

ORIGINAL ARTICLE

Semi Quantitative Risk Assessment of a Hydrogen Production Unit

MOHAMMAD JAVAD JAFARI^{1*}, SHIMA SADAT LAJEVARDI², and IRAJ MOHAMMAD FAM³

¹Department of Occupational Health Eng, Faculty of Health, Shahid Beheshti University of Medical Sciences, Evin, Chamran freeway, Tehran, Iran; ²Department of Environment and Energy, Islamic Azad University, Science & Research Branch, Simon Bolivar Blvd, Poonak, Tehran, Iran; ³Department of Occupational Health Eng, Faculty of Health, Hamadan University of Medical Sciences, Hamadan, Iran.

Received February 8, 2013; Revised April 3, 2013; Accepted May 18, 2013

This paper is available on-line at <http://ijoh.tums.ac.ir>

ABSTRACT

The safety of hydrogen generation facilities is the main concern in their process operation. This study was conducted to identify the hazards and evaluate the risks of a hydrogen generation plant. For this purpose, PrHA (Process Hazard Analysis) was applied for hazard identification while LOPA (Layer of Protection Analysis) was used for risk assessment. The study was conducted in the hydrogen production unit of Behshahr Industrial Complex, Iran in 2011 and 2012. In the process of risk assessment, the records of the accidents and plant flow diagrams were studied. Then, the knowledge of the experts and operators were used through brainstorming prior to the application of LOPA technique. LOPA standard template was applied using PHA-Pro6 software. The initiating events, consequences, independent protection layers and probability of failure were determined for 16 scenarios in 7 nodes. The results showed that without the application of IPLs, the risks of 2 scenarios needed immediate action, 9 scenarios required action at next opportunity and 5 scenarios were operational. The application of IPLs would significantly decrease the risks. The study concluded that LOPA has sufficient credibility for semi quantitative risk assessment of high potentially hazardous plants.

Keywords: Hydrogen, Analysis, Risk, Assessment, Layer, Protection

INTRODUCTION

Nowadays, many countries are increasingly trying to establish the full commercialization of hydrogen technologies. They want to diversify energy resources and raise their economic growth with the development of environmentally friendly renewable energy sources. The industry's relationship with the material, dangerous products and manufacturing processes, usually have been the causes of many historical events. In the process of generating, storage, transmission and consumption of

hydrogen, the safety of the process is the main issue. US Energy Database Department has collected 190 hydrogen incidents from 1995 to 2011 which plots the image of the subject [1].

Different methods of risk assessment namely qualitative, semi-quantitative, and quantitative methods have been developed and successfully applied to the industry. Each of these categories has its own limitation when applied to the industry. Qualitative methods are usually applied to identify the hazards because they are not able to supply enough data for control plans. The man power required for their application is usually low and does not include complicated techniques. On the other hand, the quantitative methods are usually able to

* Corresponding author: Mohammad Javad Jafari, Email: jafari1952@yahoo.com, m_jafari@sbsmu.ac.ir

Table 1. The nodes and scenarios

Node	Node No	Scenario	Scenario Code
Feed compression unit	1	1. Failure or poor performance of 11424 control valve.	S1-1
		2. A puncture at compressor transducer.	S1-2
Feed pretreatment	2	1. The blockage of natural gas flow in reformer furnace tubes.	S2-1
		2. High temperature in compressor gas	S2-2
Reforming and Steam generation	3	1. Poor performance of 21434 control valve.	S3-1
		2. Failure of reformer furnace torches.	S3-2
		3. Failure of p10 pump	S3-3
High temperature conversion	4	1. The failure of iron oxide catalyst	S4-1
		2. Gas leakage from flange.	S4-2
Heat exchanger unit	5	1. water leakage from the flange or shell e22	S5-1
		2. Failure of cooling tower fan or recycle pump.	S5-2
Pretreatment of boiler feed water	6	1. Failure or poor performance of 44155 control valve	S6-1
		2. Excess steam input from the boiler to de-aerator	S6-2
Purification unit	7	1. High pressure in absorber towers.	S7-1
Hydro-swing system		2. A rupture at heat exchanger tubes e21	S7-2
		3. Lightning at purge gas buffer.	S7-3

supply enough data for hazard control plans but they are complicated and their application requires a lot of efforts. The semi-quantitative methods are between these two groups. They can be useful for some industries while in others may fail to supply enough information. Thus, their usefulness should be tested in each specific industry.

