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Quantitative Risk Assessment in Titanium Sponge Plant

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ABSTRACT

This paper presents the quantitative risk assessment for the storage of titanium tetrachloride ($TiCl_4$). It is the major reactant used for the production of titanium in the titanium sponge plant. Titanium tetrachloride readily reacts with moisture, leading to the release of toxic hydrogen chloride (HCl). Fire explosive and toxicity index analysis, and hazard and operability (HAZOP) studies for the entire titanium sponge plant were carried out. Based on these studies, the $TiCl_4$ storage section was found to be one of the most hazardous sections in the titanium sponge plant. Fault tree analysis technique has been used to identify the basic events responsible for the top event occurrence, ie, release of HCl due to the hydrolysis of $TiCl_4$ upon contact with moisture in the environment during spillage/leakage of $TiCl_4$ from the storage tanks and to calculate its probability. Consequence analysis of the probable scenarios has been carried out. The risk has been estimated in terms of fatality and injuries. Based on these results, basic input in the form of recommendations for possible changes in the design and operation of the titanium sponge plant have been made for the risk management.

Keywords: Risk analysis, hazard assessment, consequence analysis, titanium tetrachloride, risk management, fault tree analysis

NOMENCLATURE

H' Upper height up to which the atmospheric water enters into the pool

V_a Volumetric flow rate of air

Z Reference height of wind speed

Z_o Roughness length of the substrate

$U(z)$ Wind speed at a height z

f_w Kilogram of water /kilogram of total air

δt Time step

M_{aw} Mass of atmospheric water

R Pool radius

M_{cemr} Amount of free water in concrete

M_{cw} Total mass of water that liquid encounters in each time step

l Depth of penetration of concrete from the pool liquid

1. INTRODUCTION

Assessment of risks involved in the design and operation of process plants has become exceedingly important due to the trend towards setting up more complex units with toxic, flammable or otherwise hazardous chemicals at extreme temperatures and

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pressures. The potential risks of such plants get magnified with the larger units and also due to the proximity of location to densely populated areas, if any. Increasing public awareness of technological risks of such units, thus, has placed an onerous responsibility on the process industries to review their current safety practices and scientifically devise these to make the technologies, both intrinsically and extrinsically safer. Towards this goal, risk and hazard analysis has emerged as a modern tool, to define the potential occupational hazards to titanium sponge plant personnel and surrounding environment, and public and enable computing the associated risks based on the probability of likelihood and consequence levels.

This study relates to the storage of large quantity of $TiCl_4$ in tanks required for the production of titanium sponge in large, commercial- size batches. Titanium tetrachloride is a colourless, clear, fuming liquid with low viscosity and suffocating odour[1]. Some of its properties[2-4] are shown in Table 1. Titanium tetrachloride contains the *Ti-X* bond and has pronounced haloanhydride character, being highly reactive and aggressive[5-7]. On escape from the containment and exposure to moisture, it reacts readily, violently, and exothermically with water, releasing copious volume of HCl gas and producing titanium oxy chloride ($TiOCl_2$) solid.

Table 1. Physical data of titanium tetrachloride

Parameter	Value
Colour/state	Colourless to pale yellow liquid at room temperature
Critical temperature (°C)	358
Freezing point (°C)	-25
Boiling point (°C)	135.80
Molecular weight	189.73
Specific gravity at 20 °C (g/ml)	1.72
Specific heat of liquid at 25 °C (cal / mol / °C)	37.53
Dielectric constant at 20 °C	2.79
Conductivity	Negligible

A survey of accidents that occurred in USA between January 1990 and November 1999 revealed that there had been 473 incidents involving spillage of $TiCl_4$ alone, out of which 13 involved evacuation, injuries, or deaths[8-11]. In an accident in 2001, the $TiCl_4$ evolved was as little as a few hundred milliliters, which was enough to generate a considerable volume of HCl affecting the employees at the titanium sponge plant and the staff of the neighbouring premises, as the resultant escaping gas drifted towards them[12]. Thus, this study aims at quantifying the hazards and consequences relating to the storage of $TiCl_4$ using the fault tree and consequence analysis techniques for estimating the risk to the environment and to identify the measures to be incorporated in the design and operation of $TiCl_4$ storage tanks.

2. HAZARD IDENTIFICATION–TITANIUM TETRACHLORIDE STORAGE

Fire explosion and toxicity index (FETI) analysis and hazard and operability (HAZOP) studies have been used to identify the hazardous sections of the titanium sponge plant. One of the major hazards identified from the HAZOP studies is the release of HCl due to the hydrolysis of $TiCl_4$ upon contact with moisture in the environment during the spillage/ leakage caused by the rupture of $TiCl_4$ from the storage tanks.

On the basis of FETI analysis, the storage section has been categorised as medium toxicity hazard and low fire and explosion hazard. The storage section comprises three, 25 T capacity, horizontally placed SS 304L tanks. Titanium tetrachloride is transferred to the adjacent sections and the standby tanks through pipelines. As the inventory of the $TiCl_4$ material in the storage section is large, it has been taken up for detailed qualitative and quantitative assessments.

3. FAULT TREE ANALYSIS TECHNIQUE

The fault tree analysis technique gives all possible minimum combinations of basic equipment, instrument, and operator's failures, called minimum cut sets, which could lead to the occurrence of the critical event, commonly known as the top event. The fault tree is solved to obtain the set of basic events whose combination could lead to the occurrence of an unwanted top event. On the basis of FETI analysis and HAZOP studies, the fault tree for the critical event, ie, release of *HCl* gas has been constructed.

3.1 Fault Tree Construction

The complete fault tree is shown in Fig. 1(a) to 1(e). The failure rates of the events are based on the data from several sources[13,14], suitably modified, whenever necessary, to account for the Indian conditions.

3.2 Fault Tree Analysis

The total number of minimal cut sets for this fault tree has been computed to be 414. The minimal cut sets in order of increasing the number of years or decreasing the number of occurrence of top event are listed in Table 2.

