American Journal of Engineering Research (AJER)
e-ISSN: 2320-0847 p-ISSN : 2320-0936
Volume-5, Issue-2, pp-01-09
www.ajer.org
Research Paper Open Access

Influence of Chlorine Induced Corrosion and Temperature of Exothermic Reaction on Failure of Methyl Isocyanate (MIC) Storage Tanks

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ABSTRACT : *The aim of the present work was to know the facts of Methyl Isocyanate (MIC) gas leakage and burst of its storage tank. The failure of the tank was evaluated based on the Tresca, von Mises criteria, Weibull criteria. The significance of chlorine induced corrosion and temperature derating factor were recognized using Taguchi techniques. The bursting pressure of the storage tank was highly dependent on the temperature derating factor and the crack depth. The reasons for the failure of experimental storage tanks used in the present work would satisfy the causes for the leakage of Methyl isocyanate gas and failure of the storage tank during the Bhopal gas disaster.*

Keywords : *Methyl Isocyanate, stainless steel, temperature degrading factor, crack depth, bursting pressure, Tresca criterion, von Mises criterion.*

I. INTRODUCTION

Methyl isocyanate (CH_3NCO) is utilized to produce carbamate pesticides. It reacts exothermically with water through an evolution of heat (325 calories per gram of CH_3NCO). Methyl isocyanate vapors are explosive when exposed to heat, flame or sparks. When it is decomposed in the presence of water, the solvent chloroform generates chlorine ions. Chlorine ions can corrode the stainless steel tank used for storage of CH_3NCO. Due to the exothermic reaction, the temperature and pressure in the tank increase causing the burst of storage tank. This was the main cause for Bhopal gas tragedy (Fig. 1) which occurred on the night of 2–3 December 1984 at the Union Carbide India Limited (UCIL) pesticide plant in Bhopal, Madhya Pradesh [1]. The government of Madhya Pradesh established a total of 3,787 deaths associated with the Bhopal gas tragedy [2]. A government affidavit in 2006 confirmed that the leak caused 558,125 injuries, together with 38,478 short-term injuries and about 3,900 severely and permanently disabling injuries [3].

An initial investigation by UCC showed that a large volume of water had been transported into the methyl isocyanate (MIC) tank. On account of exothermic reaction of MIC in the presence of water, hydrogen chloride was generated. The hydrogen chloride dissolved iron from stainless steel of the tank.

The reaction was accelerated by the presence of iron from corroding non-stainless steel pipelines [4]. The exothermic reaction increased the temperature inside the tank to over 200 °C and raised the pressure. This forced the emergency venting of pressure from the MIC holding tank, releasing a large volume of toxic gases. Also, the material of the storage tank lost due to chlorine initiated corrosion; the tank '610' was burst with lack of material's strength to withstand 42 tons of MIC. Based on several investigations, the safety systems in place could not have prevented a chemical reaction of this magnitude from causing a leak. The causalities of Bhopal gas tragedy are illustrated in Fig. 2. Not only ladies, gents, children, but also birds, dogs and cattle lay dead on the streets of Bhopal. The extremely hazardous gas had also left the surrounding land, lake and vegetation polluted with a toxic cocktail of chemicals. It is not just the aged but the young also put up with the plague of the toxic leak even today. According to the activists and organizations working for the welfare of the Bhopal gas tragedy victims, the rationale at the rear the birth of children with defects (Fig. 3) is due to exposure of their families to toxic chemicals that poisoned the entire area and contaminated groundwater.

The passive layer on stainless steel can be exposed to the chloride ion (Cl^-). With hydrochloric acid, the passive layer on stainless steel may be attacked depending on concentration and temperature and the metal loss is made available over the entire surface of the steel (Fig. 4). Stress corrosion cracking (SCC) is also possible owing to the specific combination of tensile stress, temperature and chloride ions. If the carbon level in the stainless steel is too high, intergranular corrosion is probably on account of reaction between chromium with carbon to form chromium carbide.

Fig. 1 Bhopal gas tragedy.

Fig. 2 Causalities of the Bhopal gas disaster.

