

ORIGINAL ARTICLE

Analysis and Simulation of Severe Accidents in a Steam Methane Reforming Plant

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ABSTRACT

Severe accidents of process industries in Iran have increased significantly in recent decade. This study quantitatively analyzes the hazards of severe accidents imposed on people, equipment and building by a hydrogen production facility. A hazard identification method was applied. Then a consequence simulation was carried out using PHAST 6.54 software package and at the end, consequence evaluation was carried out based on the best-known and different criteria. Most hazardous jet fire and flash fire will be occurred in desulfurization and reformer units respectively. The most dangerous vapor cloud explosion will be caused by a rupture in desorfurizing reactor. This incident with an overpressure of 0.83 bars at a distance of 45 m will kill all people and will destroy all buildings and equipments that are located at this distance. The safety distance determined by TNO Multi-Energy model and according to the worst consequence is equal to 260 m. Vapor cloud explosion will have the longest harmful distance on both human and equipment compared to jet fire and flash fire. Atmospheric condition will have a significant influence on harmful distance, especially in vapor cloud explosion. Therefore, the hydrogen production by natural gas reforming is a high-risk process and should always be accompanied by the full implementation of the safety rules, personal protection and equipment fireproofing and building blast proofing against jet fire and explosions.

Keywords: Hydrogen, Accident Prevention, Chemical Hazard Release, Fires, Explosions

INTRODUCTION

The fast progress of hydrogen technologies and vast investment on its production, storage and transportation are accelerating the early transfer to a hydrogen economy [1, 2]. Severe accidents involving hydrogen utilized in industries as well as in other applications in the past [1, 3-6], essentially requires a high level of safety in hydrogen facilities for preventing such accidents in the future.

The level of precautions that have been taken or

should be improved to prevent fatality, injury and destruction of probable accidents in hydrogen process industries need to be assessed using a reliable technique. Different techniques have been introduced for such a purpose. They include qualitative, semi-quantitative and quantitative methods. Among them, consequence analysis is a quantitative method that can be used to assess the hazardous consequences of the accidents in process industry [7].

Consequence analysis is an integral part of a risk assessment process, which gives an estimation of the damages that a probable accident may bring to the properties and human beings. This method enables not only safer design of a hydrogen infrastructure but also

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early adoption of hydrogen technologies, eliminating unnecessary additional costs to deploy them [7]. The trend towards larger and more complex units has brought about the need for consequence analysis of hydrogen process plants.

In the process of consequence analysis, the consequence modeling is the most important part and has four steps. The first step is source models, which provide how materials are discharged from the process. The source models provide necessary data to describe the rate, total quantity and the state of discharge. The state of material discharged from the process may be liquid, vapor or slash (a combination). In the second step, dispersion models are subsequently used to provide how the material is transported downwind and dispersed to some concentration levels. The third step is the modeling of the predictable incident outcomes. The incidents include jet fire, flash fire and vapor cloud explosion (VCE). In its final step, the application of these results along with appropriate probit models is used to evaluate the effects of the studied scenarios on the exposed environment and human beings [7, 8].

In the process of hydrogen production through Steam Methane Reforming (SMR) in large scales, the presence of highly explosive and flammable materials such as methane and hydrogen along with high purity in large volumes can potentially cause large-scale incidents that may harm humans, properties or the environment. To consider these perspectives, the consequence analysis method applied should identify and evaluate the hazardous points and incidents of the SMR plant. Not many consequence analyses have been applied to the hydrogen production facilities. In 2010, Zhiyong *et al* studied the harmful distances of a gaseous hydrogen refueling station [9]. The gaseous hydrogen refueling station seems to have less severe consequences than hydrogen generators that use natural gas reforming process.

Process description

In this large plant, the hydrogen is produced using natural gas reforming method. The process is based on the catalytic endothermic conversion of methane to give hydrogen and carbon monoxide. Carbon monoxide is then converted to carbon dioxide. Finally, hydrogen is purified by separation (Fig. 1). More details may be found in Zarei (2012) [10] and Jafari et al. (2012) [11].