PrHA is one of the most important analysis techniques for system safety. It might be used in serious attempts to identify and determine the hazards of a system. In some cases, it can be considered as a basis for controlling risks of an altered system. This requires further studies and using more accurate techniques in the system and subsystem's analysis. PrHA was used to identify and determine the hazards in present study

LOPA (Layer of Protection Analysis) is a semi-quantitative method of risk analysis which is used for risk assessment of dangerous scenarios through estimating of the risk. In this method, quantitative values of the likelihood of the failures and the severity of the consequences are required for conservative estimates of risk [2]. Few studies using LOPA technique conducted in Iran had been limited to other industries rather than hydrogen related industries. In 2009, Shojaee applied the LOPA technique to nitroglycerin production units [3]. In 2010, Shirzadian applied this technique to the boilers in an oil and gas company in order to obtain the model of risk and review the safety of the system based on independent protective layers [4].

In comparison with other techniques, the application of LOPA in process industry is simple. ACCORDING TO Arthur Dowell (1998), LOPA technique is suitable for determining the safety integrity level of an instrumentation system and to review the independent protective layers [5]. In 2004, Sanders explained the low

public perception of safety in chemical plants and refineries. He proposed comparing the risk of these units with some of the more traditional jobs. He raised the prospect of many world-class safety processes which prevent the people, facilities, assets and environment. For proving this theory, he studied on the protective layers of chemical units, including process units [6]. Schupp et al. (2006) introduced a complex procedure that was called design for safety (Dfs). That technique was a combination of methods that are currently used with other techniques such as LOPA. That technique was investigated to determine the safety layers of a reactor unit [7]. In 2007, Fang et al. studied on safety risks and they focused on ethylene cooling compressor. They applied the ETA technique to determine the safety risks of the compressor [8]. Wei et al. (2008) applied semi-quantitative technique of LOPA to a hydroxylamine production unit to estimate the chemical reactive risks, determining the probability of failures, and the severity of consequences of scenarios [9].

Different versions of LOPA have been developed. Markowski and his colleagues introduced pfLOPA (fuzzy logic for piping risk assessment) technique for risk assessment of major accidents in pipelines carrying flammable materials. This technique consists of three main elements of FLS (fuzzy logic systems). They applied this technique in their study and compared the results of this approach with the results of the classical LOPA. This study was considered as a good introduction to the results of extensive research for Fuzzy LOPA technique in later years. These researchers introduced new approaches of LOPA technique that involves ExSys-LOPA, ExLOPA and Bow-tie model in LOPA. All of these models were based on fuzzy logic systems [10-13].