Operator's error and electricity failures have been identified as the basic failures which result in high frequency of top event occurrence. The failure rate of the top event has been calculated to be 1.55 E-03. Previous studies[15,16] reveal that the operator-related failures are generally more common than the instrument-related failures, and due to their unpredictability, the complexity of the situation increases manifolds. On the basis

Table 2. Fault tree analysis of top event occurrence

Minimal cut sets	Failure rate
(106)(230)(231)(234)(229)(226)	1.55E-03
(107)(230)(231)(234)(229)(226)	1.55E-03
(220)(230)(231)(234)(229)(225)	8.01E-04
(222)(230)(231)(234)(229)(226)	1.55E-05
(106)(230)(231)(234)(229)(225)	1E-05
(107)(230)(231)(234)(229)(225)	1E-05
(106)(230)(231)(234)(229)(227)	1E-05
(107)(230)(231)(234)(229)(227)	1E-05
(220)(230)(231)(234)(229)(227)	5.17E-06
(220)(230)(231)(234)(228)(225)	5.17E-06
(106)(230)(231)(234)(228)(226)	3.1E-06
(107)(230)(231)(234)(228)(226)	3.1E-06
(220)(230)(231)(234)(228)(226)	1.6E-06

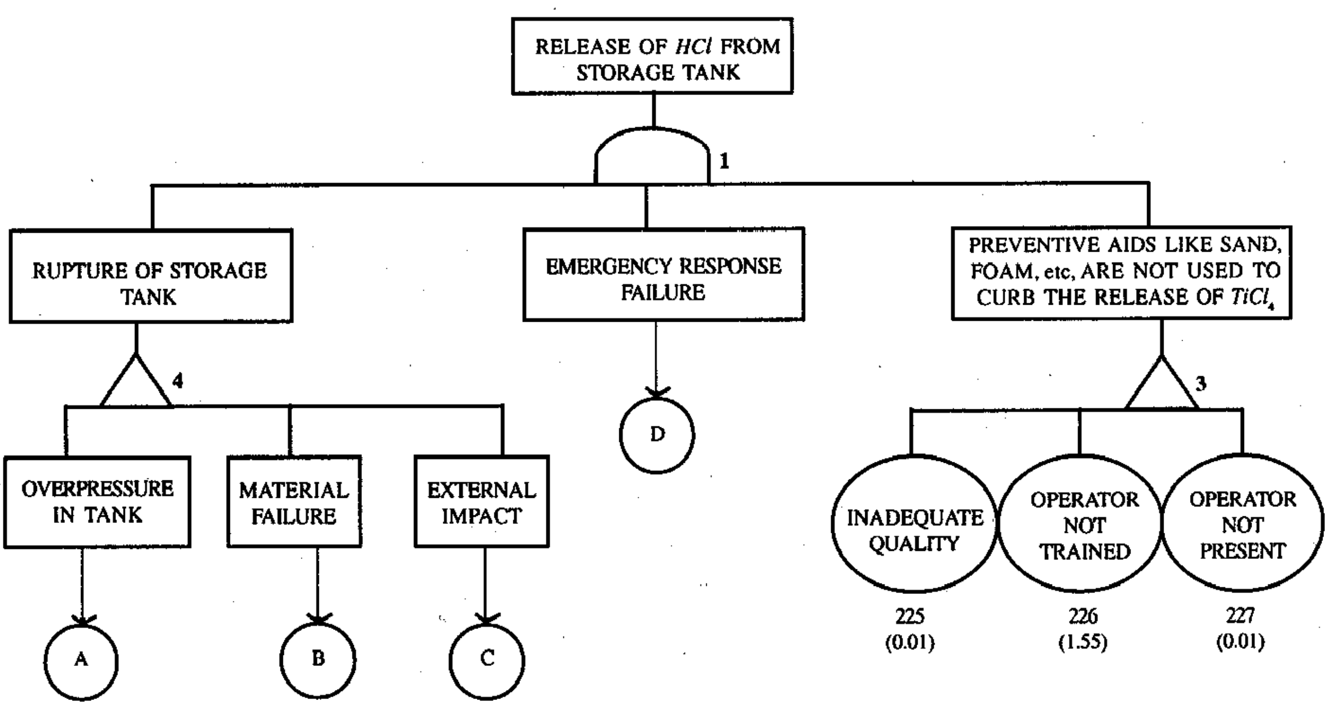

Figure 1(a). Fault tree for the release of *HCl* from the storage tank

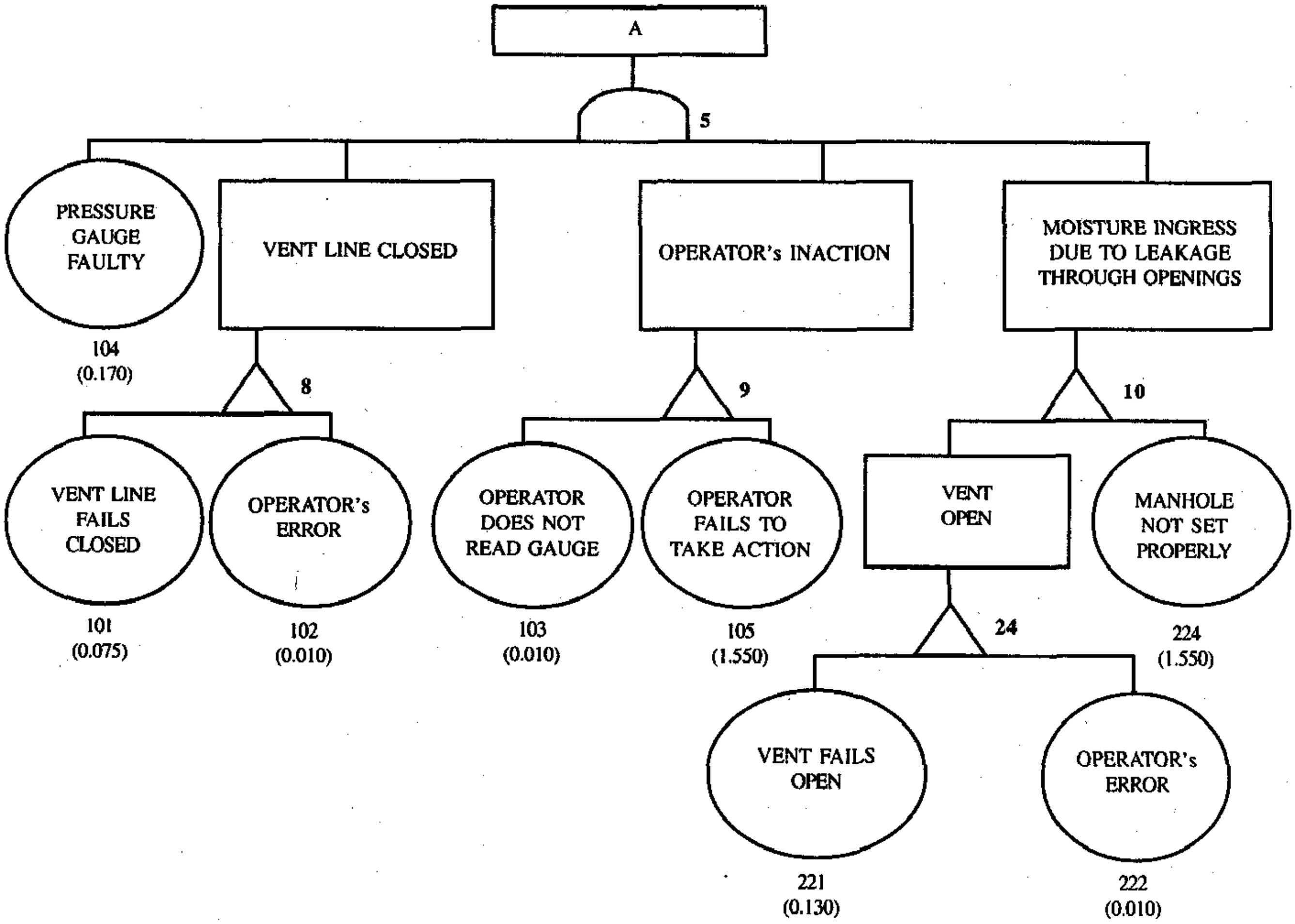

Figure 1(b). Fault tree for the release of *HCl* from the storage tank

of the observations brought forward by fault tree analysis technique, recommendations regarding maintenance/operator's training have been made.

3.3 Sensitivity Analysis

Sensitivity analysis has been carried out to determine the effect of incorporating the suggested modifications on the system safety. The results of the analysis are shown in Table 3. It is apparent from this table that incorporation of the suggested modifications in the design and operation can bring improvement of several orders of magnitude in the system safety.

3.4 Consequence Analysis

Titanium tetrachloride is used and transported in its liquid phase, and therefore on spillage, it

Table 3. Sensitivity analysis

Basic event	Recommendation	Top event occurrence	
		Before	After
Design of the tank	•Provide rupture disks •Modify the design as jacketed tanks	1.55E-03	8.01E-04
Electricity failure	Generator for auto takeoff	8.01E-04	9.61E-06
Operator's error	Operator's training for normal and remedial measures	9.61E-06	3.32E-07
Emergency transfer system failure	Preoperational checks	3.32E-07	8.98E-08