Fig. 3 Birth defects

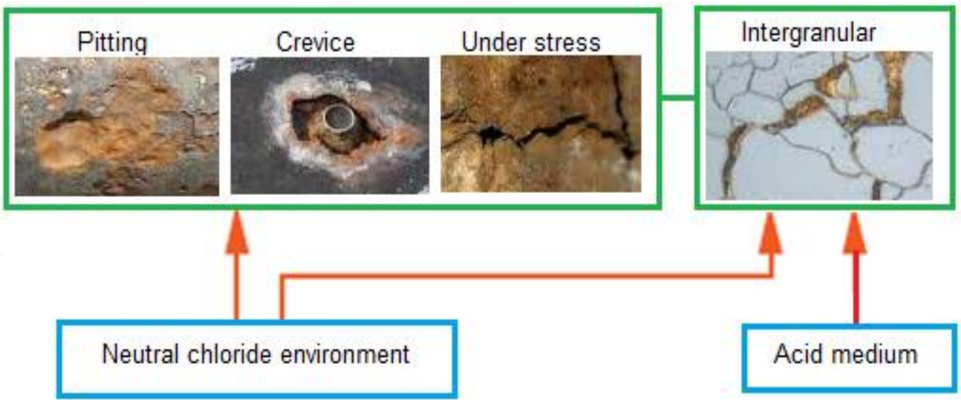


Fig. 4 Corrosion of stainless steel.

Most popular failure pressure methods for pressurized vessels with active corrosion defects are ASME B31G [5, 6] and modified ASME B31G [5, 7], DNV-RP-F101 [8, 9], SHELL-92 [10, 11], RSTRENG [12, 13], PCORRC [14, 15], LG-18 [16, 17], Fitnet FSS [18, 19] and Choi criteria [20, 21].

The present work was tantamount to predict the failure of MIC storage tanks due to chlorine induced corrosion and temperature developed in exothermic reaction of MIC with water. The failure analysis was investigated using modified ASME B31G criterion based on Taguchi design of experimentation [22]. The results were further cross-checked with those computed from ASME B31G, DNV-RP-F101, SHELL-92, PCORRC, LG-18, RSTRENG, Fitnet FSS and Choi criteria.

II. MATERIAL AND METHODS

The material of pipes was stainless steel. In the present study, the dimensions of the test tank were 200 mm outer diameter and 6000 mm length. The chosen control parameters are shown in table 1. The control factors were assigned to the various columns of an orthogonal array (OA), L9 is given in table 2. The corrosion pits were modeled as a single crack (because of their near proximity) as given in table 3. The dimensions of crack are given in Fig. 5.

Table 1. Control factors and their levels

Factor	Symbol	Level–1	Level–2	Level–3
Temperature derating factor	A	0.6	0.8	1.0
Length of crack, mm	B	200	250	300
Depth of crack	C	40%t	50%t	60%t
Type of steel	D	AISI 304	SAE J405	A516 G 70

where t is pipe thickness.

Table 2. Orthogonal Array (L9) and control factors

Treat No.	A	B	C	D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

Table 3: Interaction criterion of cracks

Interaction criterion	Dimensions of crack after interaction
$c_1 + c_2 \geq d$	$2c = 2c_1 + 2c_2 + d$
	A = max[a_1, a_2]

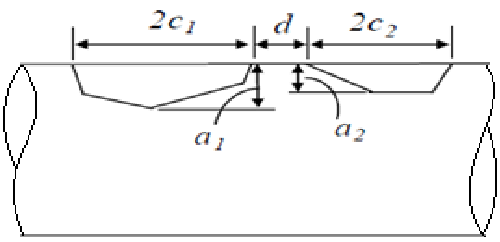


Fig. 5 The crack dimensions.

The Tresca and von Mises criteria were applied to investigate the failure analysis. In principal stress space (σ_1, σ_2, σ_3), the Tresca criterion can be expressed as

$$\tau_{max} = \max\left(\frac{|\sigma_1 - \sigma_2|}{2}, \frac{|\sigma_2 - \sigma_3|}{2}, \frac{|\sigma_1 - \sigma_3|}{2}\right) = \frac{\sigma_{YS}}{2} \quad (1)$$

where τ_{max} is the maximum shear stress and σ_{ys} is the yield strength in tension.