The hydrogen generator with 65 m in length and 25 m in width is located in an industrial plant with 490 m length and 360 m width. Five vulnerable targets neighboring the hydrogen plant including workers in packaging industries, customs warehouses, Paxan Co and IAC center as well as the vehicles passing the highway will be exposed to the proposed accidents of this hydrogen generation facility. In addition, there are several potential vulnerable targets inside the plant, such as large vegetable oil storage tanks, office buildings, vegetable oil transport train, natural gas transferring pipeline and central restaurant.

The objective of present study was the comprehensive and quantitative consequence analysis of severe accident on a steam methane reforming plant in Tehran.

MATERIALS AND METHODS

The consequence analysis scheme followed in present study involves four steps [7] shown in Fig. 2. They are described in the following.

Identification of hazards and selection of scenarios

The identification of vulnerable areas and specific hazards is of fundamental importance in consequence analysis. Different methods are required at different



Fig 1. The block diagram of hydrogen generation process by steam methane reforming

Table 1. Credible scenarios and their mass flow rate in studied plant

Location	Scenario No.	Leak size (mm)	Mass flow rate (kg/s)
	S-1	5	0.06
Desulfurization reactor	S-2	30	0.25
	S-3	300	225
	S-4	5	0.05
Heat exchanger	S-5	30	0.20
	S-6	300	183
	S-7	5	0.07
Reformer (furnace)	S-8	30	0.30
	S-9	300	268
Hudrogan purification	S-10	5	0.02
abaarbarra	S-11	30	0.07
absorbers	S-12	300	59
	S-13	5	0.02
Purge gas buffer	S-14	30	0.07
	S-15	300	62

stages of a project to identify hazards. One of the first systematic methods of hazard identification used in chemical industry is HAZID method [12]. Scenarios begin with an incident, which usually result in the release of containment of material from the process. Typical incidents might include rupture, break of a pipeline and a hole in a reactor or pipe [12]. For this purpose, all necessary information for hazard identification was collected from the production process. The process hazards were identified by application of HAZID technique. Finally, after screening low consequence scenarios the most credible ones in the selected hydrogen plant were determined as summarized in Table 1. The pipe diameters used in this plant were from 150 to 300 mm. On this basis, all scenarios were categorized in three groups including small (5 mm) holes, medium (30 mm) holes and Fullbore rupture (300 mm). A total of 15 scenarios were modeled and their consequences were quantitatively assessed based on this categorization. In this study, the likelihood of these events happening was not considered.

Consequence simulation

The consequence modeling input data and assumptions shown in Table 2 were used for the consequence modeling of the hydrogen generation facility. The data in Table 2 along with those in Table 1 describe the rate, total quantity and the state of discharged material in each scenario. The consequence models employed in the study are those of the Process Hazard Analysis Software Tool (PHAST) developed by DNV. PHAST is professional software used for consequence modeling in chemical process risk assessments [3, 10-11]. This software was specifically validated for the release of hydrogen [14].

The representative atmospheric conditions in present study comprise average wind speed, atmospheric stability, ambient temperature and humidity. All of the credible scenarios were modeled in two different atmospheric conditions corresponding to day (springsummer, D5) and night (fall-winter, F2), (Table 3).

Jet fires, flash fires (VCF) and vapor cloud explosions (VCE) were considered as the major outcomes of incidents in a hydrogen generation facility.



Fig 2. Flow diagram of the procedure used for consequence analysis [7]

	Process condition		Material	M - 10/		
Scenario location –	P(bar) T(°C)		composition	Molar%	Mixture LFL (ppm)	
Desulfurization reactor	25	200	NG	85		
			CO_2	0.1	40211	
			H_2	5		
Heat exchanger	27	530	NG	52		
			H_2O	46	73711	
			H_2	2		
Reformer (furnace)	35	300	CH_4	5		
			H_2	60		
			CO_2	8	61124	
			H_2O_2	25		
			CO	2		
Hydrogen purification absorbers (HPA)	15	40	H_2	99.99	81517	
Purge gas buffer	4	35	CH_4	12		
			H_2	34		
			$\tilde{O_2}$	40	40000	
			CO	13		

Table 2. Consequence modeling input data and assumptions

The best-known models were used to estimate the effects of these outcomes (Table 4) [7-8].

Finally, in last stage by using appropriate probit models and estimating the population distribution the number of fatalities was estimated. In a jet and flash fire, the fatality is caused by the radiation intensity while in VCE it is caused by the overpressure. For estimating the number of fatalities from jet fires and VCEs, probit models were applied but in flash fires it was assumed that all people exposed to low flammability limit will die [12-13].

