accumulation of unreacted constituents ( $\text{TiCl}_4$ ) had occurred over time and was then allowed/induced to react at a later point in time.

Given the timing of the incident relative to the changeover of the pump, it seems likely that a substantial amount of  $\text{TiCl}_4$  was present in vessel D650 but separated in such a manner as to have avoided reaction. The starting of the reserve pump restarted effective mixing/contact between the separated reservoirs of accumulated  $\text{TiCl}_4$  and aqueous hydrochloric acid solution, resulting in the violent reaction observed.

Therefore, it is our opinion that, whilst both scenarios are possible, and facts are not available to conclusively demonstrate one scenario in favour of the other, the timing of the incident, immediately after the pump changeover, leads us to believe that the second scenario is rather more likely than the first.

## Dedication

This paper is dedicated to the memory of Paul Dooley.

## References

- Buston, J. E., Vechot, L. N., Kay, J., Round, G. A., Masharani, S., Tickle, G. A. and Rowlands, R., 2011, Experimental Study of the Liquid Phase Hydrolysis Reaction of Titanium Tetrachloride, *Hazards XXII*, 238-245
- Cruse, H. A., Buston, J. E., Vechot, L. N., Tickle, G. A. and Rowlands, R., 2011, Modelling spills of water reactive chemicals, *Process Safety and Environmental Protection*, 415-423
- HPA, "Titanium Tetrachloride Incident Management," 2010, [http://www.hpa.org.uk/webc/HPAwebFile/HPAweb\\_C/1279889227778](http://www.hpa.org.uk/webc/HPAwebFile/HPAweb_C/1279889227778).
- HPA, "Hydrogen Chloride / hydrochloric acid Incident Management," HPA, 2011, [http://www.hpa.org.uk/webc/HPAwebFile/HPAweb\\_C/1194947387098](http://www.hpa.org.uk/webc/HPAwebFile/HPAweb_C/1194947387098).
- HSE, EH40/2005 Workplace Exposure Limits, 2nd Edition, HSE, 2011.

US CDC NIOSH, “Documentation for Immediately Dangerous to Life or Health Concentrations (IDLHs)”  
<http://www.cdc.gov/niosh/idlh/7647010.html>.