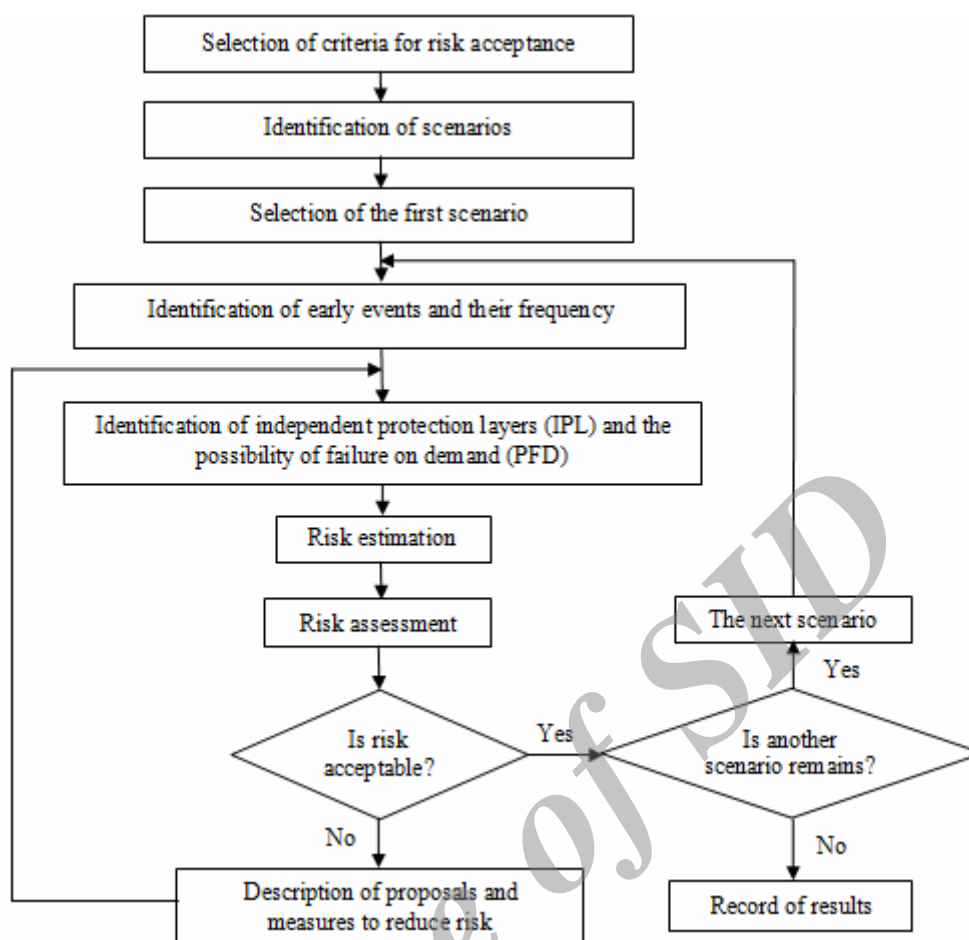


Fig 1. The flowchart of LOPA

Because the quantitative risk assessment methods are time consuming and costly thus, in many cases their application is limited. They require a great deal of information and efforts to determine the probability and consequence of hazards. Such information may not be available or difficult to be provided. LOPA technique is a semi-quantitative risk analysis method and it does not require very detailed information. However, it categorizes various scenarios of the risks and helps safety engineers to decide on risk mitigation. LOPA is used for simplification of risk assessment techniques in industrial accidents that are supported by the European Union [14].

The objective of this work was to identify hazards using PrHA (Process Hazard Analysis) technique, investigate the initial events and study the outcomes of different protective layers using LOPA method in a hydrogen generation unit that uses natural gas reforming process.

MATERIALS AND METHODS

The study was conducted in the hydrogen production unit of Behshahr Industrial Complex in 2011 and 2012.

The complex had 1200 (800 in day shift and 400 at night shift) employee. The hydrogen generator was a 1.676 Nm³/h fully automatic unit. It was operated and monitored through a process control center. The study consisted of two main parts including hazard identification and risk assessment. Hazards of the process unit were identified using PrHA. The LOPA was applied for risk assessments of the identified failures. Details may be found below.

Hazard Identification

As described earlier [15, 16], a multidisciplinary team of diverse expertise including Management, HSE Manager (as the team leader), Process Control Engineer, Instrumentation Engineer (Electrical Engineer), and Maintenance Technician were established to identify scenarios. The hydrogen production unit was divided into 7 nodes by the team based on the PFD (process flow diagram) of the plant. The more likely scenarios for each node (16 scenarios in total) were identified and coded as in Table 1. In next step, early events of each scenario and their likelihood were identified. IPLs (Independent protection layers) of each failure were also proposed.

Table 2. Severity numbers corresponding to the consequence categories

Severity	Description	Simplified Injury/Fatality Categorization
1	Low Consequence	Same as category 2
2	Low Consequence	PERSONNEL- Minor injury or no injury, no lost time; COMMUNITY- No injury, hazard or annoyance to public; ENVIRONMENT- Recordable, event with no agency notification on permit violation; FCILITY- Minimal equipment damage at an estimated cost less than 100000 US\$ and with minimal loss of production.
3	Medium Consequence	PERSONNEL- Single injury not severe, possible lost time; COMMUNITY- Odor or noise annoyance complaint from the public; ENVIRONMENT- Release that results in agency notification on permit violation; FCILITY- Some equipment damage at an estimated cost greater than 100000 US\$ and with no loss of production.
4	High Consequence	PERSONNEL- One or more severe injuries; COMMUNITY- One or more injuries; ENVIRONMENT- Significant release with serious offsite impact; FCILITY- Major damage to process area(s) at an estimated cost greater than 1000000 US\$ or some loss of production.
5	Very High Consequence	PERSONNEL- Fatality or permanently disabling injury; COMMUNITY- One or more severe injuries; ENVIRONMENT- Significant release with serious offsite impact and more likely than not to cause immediate or long-term health effects; FCILITY- Major or total destruction of process area(s) at an estimated cost greater than 10000000 US\$ or a significant loss of production.