The von Mises criterion can be expressed by the principal stresses in the form:

$$\tau_{vm} = \sqrt{\frac{1}{6}[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2]} = \frac{\sigma_{YS}}{\sqrt{3}} \quad (2)$$

where τ_{vm} is the von Mises effective shear stress.

Chloride pitting initiated on tank inner diameter (ID) surfaces was observed (Fig. 6). Acidification was made by adding hydrochloric acid at different temperatures. The test period was 72 hours depending on the standard. A critical value of pH exists, under which the corrosion rate sharply increases. Of the steel Cr18Ni9, the critical pH value is 1.5 [23]. The temperature rise is mitigated through heat transfer from the gas to the cylinder walls. The depth of corroded pits was measured using pit depth gage (Fig. 7). Corroded pits in a sample coupon are shown in Fig. 8.

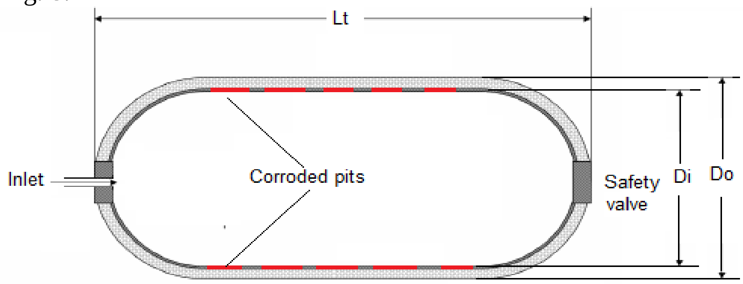


Fig. 6 The storage tank for experimentation.

Fig. 7 The pit depth gage.

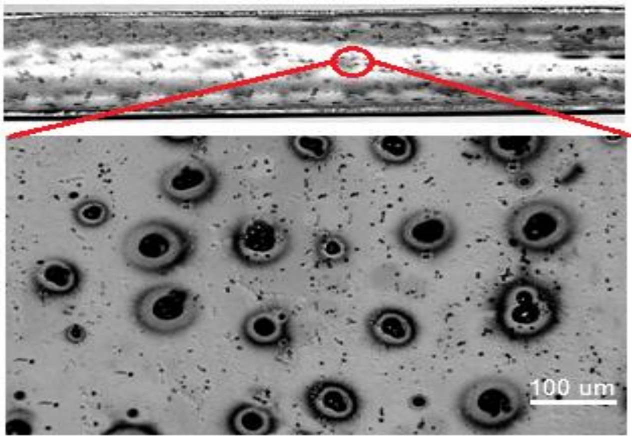


Fig. 8 Corrosion pits in the test specimen.

III. RESULTS AND DISCUSSION

The bursting pressures were computed from PCORRC, ASME B31G, modified ASME B31G, DNV-RP-F101, SHELL-92, RSTRENG, Fitnet FSS, LG-18 and Choi criteria are given in Fig. 9. The lower limit represents the results computed from ASME 31G criterion and the upper limit stands for the results calculated from RESTRENG criterion.

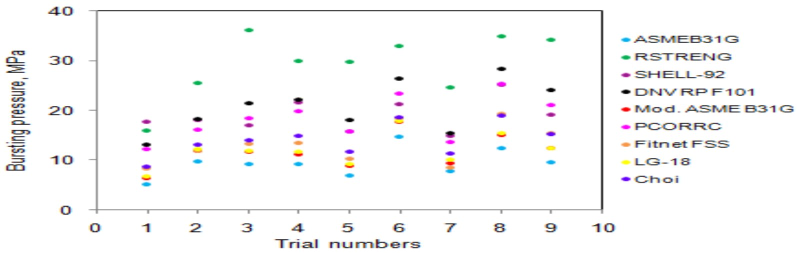


Fig. 9 Bursting pressures computed from different methods.