Effect models convert these incident's specific results into effects on people (injury or probability of death) and structures. Probit equations are commonly used to quantify the expected rate of fatalities of jet fire for the exposed population. These equations expressed as [7, 15]:

$$p = K_1 + K_2 \times Ln(V)$$
(1)
 $K_1 = -14.9, \quad K_2 = 2.56, \quad V = t.q^{4/2}$

Where *p* is the probit variable, K_1 and K_2 are constants and *V* represents the dose of hazard (radiation), t is exposure time (sec) that was assumed 20 s for this case and q is radiation power (kW/m²).

One of the most commonly used probit models which determines the fatalities of outdoor persons from the blast overpressure is the Hurst, Nussey and Pape (1989) probit model [7, 16]. The relationship of this probit variable is generally quoted as:

$$p = 1.47 + 1.35Ln(Pressure)$$

Where: pressure is in psi. A useful expression for converting of probit variable (p) to probability of fatality (P) is given by [15]:

(2)

$$P = 0.5 \left[1 + \frac{p-5}{|p-5|} erf\left(\frac{|p-5|}{\sqrt{2}}\right) \right]$$
(3)

In the case of Flash Fire, the above equation has only two values of 1 and 0 for the areas in which gas concentration is above and below flammable concentrations respectively. Combining the above equation and population distribution data will give the number of fatalities in all incident outcomes by using the following relationship [8, 15]:

$$N = \int_{A} P \times dA \tag{4}$$

Where N is the number of fatalities, P is uniform population distribution and A is the area affected by the incident. In this study, the probability of fatalities was considered to be 1 in these equations, In other words, only the area where the probability of death is 1 was considered.

Consequence assessment Jet fire

The thermal consequences of Jet fires were assessed using the radiation intensity of each jet fire from table 5 [7-8].

Flash fire

The consequences of flash fires were determined using their Lower Flammable Level (LFL) as the following [7, 12].

• LFL zone: People who are in direct contact with the flames will die.

Atmospheric parameter	Day	Night
Wind velocity (m/s)	5	2
Atmospheric stability class	D	F
Ambient temperature (°C)	28.33	2.77
Relative humidity (%)	19.35	67.27

Table 3. Atmospheric conditions corresponding to day and night

Table 4. Models used for estimating the harm effect of different incident outcomes [7]

Incident outcome	Model		
Flash Fire	Eisenberg, Lynch and Breeding model (vulnerability model)		
Jet Fire	Cone model		
VCE	TNO Multi-Energy model		

Table 5. Effects of thermal radiation from Jet fires (duration 20s) [7, 16]

Radiation intensity (kW/m ²)	Observed effect
Λ	Sufficient to cause pain to personnel if unable to reach cover within 20s. However second degree
4	burns is likely; 0% lethality
12.5	Minimum energy required for piloted ignition of wood, melting of plastic tubing
37.5	Sufficient to cause damage to process equipment

• ¹/₂LFL zone: People who are in this zone will suffer from inhalation effects and diseases

Vapor cloud explosion

The consequences of VCEs were determined using the overpressure intensity of each VCE according to the following [3]:

Persons indoors

The purpose of this model is to determine the fatality probability of the occupants of buildings subject to blast loading. This is dependent on the level of blast loading, the type and construction of the building. The Center for Chemical Process Safety (CCPS) has published relationships between the probability of fatality for occupants and the level of blast overpressure for 5 different types of building [17-18]. In this study, only primary injury due directly to the blast wave overpressure was analyzed.

Property damage

This will enable authorities to take the economic risks to the properties, structures and businesses into account as part of any land use planning decision. Explosion overpressure level and its' damage effect on structures and corresponding to fatality are shown in Table 6 [16, 18].

RESULTS

Consequence modeling revealed that the main hazards of hydrogen generation by natural gas reforming are the vapor cloud explosion (VCE), jet fire and flash fire, which are mainly due to the physical and chemical specifications of hydrogen and other material involved in hydrogen generation cycle. Therefore, consequences of VCE, flash fires and jet fires for different scenarios were modeled. The results showed that the VCE, flash fire and jet fire caused by small and medium holes size (e.g. 5 & 30 mm holes) would not have any fatality in day and night. Therefore, the consequence evaluation results of these scenarios have not been shown in Table 7. This table shows the fatality of VCE, jet fire and flash fire caused by a fullbore rupture at studied units in day and at night.