Risk Analysis

The LOPA technique was applied according to the flow chart depicted in Fig 1. For this purpose, the risk acceptance criteria were selected from a risk matrix presented in PHA-Pro6 software. This matrix was proposed by US-CCPS (Center for Chemical Process Safety), specifically for LOPA studies [2]. This 5×7 matrix is a table that each box has a number from 1 to 13 proportional to the risk priority number (Fig 2).

The acceptable level of risk varies from plant to plant according to engineering decisions, regulatory restrictions, safety standards, financial status of the organization and etc [17]. Based on these factors, THE acceptable level of risk was considered to be 5 in this study. Risks higher than acceptable level need to be reduced. The risk matrix of Fig 2 and its' assigned numbers are standard and recommended for chemical industries.

The risk of each scenario was derived from the combination of its likelihood and severity of consequence. The severity of the consequence is categorized in 5 groups, considering human, property and environment losses (Table 2). The likelihood of the consequence is based on the probability of the accidents and it is categorized in 7 groups (Table 3). The possibility of failure on demand was determined for two cases of with IPLs and without IPLs applied. The RPN

(Risk Priority Number) of each failure was estimated using LOPA risk matrix (Fig 2). As shown in this figure, risks are ranked in 13 categories based on risk priority number [2]. The risk of each failure was ranked and evaluated using measures shown in Fig 2. The influence of the proposed independent protection layers on risk priority number of each scenario was also studied.

5	5	7	8	10	11	12	13
4	4	5	6	7	10	11	12
3	3	4	5	6	7	8	9
2	2	3	4	5	6	7	8
1	1	2	3	4	5	6	7
	1	2	3	4	5	6	7

Fig 2. LOPA Risk Matrix [2]

Table 3. Likelihood numbers corresponding to the likelihood of consequence

Likelihood	Consequence frequency per year
1	1×10^{-6} to 1×10^{-7}
2	1×10^{-5} to 1×10^{-6}
3	1×10^{-4} to 1×10^{-5}
4	1×10^{-3} to 1×10^{-4}
5	1×10^{-2} to 1×10^{-3}
6	1×10^{-1} to 1×10^{-2}
7	1 to 1×10^{-1} or higher

RESULTS

Severity of Consequences

The hazard identification of the study revealed that there are 7 nodes and 16 scenarios to be studied (Table 1). The layer of protection analysis showed that the failure of reformer furnace torches (S3-2) has the highest severity of 5 among all studied scenarios. The average severity of studied scenarios was 3.7 ± 0.60 while 6 scenarios had the minimum severity of 3 (Fig 3).

Likelihood of Failures

The likelihood of each failure was determined for two cases of “with IPLs” and “without IPLs”. Fig 3 shows the likelihood of each failure for two cases of with IPLs and without IPLs. The results showed that without IPLs, the average likelihood of all scenarios were 5.9 ± 0.85 .

Risk Determination

The RPNs (Risk Priority Numbers) were determined from LOPA matrix in Fig 2 by applying the severity of the consequence (consequence category) and the likelihood of failures (frequency of consequence). Fig 5

shows the RPNs of all scenarios with and without proposed IPLs applied. The risk estimated with each proposed IPL applied, represents the residual risk of each scenario.

Risk Assessment

The determined risk for each scenario was then ranked and assessed for two cases of with and without IPLs applied. Table 4 shows the risk assessment of each scenario in two mentioned cases.

DISCUSSION

The failure of reformer furnace torches (S3-2) has the highest severity category among all studied scenarios. The failure of reformer furnace reduces furnace temperature. This can increase the possibility of no reaction in furnace leading to no hydrogen production.