3.1 Influence of temperature degrading factor, crack dimensions and tube material on bursting strength

Table 4 gives the ANOVA (analysis of variation) summary of bursting pressure. All the process parameters could satisfy the Fisher's test at 90% confidence level. The temperature degradation factor (A), all by itself contributed to a two-third of the total variation observed. Crack length (B), crack depth (C) and type of steels (D) shared, respectively, 4.01%, 19.56% and 15.62% of the total variation in the bursting pressure.

Table 4: ANOVA summary of the bursting pressure based on modified ASME 31G criterion.

Source	Sum 1	Sum 2	Sum 3	SS	v	V	F	P
A	22.44	33.34	40.99	57.93	1	57.93	13984.72	60.82
B	29.49	33.68	33.59	3.82	1	3.82	922.18	4.01
C	37.39	32.54	26.83	18.63	1	18.63	4497.42	19.56
D	26.80	406.20	96.76	14.88	1	14.88	3592.14	15.62
e				0.0166	4	0.0041	1.00	-0.01
T	116.12	505.76	198.17	95.24	8			100

Note: SS is the sum of square, v is the degrees of freedom, V is the variance, F is the Fisher's ratio, P is the percentage of contribution and T is the sum squares due to total variation.

Figure 10a shows in the dependence of bursting pressure on the temperature degrading factor. As the degrading factor de-creased the pressure needed to burst the pipe would also de-crease. Degrading factor is temperature dependent. It decreases with the increase of temperature. The temperature would build up over the exothermic reaction of MIC in the presence of water. The storage tank with no leakage contains a fixed mass. For a fixed mass of gas in the storage tank, at a constant volume, the pressure (P) is directly proportional to the absolute temperature (T). The gas pressure increases by the collision of the moving gas particles with each other and against the walls of the storage tank. The effect of crack length was very slight on the bursting pressure (figure 10b). This implies that the interaction effect of corrosion pits was very low on the bursting pressure. If the crack depth increased, the pipe could fail even at low bursting pressure (figure 10c). In presence of chloride ions, pits grow by an autocatalytic mechanism. Pitting corrosion of stainless steel is illustrated in the figure 11. AISI 304 failed at low bursting pressure while SAE J405 and ASTM A516 grade 70 required high bursting pressure to fracture (figure 10d).

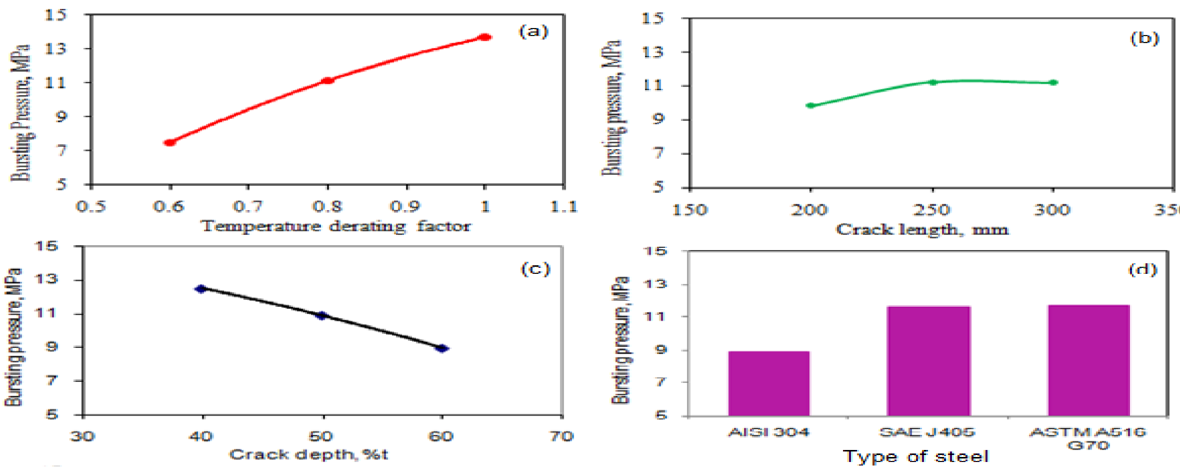


Fig. 10 Effect of process variables on bursting pressure.