According to the results, a jet fire and VCE set by a full-bore rupture at desulfurization reactor will have the highest fatality of 26 persons among all scenarios. A flash fire set by a full-bore rupture at reformer will have the highest fatality of 8 persons in day. The VCE caused by a full-bore rupture at desulfurization reactor would have the highest fatality of five persons. The fatality of

Pressure (bar)	Description of Damage	Fatality Outdoor (%)	Fatality Indoor (%)
0.01	*Safe Distance	-	-
0.17	Moderate Damage	-	5
0.34	Severe Damage	15	50
0.83	Total Destruction	50	100

Table 6. Explosion overpressure level and damage effects on structure and people

*Threshold for glass breakage

Table 7. Lethality of accidents from hydrogen generation facility in day and at night

Consequence		Jet Fire		Flash Fire		VCE	
Scenario Location		Day	Night	Day	Night	Day	Night
Desulfurization Reactor		26	10	6	2	5	2
Heat Exchanger		14	6	2	1	2	0
Reformer		15	6	8	3	3	0
Purification Absorbers		20	6	3	1	4	1
Purge Gas Buffer		1	0	0	0	0	0

all incidents caused by a full-bore rupture at night would be less than them in day (Table 7).

Jet fire

Flash fire

In the case of VCF (flash fire) only two values of 1 and 0 are considered for the areas in which gas concentration is above or below the flammable concentrations respectively. When the flammable gas reaches to a source of ignition, there will be flash fire. Flash fire flames will cause extreme damages to the equipment's as well as serious injuries to the employees. In its worst case, especially at the maintenance time, it can claim lives. People within the flash fire envelope (the lower flammable limit, LFL) will be killed because of extremely radiation doses [7]. Flash fire effect zone diagrams show that there are flammable concentrations of material in the plant area. The analysis of radiated distance of flash fire on equipment and people showed that the worse case is related to full-bore rupture of reformer and desulfurization reactor respectively (Fig. 3). The most hazardous flash fire will occur in the reformer unit. In this scenario, the concentration of the material released in LFL zone (area of 1505 m²) will be from 61125 ppm down to 40000 ppm as it goes further from the incident point. The concentration of the material released in this scenario is high enough to kill all the people (8 people) in the area (Table 7).

The radiated distance of different intensities from a jet fire caused by a full-bore rupture at studied units is shown in Fig. 4. The longest radiated distance of different intensities belongs to a jet fire caused by a full-bore rupture in desulfurization reactor. The results show that if a jet fire is set by a full-bore rupture in desulfurization reactor then the radiation level at a distance of 135m will be high enough to cause damage to process equipment. This is the highest harm full distance, which has enough radiation intensity to destroy all equipment in this area.

Vapor cloud explosion

The distance imposed by different levels of overpressure from a VCE caused by a full-bore rupture in different units is shown in Fig. 5. The results showed that desulfurization reactor would impose the largest area to different overpressures than other units. In case of a VCE caused by a full-bore rupture in desulfurization reactor, the safe distance from the rupture will be 260 m at nights and 250 m during the days. This distance is safe for other scenarios studied in present work. The shortest distance imposed by different levels of overpressure belongs to the VCEs caused by a full-bore rupture in purge gas buffer.



Fig 3. Distances imposed by flash fire in day and night at different units

Average Harmful Distance

A further analysis was performed based on IGC harmful criteria to study the harmful distances for the people and the equipment at different parts of the hydrogen generation facility. For this purpose, average harmful distance of three groups of leaks (Table 1) from different units of hydrogen generation facility was considered. The results revealed that a VCE caused by a full bore rupture at desulfurization unit will lead to the longest average harmful distance both the people (160 m, Fig. 6) and for the equipment (123 m, Fig. 7). Reformer unit will have the longest harmful distances for the people and the equipment among all flash fires caused by a full-bore rupture at different studied units. Desulfurization unit will have the longest harmful distances both the people and the equipment when a jet fire is set by a full bore rupture at different units. The results showed that all incidents of VCE, flash and jet fires at all studied units except a flash fire in purge gas buffer will harm all facilities located in the hydrogen generation plant's boundary limit.