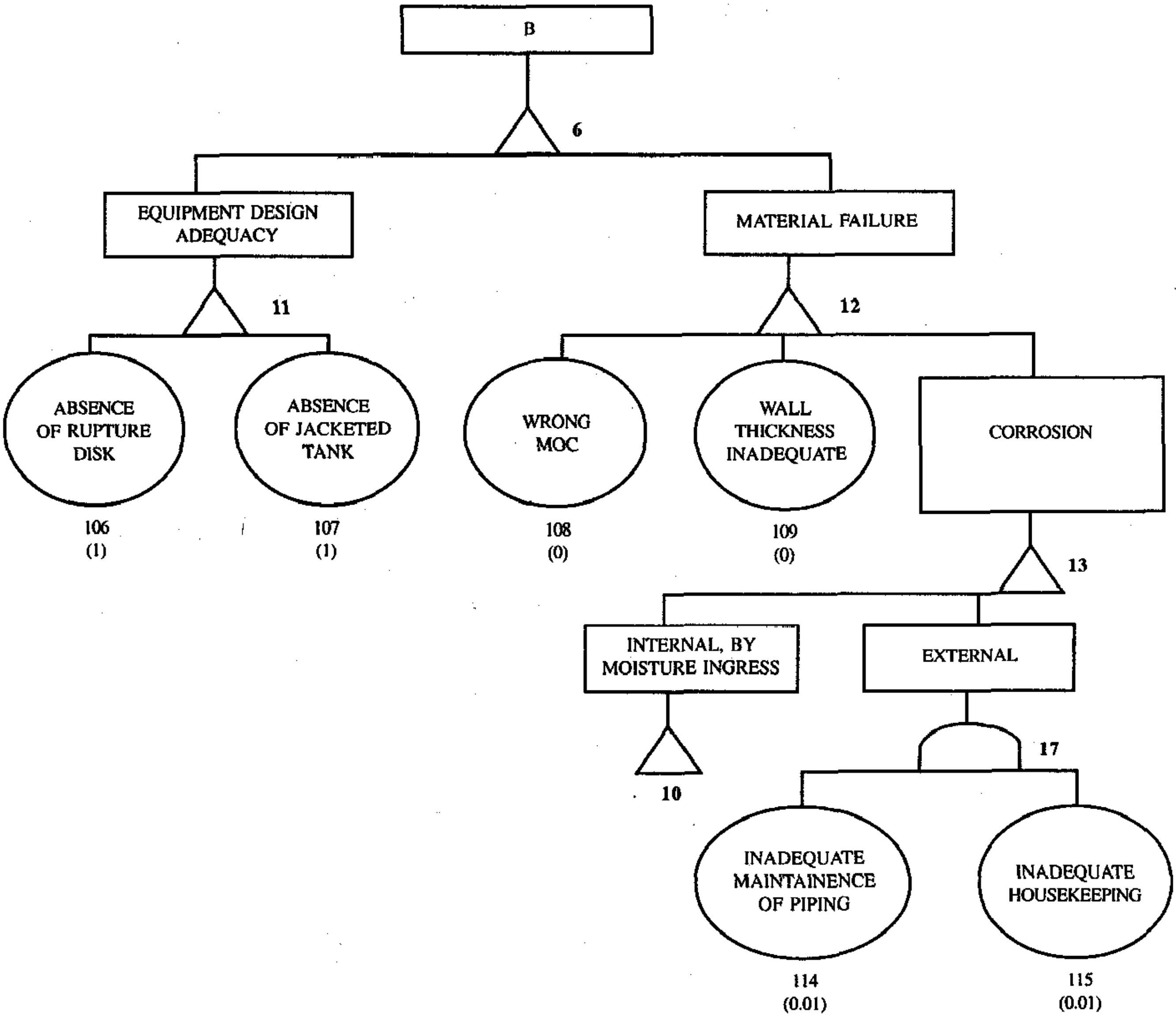

Figure 1(c). Fault tree for the release of *HCl* from the storage tank

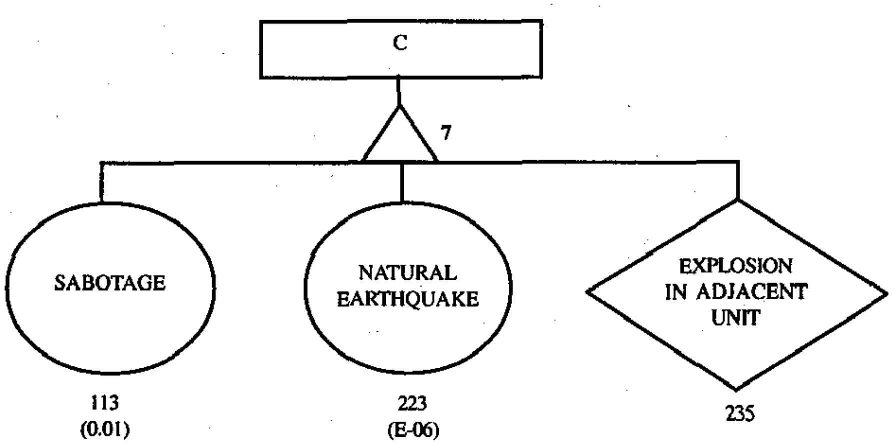

Figure 1(d). Fault tree for the release of *HCl* from the storage tank

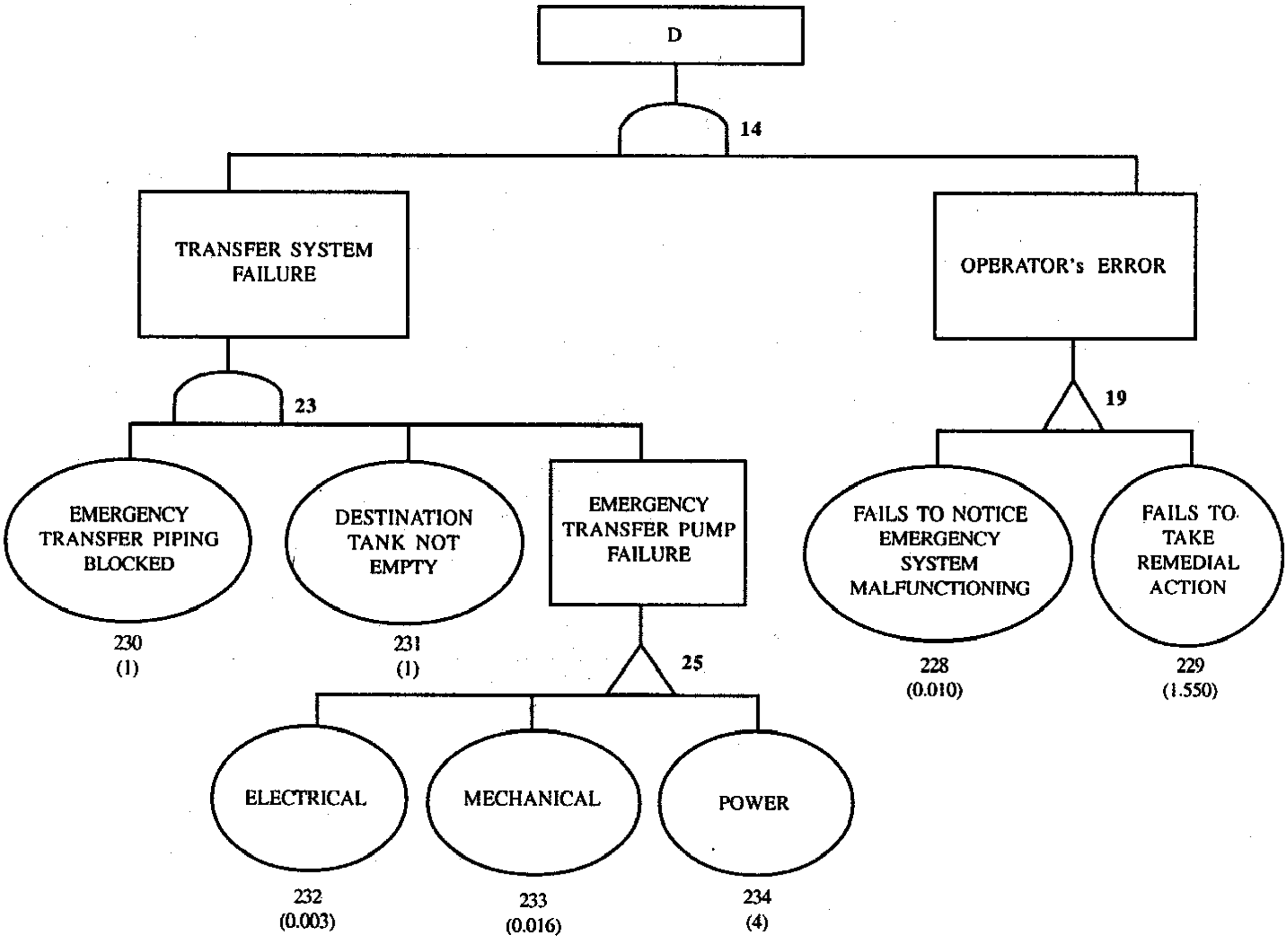

Figure 1(e). Fault tree for the release of *HCl* from the storage tank

creates liquid pool. Titanium tetrachloride reacts violently with water in the environment (ground, substrate) releasing *HCl* gas and $TiOCl_2$ solid as shown below.

$$TiCl_4 + H_2O \xrightarrow[\text{in excess}]{\text{When chloride}} TiOCl_2 + 2HCl \quad (1)$$

$$TiCl_4 + 2H_2O \xrightarrow[\text{in excess}]{\text{When water}} TiO_2 + 4HCl \quad (2)$$

This highly exothermic reaction supplies the pool with energy, thereby raising its temperature and vapour evolution rate. The pool formed usually contains only $TiCl_4$ liquid, as there is not enough water to allow *HCl* to enter into the solution.

4. EFFECTS & DAMAGE CALCULATIONS

Neutral dispersion model has been used to assess the effects of *HCl* dispersion into the surrounding atmosphere. TNO effects model and TNO yellow book[17] have been used to carry out the consequence analysis.

4.1 Pool Radius Calculation