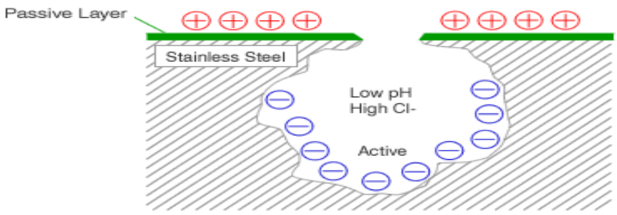


Fig. 11 Pitting corrosion mechanism.

Table 5: ANOVA summary of the Tresca criterion

Source	Sum 1	Sum 2	Sum 3	SS	v	V	F	P
A	147.02	199.29	244.93	1600.27	1	1600.27	1760779.5	55.02
B	190.30	201.54	199.40	23.74	1	23.74	26121.2	0.82
C	237.09	194.27	159.88	997.49	1	997.49	1097539.8	34.3
D	173.13	14531.00	591.24	286.85	1	286.85	315621.5	9.86
e				0.00364	4	0.00091	1.00	0
T	747.54	15126.09	1195.45	2908.35	8			100

3.2 Failure criteria

Table 5 and 6 give the ANOVA summary of the Tresca criterion and von Mises criterion respectively. Even though all the process parameters could assure the Fisher's test at 90% confidence level, only temperature degrading factor and crack depth had leading roles in the total variation of Tresca and von Mises criteria. The degrading factor (A) and crack depth (C) contributed, respectively, nearly 55.02% and 34.30% of the total variation in the Tresca and von Mises criteria. The type of stainless steel (D) put in 9.86% of the total variation in the Tresca and von Mises criteria. The crack length was insignificant in the variation of Tresca and von Mises criteria.

Table 6: ANOVA summary of the von Mises criterion

Source	Sum 1	Sum 2	Sum 3	SS	v	V	F	P
A	254.64	345.18	424.23	4800.81	1	4800.81	21193252	55.02
B	329.61	349.07	345.37	71.2	1	71.2	314314	0.82
C	410.65	336.48	276.92	2992.47	1	2992.47	13210306	34.3
D	299.87	43593.01	1024.05	860.55	1	860.55	3798912	9.86
e				0.00091	4	0.00023	1.00	0
T	1294.8	44623.74	2070.58	8725.03	8			100

The maximum shear stress as a function of temperature de-grading factor is shown in figure 12a. The maximum shear stress at failure decreased with decrease of degrading factor (or increase of temperature). The crack length (or integration of corrosion pits) did not influence much on the failure shear stress (figure 12b). The failure shear stress decreased with increase of crack depth (or depth of corrosion pits) as revealed in figure 12c. The failure shear stress induced in the AISI 304 was smaller than those of AE J405 and ASTM A516 grade 70 steels (figure 12d).

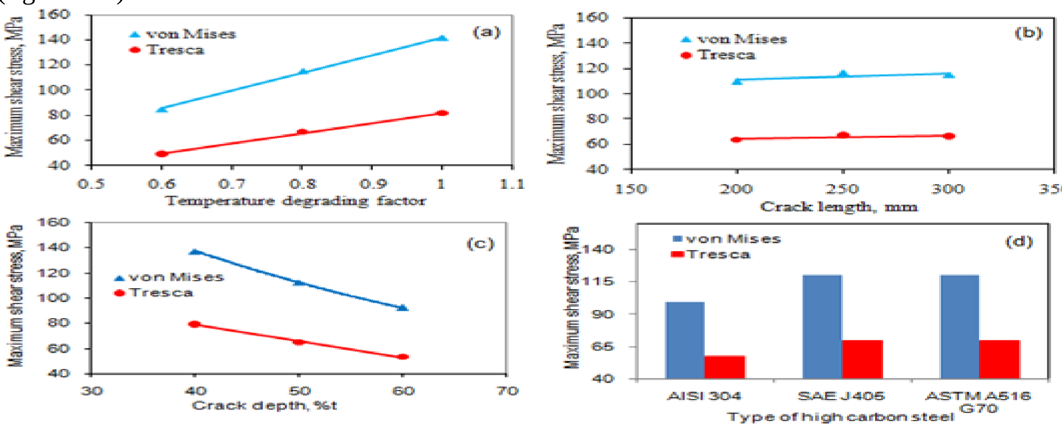


Fig. 12 Effect of process variables on failure criteria.