The studied hydrogen generation facility was located in an industrial complex with total area of 176400 m^2 and a total number of 1200 workers that 800 of them were working in day and 400 at night. The average population distribution was 5 and 2.5 persons per 1000 square meter in the day and night respectively. The term "Safety distance" will be used in this study to show the distance from the leaking point that will be safe. The safety distance was determined according to worst-case consequence. This indicates that the worst case may be used as a decisive consequence to determine the safe distances for hydrogen generation plant. Worst-case consequence is a VCE caused by a full-bore rupture at desulfurization reactor. The safety

distance was determined based on IGC criteria (harmful exposure threshold value to people and equipment e.g. 0.07 bar (160 m, Fig 6) & 0.2 bar (123 m, Fig. 7) of overpressure respectively) as well as Health and Safety Authority criteria (0.01bar, Threshold for glass breakage, Table 5).

Safety distance of hydrogen generation facility is equal to 260 m according to Fig. 3. This means that the distance of hydrogen unit's boundary limit to 0.01bar overpressure contour is equal to 260 m. Any activity or construction of any new unit is only allowed further than this interval. This distance covers not only the studied hydrogen generation plant but also neighboring premises.

DISCUSSION

Flash Fire

The results of present study showed that the most dangerous flash fire will occur in case of a full bore rupture in reformer unit. In this incident the concentration of the material released in LFL zone (in an area of 1505 m^2) will be from 61125 ppm down to 40000 ppm and enough to kill all the exposed people (8 persons) in the area. Gas detectors installed in the hydrogen generation facility will be able to detect the release of the gases, alarming the operators to take appropriate actions prior to any combustion. High process operating temperature (300 °C), the highest operating pressure (35 bar), high molar rates of flammable gases (60% H₂, 5% CH₄ and 2% CO) in reformer unit and large release hole size in studied scenario are the main reasons for having the most dangerous flash fires in this unit.

According to the guidelines for chemical process quantitative risk analysis issued by AIChE [7] the



Fig. 4. Thermally radiated distance from jet fires set by a full-bore rupture at studied units



Fig. 5. Distances imposed by different overpressure levels from VCEs caused by a full-bore rupture

probability of death outside the LFL zone is very low but flash fire is usually widely distributed and can reduce oxygen in the environment thus causing inhalation effects [7]. The analysis of radiation imposed on the equipment and people showed that the flash fires caused by a full bore rupture in reformer and desulfurization reactor will affect the longest distances of 182 m and 158 m respectively (Fig. 3).

Zhiyong et al. estimated that the harmful distance due to a flash fire of a hydrogen refueling station would be 47 m [9], which is far lower than the results of in present study. This could be due to large release leak size in present study (300 mm) compared to Zhiyong study (15mm). A valid comparison between the results of flash fire simulations in different meteorological conditions conducted by Yousefzadegan et al. in filter separators installed in gas pressure reduction stations showed that the flammable concentrations of natural gas will encompass the larger area in hot weather [19] which is almost consistent with the present study (Fig. 3).

Jet Fire

Results showed that the jet fire caused by a full-bore rupture in desulfurization reactor has the highest lethality (26 people) compared to the similar accident in other studied units. The jet fire set by a full-bore rupture in desulfurization reactor will also harm the largest area





Fig 6. Average harmful distance to people in different incidents caused by a full bore rupture at different Units



Fig 7. Average harmful distance for equipment in different incidents caused by a full-bore rupture at different units

as far as 249 m at night and 242 m during the day (Fig. 4).

The longest distance imposed by 37.5 kw/m^2 radiation is 28 m [7]. In the present study, even the purge gas buffer (with the shortest radiated distance) has a longer (42 m at night and 44m during the day) harmful distance for 37.5kw/m^2 radiation. The molar rates of different gases in this unit (e. g. 34% of H₂, 12% of CH₄ and 13% of CO) is the likely reason for longer harmful distances compared to the gas refueling station studied by Zhiyon et al.

According to the results maximum radiation from the worst jet fire may get up to 350 kw/m^2 in warm weather (e.g. spring & summer) and 370 kw/m^2 in cold

weather (e.g. fall & winter), that are much higher than the sufficient level to cause damage to process equipment (e.g. 37.5 kw/m^2 , Table 3), harmful exposure threshold value to the people (e.g. 9.7 kw/m^2) [20] and safe limit of radiation flux (e.g. 0.139 w/cm^2) [21].