Generally for chemical storage tanks, release of half of the tank capacity is normally considered. However, for the storage in close grouping of three or more tanks, a large quantity is assumed to be released, 90 per cent in the case of vertical tanks and 80 per cent in horizontal tanks. It is assumed that out of 25T of $TiCl_4$ stored in the tank, 20T is released on rupture of the tank, forming a pool. Based on these, the radius of the pool has been calculated to be 22.6 m.

4.2 Moisture Availablility

In most cases, the reaction of $TiCl_4$ with moisture proceeds under excess of $TiCl_4$, with HCl dispersing into the atmosphere. During spreading, the pool encounters free ground water, substrate water, and also absorbs atmospheric moisture. After spreading has ceased, the water is absorbed only from the substrate and the atmospheric moisture.

4.3 Dispersion Calculations

Assuming a time period of 30 min for the reaction of $TiCl_4$ released with the available water, the source strength of HCl evolved was calculated to be 2.12 kg/s (*Appendix* 1). Figure 2 depicts the directional IDLH (145 mg/m^3) contour during monsoon. Figures 3 and 4 give the variation of concentration with the downwind distance up to TLV and IDLH limits. The population staying within a radial distance of 1300 m needs to be evacuated within 30 min, while the population staying within a radial distance of 8650 m needs to be alerted. The data for the model is based on the wind speed data provided, and the scenario has been estimated (*Appendix* 1) using a wind speed of 2 m/s and ambient temperature of 33 °C.