The stainless steel 304 alloy contains 18% Cr, 8% Ni and 2% Mn. This alloy has an austenitic structure. The stainless steel 405 alloy contains 13% Cr, and 1% Mn. This alloy has a martensitic structure. The steel ASTM A516 grade 70 contains 0.2%C, 1.05% Mn and 0.32% Si. The depths of corroded pits of all trials tested experimentally are presented in figure 13. The average of three maximum depths (green continuous line) was used in the present investigation to estimate the bursting strengths. Fig. 14a depicts the corroded pit induced in AISI 304 stainless steel subjected to testing conditions of trial 9. Fig.14b represents the corroded pit developed in SAE J405 stainless steel subjected to testing conditions of trial 6. Fig. 14c reveals the corroded pit produced in ASTM A516 grade 70 steel subjected to testing conditions of trial 8. For trials 6, 8 and 9, the average maximum depths of corroded pits were, respectively, 2.43 mm, 2.54 mm and 3.11 mm. Fig. 15 shows the interaction among local corrosion pits forming chainlike flaws.

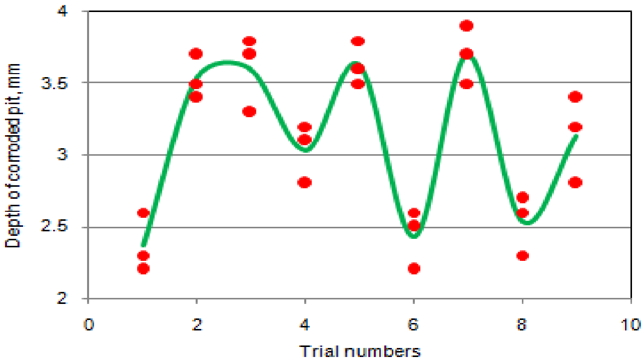


Fig. 13 Depths of corroded pits.

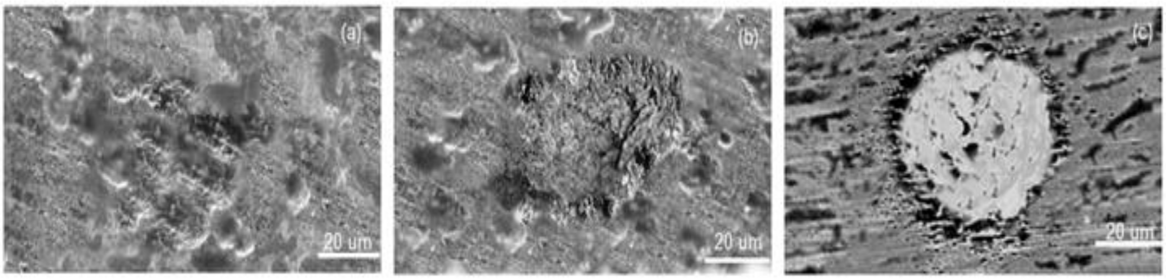


Fig. 14 SEM images of corrosion pits: (a) AISI 304, (b) SAE J405 and (c) ASTM A516 G70 steels.

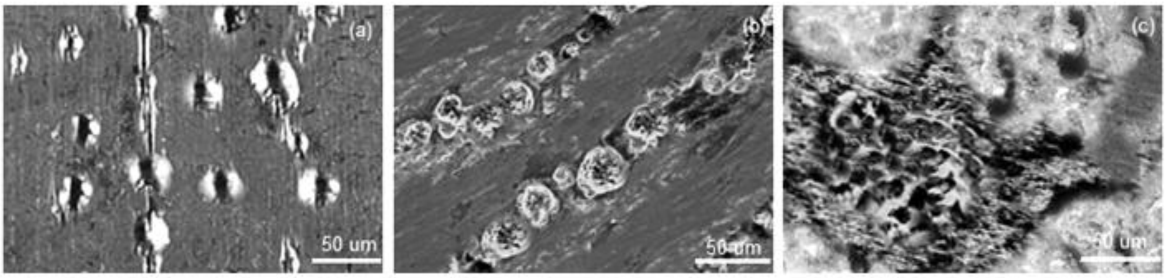


Fig. 15 Interaction of local corrosion pits: (a) AISI 304, (b) SAE J405 and (c) ASTM A516 G70 steels.