Results showed that the jet fire travels further (except for desulfurization reactor, Fig 4) in windy condition (daytime) rather than calm condition (nighttime), which is consistent to the results of Zhiyong et al. [9].

Vapor cloud explosion

Considering the results of VCEs, it may be concluded that the explosions of vapors in

desulfurization reactor set by a full-bore rupture is the worst scenario. This incident has the most lethality rate (5 people, Table 7) and influences the largest area (Fig. 5). The worst case may be used as a decisive consequence for determination of safe distances in hydrogen generation facility. Severe consequence of VCE in desulfurization reactor is likely because of high purity of methane gas (85%) content in this unit.

The results also showed that the purge gas buffer unit has the lowest consequence of VCE caused by a full-bore rupture in this unit (Fig 5 and Table 7). Low molar combination of flammable substances (e.g. 12% CH_4 , 34% H_2 & 13% CO, Table 2) in this unit is likely the main reason for such a low consequence. Low process operating pressure (4 bar), and temperature (35 $^{\circ}C$) as well as having 40% of CO₂ in its material mixture are other likely reasons for low consequence in this unit.

Further modeling revealed that the explosions of vapor set by a full-bore rupture in desulfurization reactor and purification absorbers will lead to a peak overpressure of 0.3 bar. The peak overpressure from these scenarios (purification units and desulfurization reactor) is much more than the harm exposure threshold values adopted by IGC for the people (e.g. 0.07 bar) and the equipment (e.g. 0.2 bar) [20]. According to the results, large leaks expected to be in large size piping have longer effected distances mainly because of higher mass of released flammable material. Therefore, smaller pipe work is expected to be an effective mitigation measure to reduce the harmful distances.

Fig. 5 shows that the VCEs are more harmful at night rather than day. It is generally accepted that higher wind speeds (expected during the day Table 3) will help the dispersion of hydrogen and other flammable gases, leading to less harmful VCEs. Lower ambient temperature, higher relative humidity and stable atmosphere at night (Table 3) are also expected to help the hydrogen cloud to travel a longer distance nearby ground before it rises, leading to a stronger explosion at night rather than day.

The results of the present study well agree with the results of Zhiyong et al., which showed that a VCE in gaseous hydrogen refueling station has the longest harmful distance among all studied incidents [9]. Of course, the effected distances by VCE in present study are higher than those in Zhiyong et al. study. The application of suitable ventilation system, smaller release hole size, new installation, slight shift in temperature and no chemical reaction between materials released from a refueling station could had led to lower harmful distances compared to the present study.

Considering the overpressure of 0.01 bar as a safe criterion (Table 5), the safety distance of studied hydrogen generation facility during a vapor explosion is then 260 m. Any activity or construction of any new unit is forbidden near this area. This distance covers not

only the studied hydrogen generation plant but also neighboring premises.

According to this result, the application of gas detectors and emergency shutdown valve in hydrogen plant particularly in desulfurization reactor and reformer, elevating hydrogen piping and instrumentation as well as preventing from severe mechanical impacts, are the logical and practical measures for decreasing the probability and severity of potential accidents.

CONCLUSION

In present study, a new and comprehensive method for consequence analysis of probable accidents in a hydrogen generator facility, which uses natural gas reforming process, was applied. The main conclusion can be summarized as follows:

- 1. Consequence modeling revealed that the main hazards of hydrogen facility are the vapor cloud explosion (VCE), jet fire and flash fire, which jet fire will have most fatality and VCE will have the longest harmful distances for the people and the equipment among all accident at different studied units
- 2. Reformer unit will have the longest harmful distances and highest fatality among all flash fires at different studied units
- 3. Desulphurizing reactor unit will have the longest harmful distances and highest fatality among all jet fires and VCEs at different studied units
- 4. The jet fire's harm effect distances, increase with the growth of wind velocity (day) and in flash fire released material will encompass the largest area in hot weather (day), whereas VCE will have larger harm effect distances at night.
- 5. Safety distance of hydrogen facility based on the worst-case consequence is equal to 260 m, which is outside of hydrogen plant and related site plant boundary and this is high stakes imposed on neighborhood and public.

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