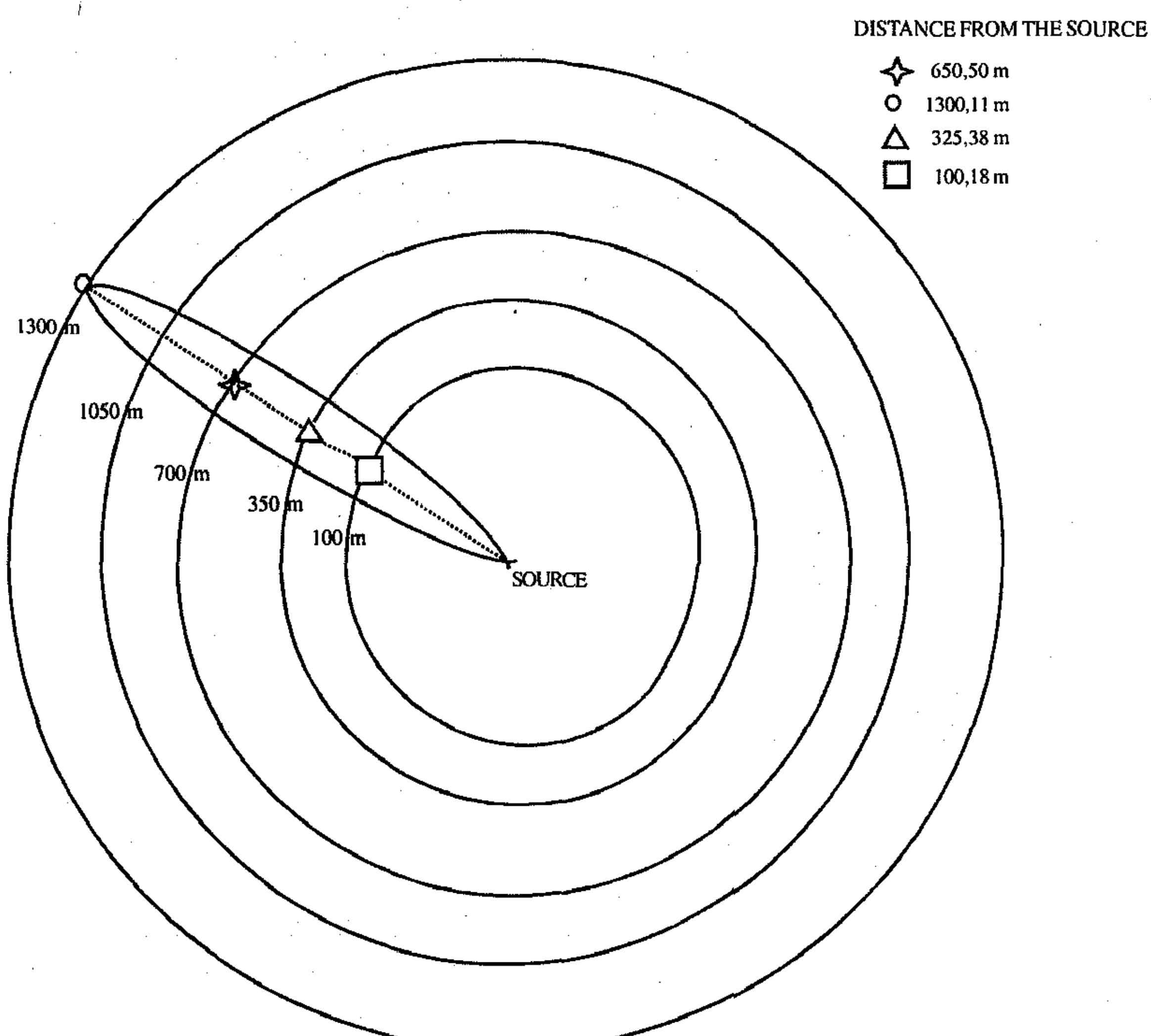

Figure 2. Depiction of an IDLH (145 mg/m^3) plume from the time of release to t = 1800 s in the wind direction during monsoon

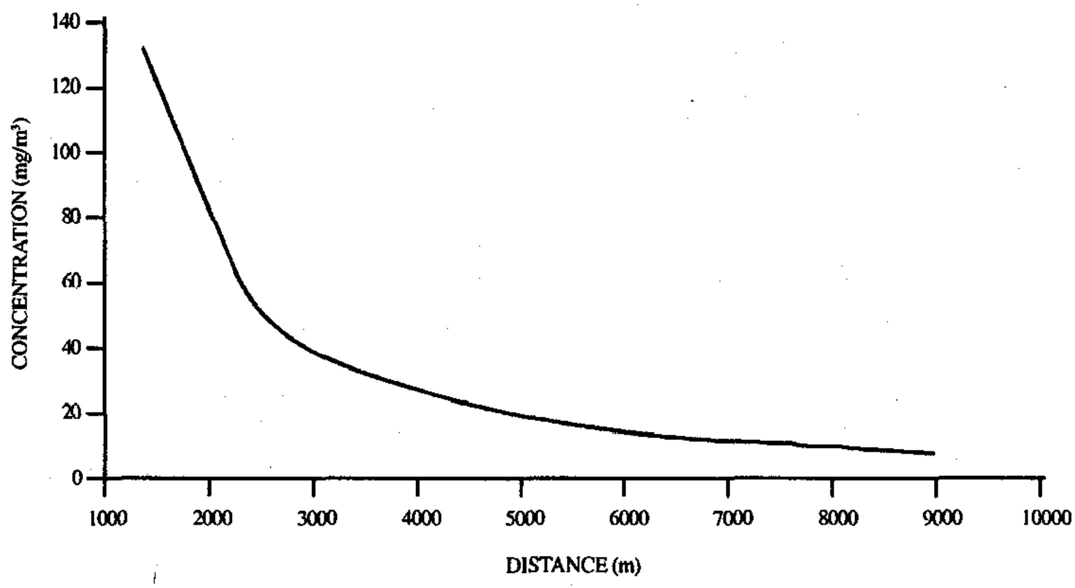

Figure 3. Variation of concentration with distance (up to TLV limit)

4.4 Effect of Seasonal Variation

Based on the wind rose pattern supplied by the local meteorological department, the predominant wind direction during monsoon (17 % of the time) is west-north-west, so the probability of *HCl* dispersing in this direction is the maximum. During winter, the wind direction is reversed with the plume pointing towards east-south-east (47 % of the time).

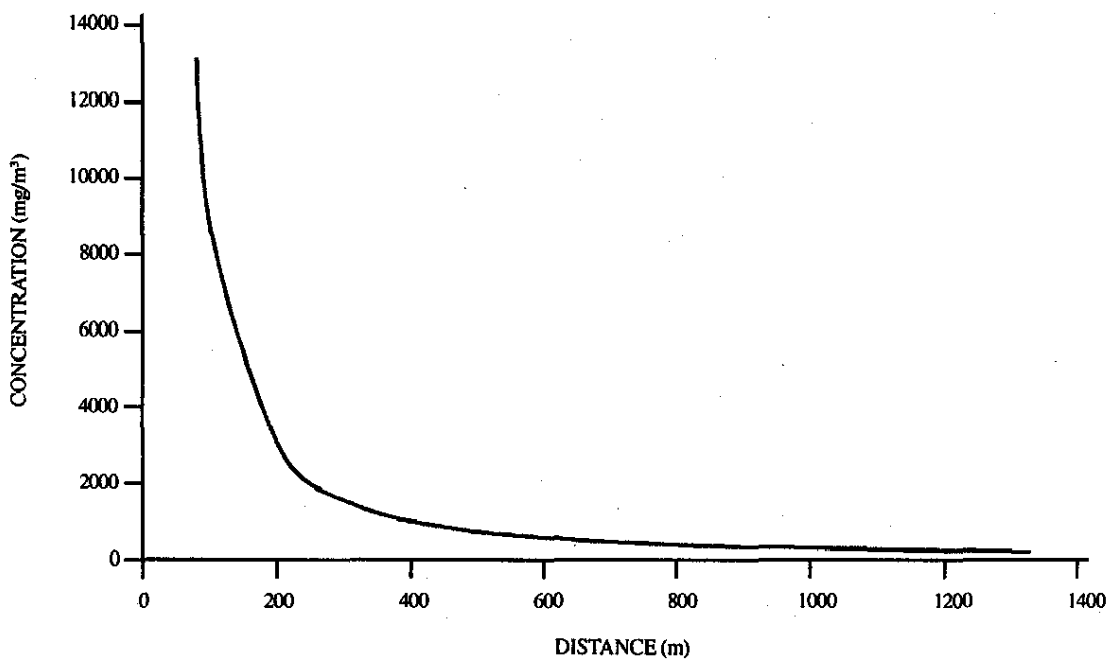

Figure 4. Variation of concentration with distance (up to IDLH limit)