As observed from F. 16a, only pipes 6, 8 and 9 were burst under von Mises failure criterion even though all the pipes were found safe under the Tresca criterion (Fig. 16b). The Wei-bull criterion was utilized to predict the reliability of all the tanks. The least reliable criterion was ASME 31G and the most dependable criterion was RESTRENG (Fig. 17). For 80% of reliability the maximum bursting pressures were, respectively, 5.52 MPa and 19.77 MPa for ASME 31G and RESTRENG criteria. For test conditions 6, 8 and 9 bursting pressures were 14.16 MPa, 16.78 MPa and 12.39 MPa at danger level of reliabilities of 0.063, 0.013 and 0.145 according ASME B31G criterion.

The reasons for the failure of tanks were due to:

- decreased temperature derating factor (i.e., increase of temperature due to exothermic reaction and consequently increase of pressure in the tank),
- increased depths of corroded pits (the depth of corroded pits depends upon the resistance to chlorine induced corrosion).

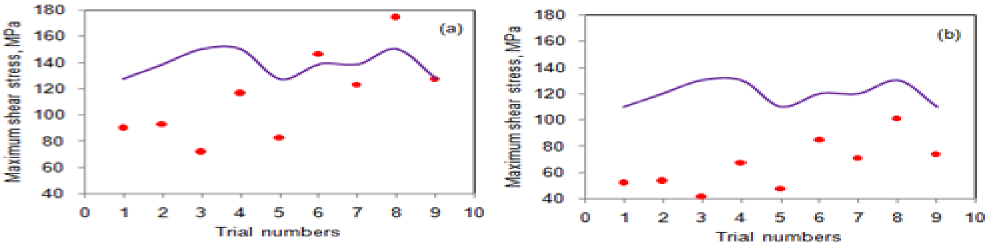


Fig. 16 Failure criterion of all pipes: (a) von Mises and (b) Tresca.

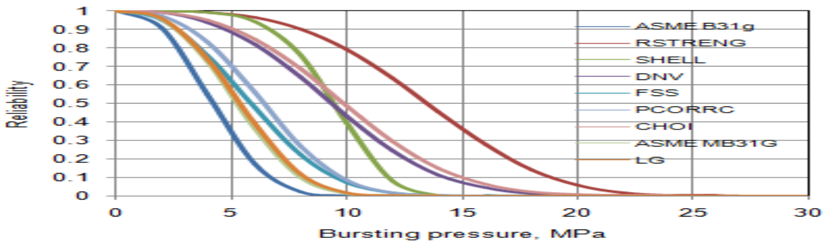
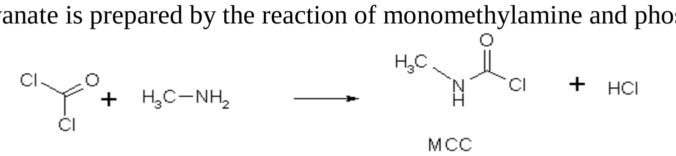
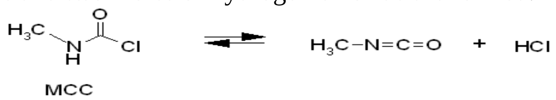


Fig. 17 Weibull failure criterion of all pipes.