4.5 Incident Outcome Frequency Calculations

The frequency of release of *HCl* due to storage tank rupture was found to be 1.55×10^{-3} per year. Based on this data and the directional wind probability, the incident outcome during monsoon and winter have been calculated. The results for monsoon and winter are summarised in Tables 4 and 5. This value is beyond the acceptable limits of 10^{-6} events/year as given by TNO for catastrophic events (with large consequences in terms of fatalities).

Table 4. Estimation of incident outcome during monsoon

Event	Incident frequency per year	Wind direction	Directional probability	Incident outcome
Release of *HCl* due to leakage of storage tank	1.55E-03	S	0.015	2.33E-05
	1.55E-03	NNW	0.070	1.09E-04
	1.55E-03	WSW	0.080	1.24E-04
	1.55E-03	SSW	0.095	1.47E-04
	1.55E-03	W	0.110	1.71E-04
	1.55E-03	SW	0.120	1.86E-04
	1.55E-03	NW	0.145	2.25E-04
	1.55E-03	WNW	0.170	2.64E-04
Total			0.805	1.25E-03

Table 5. Estimation of incident outcome during winter

Event	Incident frequency per year	Wind direction	Directional probability	Incident outcome
Release of *HCl* due to leakage of storage tank	1.55E-03	SSE	0.015	2.33E-05
	1.55E-03	N	0.020	3.10E-05
	1.55E-03	NNE	0.020	3.10E-05
	1.55E-03	WSW	0.020	3.10E-05
	1.55E-03	SSW	0.030	4.65E-05
	1.55E-03	S	0.085	1.32E-04
	1.55E-03	NE	0.140	2.17E-04
	1.55E-03	SE	0.475	7.36E-04
Total			0.805	1.25E-03

Tables 6 and 7 indicate the incident outcome after implementation of the recommendations. As is apparent, the incident outcome has been considerably reduced (7.23E-08), which is well within the acceptable limits.

Table 6. Estimation of incident outcome after implementation of the recommendations during monsoon

Event	Incident frequency per year	Wind direction	Directional probability	Incident outcome
Release of *HCl* due to leakage of storage tank	8.98E-08	S	0.015	1.35E-09
	8.98E-08	NNW	0.070	6.29E-09
	8.98E-08	WSW	0.080	7.18E-09
	8.98E-08	SSW	0.095	8.53E-09
	8.98E-08	W	0.110	9.88E-09
	8.98E-08	SW	0.120	1.08E-08
	8.98E-08	NW	0.145	1.30E-08
	8.98E-08	WNW	0.170	1.53E-08
Total			0.805	7.23E-08

Table 7. Estimation of incident outcome after implementation of the recommendations during winter

Event	Incident frequency per year	Wind direction	Directional probability	Incident outcome
Release of *HCl* due to leakage of storage tank	8.98E-08	SSE	0.015	1.35E-09
	8.98E-08	N	0.020	1.80E-09
	8.98E-08	NNE	0.020	1.80E-09
	8.98E-08	WSW	0.020	1.80E-09
	8.98E-08	SSW	0.030	2.69E-09
	8.98E-08	S	0.085	7.63E-09
	8.98E-08	NE	0.140	1.26E-08
	8.98E-08	SE	0.475	4.27E-08
Total			0.805	7.23E-08

4.6 Damage Calculations

The effect calculations give the extent of the IDLH and TLV plumes, while the probability calculations give the directional probability of the incident outcome. Their damage potential is calculated based on the extent of IDLH plume and its superimposition on the layout of the titanium sponge plant and the surrounding areas. Tables 4 and 5 give the area of exposure and population at risk during monsoon and winter. If effective measures are instituted to evacuate within 30 min the affected population residing within 1.3 km radius, the damage to the personnel present within the titanium sponge plant who might be affected, immediately comes down.

5. CONCLUSION

The release of *HCl* due to the rupture of $TiCl_4$ storage tank has been quantitatively assessed. On the basis of the probability calculations using fault tree analysis technique as well as the effect and damage calculations using consequence analysis, an assessment of the individual risk has been carried out as follows:

$$\text{Risk(fatalities/year)} = \text{Probability(events/year)} \times \text{Damage(fatalities/event)}$$

The effect of the seasonal variation on the risk values was considered as environmental conditions, namely humidity, wind direction, and wind velocity, which have a substantial bearing on the quantity of *HCl* released and its dispersion into the environment. Individual risk values for both the monsoon and winter, have been estimated and the results are summarised in the Tables 8 and 9. The total individual risk, as seen from these tables, is 2.37 fatalities/year during monsoon and 0.67 fatalities/year during winter. Incorporation of the suggested preventive measures brings down the probability of occurrence of the top event, ie, spillage of $TiCl_4$ and the subsequent release of *HCl*. This reduces the risk to 4.79E-05 fatalities/year and 3.87E–05 fatalities/year for both monsoon and winter seasons (Tables 10 and 11). After implementation of the protective measures, ie, evacuation of the people, and assuming only 5 personnel to be present at the site, the risk comes down to 3.6 E-07 fatalities/year.

On comparison with the risk assessment matrix given in the Table 12, the frequency of 1.25E-03 events/year for monsoon (before implementation of the recommendations), falls under the probable category, while the damage comes under the catastrophic category. Thus, the risk comes under the A category, ie, unacceptable. After implementation of the recommendations, the frequency of occurrence comes down to 7.23 E-08 events/year, which falls under the improbable category, while the damage comes under the marginal category. Thus, the risk comes under the C category, ie, acceptable with review.

Table 8. Estimation of individual risk during monsoon

Contributing incident	Frequency of incidence per year	Wind direction	Area of exposure (sq m)	Population	Risk and fatalities per year*
Release of *HCl* due to leakage of storage tank	2.33E-05	S	46200	200	4.66E-03
	1.09E-04	NNW	46200	500	5.45E-02
	1.24E-04	WSW	46200	600	7.44E-02
	1.47E-04	SSW	46200	600	8.82E-02
	1.71E-03	W	46200	1000	1.71E+00
	1.86E-04	SW	46200	600	1.12E-01
	2.25E-04	NW	46200	500	1.13E-01
	2.67E-04	WNW	46200	800	2.14E-01
Total					2.37

Total individual risk from $TiCl_4$ storage tank rupture is 2.37. Assuming population not evacuated within 30 min.

Table 9. Estimation of individual risk during winter

Contributing incident	Frequency of incidence per year	Wind direction	Area of exposure (sq m)	Population	Risk and fatalities per year*
Release of *HCl* due to leakage of storage tank	2.33E-05	SSE	46200	600	1.40E-02
	3.10E-05	N	46200	500	1.55E-02
	3.10E-05	NNE	46200	500	1.55E-02
	3.10E-05	WSW	46200	600	1.86E-02
	4.65E-05	SSW	46200	600	2.79E-02
	1.32E-04	S	46200	200	2.64E-02
	2.17E-04	NE	46200	500	1.09E-01
	7.36E-04	SE	46200	600	4.42E-01
Total					6.68E-01

Total individual risk from $TiCl_4$ storage tank rupture is 0.668 .
* Assuming population not evacuated within 30 min.

Table 10. Estimation of individual risk after implementation of the recommendations during monsoon

Contributing incident	Frequency of incidence per year	Wind direction	Area of exposure (sq m)	Population	Risk and fatalities per year
Release of *HCl* due to leakage of storage tank	1.35E-09	S	46200	200	2.69E-07
	6.29E-09	NNW	46200	500	3.14E-06
	7.18E-09	WSW	46200	600	4.31E-06
	8.53E-09	SSW	46200	600	5.12E-06
	9.88E-09	W	46200	1000	9.88E-06
	1.08E-08	SW	46200	600	6.47E-06
	1.30E-08	NW	46200	500	6.51E-06
	1.53E-08	WNW	46200	800	1.22E-05
Total					4.79E-05

Table 11. Estimation of individual risk after implementation of the recommendations during winter

Contributing incident	Frequency of incidence per year	Wind direction	Area of exposure (sq m)	Population	Risk and fatalities per year
Release of *HCl* due to leakage of storage tank	1.35E-09	SSE	46200	600	8.08E-07
	1.80E-09	N	46200	500	8.98E-07
	1.80E-09	NNE	46200	500	8.98E-07
	1.80E-09	WSW	46200	600	1.08E-06
	2.69E-09	SSW	46200	600	1.62E-06
	7.63E-09	S	46200	200	1.53E-06
	1.26E-08	NE	46200	500	6.29E-06
	4.27E-08	SE	46200	600	2.56E-05
Total					3.87E-05

Table 12. Risk assessment matrix

Frequency of occurrence		Hazard category			
		Catastrophic (>100)	Critical (10-100)	Marginal (1-10)	Negligible (<1)
Frequent	(0.01)	A	A	A	C
Probable	(0.001)	A	A	B	C
Occasional	(0.0001)	A	B	B	D
Remote	(E-5)	B	B	C	D
Improbable	(E-6)	C	C	C	D

A – Unacceptable, B – Undesirable (management decision), C – Acceptable with review, D – Acceptable without review

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APPENDIX **1**

Pool Radius Calculation

Amount of $TiCl_4$ spilled = 20,000 kg

Density of $TiCl_4$ = 1.728 kg/l

Hence, volume of $TiCl_4$ spilled = $11574.07 \times 10^{-3} m^{-3}$

Area of the storage section = 1600 m^2

Height of spilled liquid = 0.7 cm

Radius of pool formed $= \sqrt{\frac{V}{\pi h}}$ = 22.6 m

Moisture Calculation

$$V_a = \frac{U(z)}{\ln(Z/Z_0)}(H'[\ln(H'/Z_0) - 1] + Z_0)$$

Assuming the following:

z = 10 m

$U(z)$ = 2 ms^{-1}

Z_0 = 0.0005 m

H' = 0.002 m

$V_a = 2.545 \times 10^{-3}$ m^3/s

$M_{aw} = V_a 1.2 f_w \delta t 2R$

Considering relative humidity of 70 per cent (worst case scenario during monsoon)

$\dot{M}_{aw}$ = 0.027 kg

$M_{cemr} = \{(1/3\pi(^2(l_{tn} - l_{tn-1})\}C$

l_{tn} = 0.002 m (assumed)

l_{tn-1} = 0.001 m (assumed)

C = Cement content in concrete = 400 kg/m^3

M_{cemr} = 213.9 kg

$M_{cw} = \{\{1/3\pi r^2(l_{tn} - l_{tn-1})\} W_{cem}\} + 0.2\ M_{cemr}$

M_{cem} = 180 kg/m^3 (assumed average value)

M = 139.06

Assuming free-water film thickness on the ground as 0.0005 m

Mass of water = 802.3 kg

Total water available for the reaction:

- Total mass of water encountered in each time step (assumed time step of 10 s) from concrete = 139.06 kg
- Mass of atmospheric water = 0.027 kg
- Mass of water on the ground = 802.3 kg

Total water = 52.3 kg moles

Stochiometric Calculation

$$TiCl_4 + H_2O \rightarrow TiOCl_2 + 2HCl$$

$TiCl_4$ spilled = 105.26 kg moles

Since water is the limiting reactant, amount of HCl formed = 3818 kg.