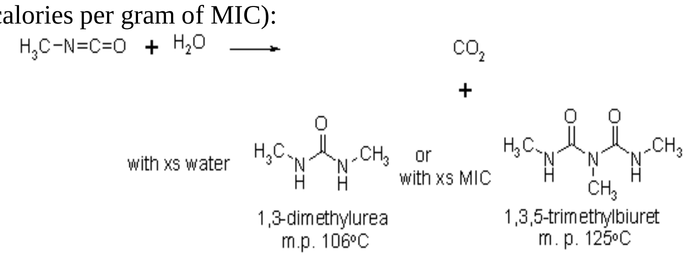
It is better to understand the exothermic reaction, rise of temperature and pressure and corrosion mechanism. Methyl isocyanate is prepared by the reaction of monomethylamine and phosgene as follows:



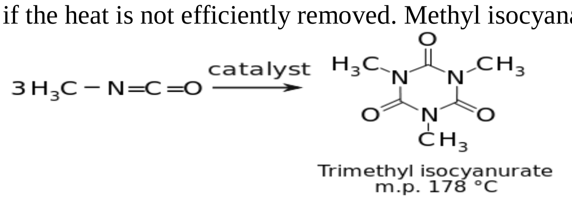
A mixture of methyl isocyanate and two moles of hydrogen chloride are formed.



Methyl isocyanate reacts exothermically with water and forms 1,3-dimethylurea and carbon dioxide with the evolution of heat (325 calories per gram of MIC):



Half of Methyl isocyanate is consumed in 9 min At 25 °C, in excess water [24]. Methyl isocyanate boils rapidly if the heat is not efficiently removed. Methyl isocyanate also reacts with itself to form a trimer.



The penetration of chloride ions is the main contributing factor for inducing corrosion of the steel. The conditions for the occurrence of corrosion are elevated chloride concentration, presence of moisture and oxygen and electrical conductivity. If the pH is greater than 12.5, the steel gets corroded. The corrosion mechanism is as follows (figure 10):

Decomposition of passivity layer: $Fe^{2+} + 2Cl^- \rightarrow FeCl_2$

Corrosion of steel: $Fe \rightarrow Fe^{2+} + 2e^-{}_2$ (reduction)

$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$ (oxidation)

Formation of rust: $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

$2Fe(OH)_2 + \frac{1}{2}O_2 + H_2O \rightarrow Fe_2O_3.3H_2O$ (rust)

The oxidation of iron atoms in steel reduces of steel cross section owing to the "rusting away" which may lead to inadequate areas of steel necessary for carrying pressure on the inner walls of the tank.

AISI 304, SAE J405 and ASTM A516 G70 steels are subjected to crevice corrosion and pitting corrosion. They make a range of incubation times. AISI 304 stainless steel can perform well where chloride levels are small. When chloride levels are high, the performance of AISI 304 stainless steel is poor. For SAE J405 and ASTM A516 G70 steels, the incubation time for non-uniform attack in chloride containing environments is very short, often only hours or a few days. Tanks made of SAE J405 and ASTM A516 G70 steels were failed due to corrosion even though they have good strength. Yield strengths of SAE J405 and ASTM A516 G70 steels are, respectively, 276 MPa and 260 MPa. The test conditions 6 and 8 represents SAE J405 and ASTM A516 G70 steels respectively. Even though AISI 304 stainless steel has yield strength of 215 MPa, the corrosion rate was slower as those of SAE J405 and ASTM A516 G70 steels.

The causalities of Bhopal gas disaster might be caused by toxic characteristic of Methyl isocyanate. The threshold limit value of MIC set by the American Conference on Government Industrial Hygienists is 0.02 ppm. Over 12 ppm level of expo-sure, MIC can result in pulmonary or lung edema, emphysema and hemorrhages, bronchial pneumonia and death [25].

IV. CONCLUSIONS

The bursting pressure of the storage tank was highly dependent on the temperature derating factor and the crack depth. The bursting pressure is decreased with the increase of crack depth and the decrease of degrading factor (or increase of temperature). The rise of temperature in the storage was caused by exothermic reaction MIC with water. The rise in temperature increased the pressure in the storage tank. The von Mises criterion was very near the failure pattern of the tanks. The failure criteria would satisfy the reliability results obtained from the Weibull criterion and ASME 31G criterion used for the estimation of the bursting strength. The reasons for the failure of experimental storage tanks used in the present work would satisfy the causes for the leakage of Methyl isocyanate gas and failure of the storage tank during the Bhopal gas disaster.

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