According to the results, without Independent protection layers, Poor performance of 21434 control valve (S3-1) had the highest likelihood of 7 (Fig 4). This failure is reluctant to pass more fuel which can increase the reformer furnace temperature, damaging the catalyst of the furnace. Without IPLs, a puncture at the compressor transducer (S1-2) had the minimum likelihood of 4 (Fig 4). This failure can lead to a pressure drop in the cycle of water into the cooling tower to transducer, increasing temperature in the compressor. This leads to an increasing of gas temperature at the outlet of E20 transducer.

The statistical paired t-test showed that the application of proposed independent protection layers are expected to significantly ($P\text{-value}=0.0000005$) reduce the average likelihood of failures. The application of IPLs changes the failure ranking of the studied scenario (Fig 4). The application of the proposed independent protective layers can decrease the average likelihood of failures by 32.2% from 5.9 ± 0.85 to 4.0 ± 1.26 . With IPLs applied, 3 scenarios of S6-1, S6-2 and S7-1 would have

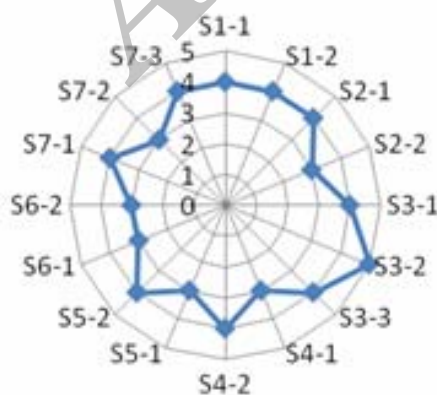
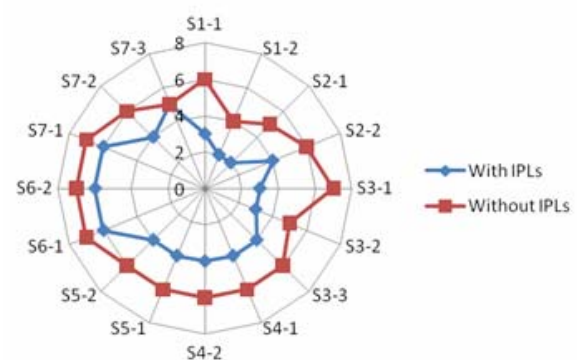
**Fig 3.** The severity of consequences**Fig 4.** The likelihood of failures with and without IPLs

Table 4. The risk assessment of the studied scenarios

Risk Ranking	Description	Without IPLs	With IPLs
1	No further action		
2	No further action		
3	No further action		
4	No further action		
5	No further action		S1-2, S2-1
6	Operational (evaluate alternatives)		S1-1, S2-2, S3-1, S4-1, S5-1, S7-2
7	Operational (evaluate alternatives)	S1-2	S3-3, S4-2, S5-2
8	Operational (evaluate alternatives)	S2-2, S4-1, S5-1, S7-2	S3-2, S6-1, S6-2
9	Action at next opportunity (notify corporate management)	S6-1, S6-2	
10	Action at next opportunity (notify corporate management)	S2-1, S7-3	S7-3
11	Action at next opportunity (notify corporate management)	S1-1, S3-2, S3-3, S4-2, S5-2	S7-1
12	Immediate action (notify corporate management)	S3-1, S7-1	
13	Immediate action (notify corporate management)		

the highest likelihood of 6.

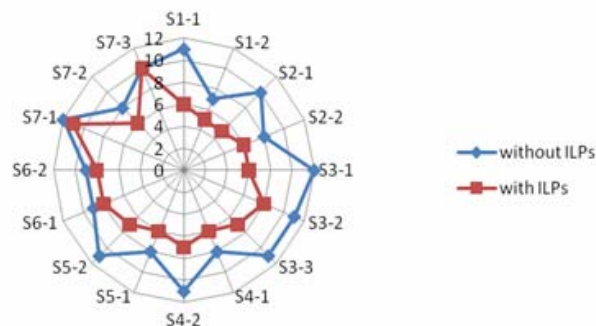
Failure or poor performance of 44155 control valve (S6-1) will increase the water flow rate to de-aerator. This can increase the temperature of outlet water with the possibility of damage to the boiler and P10 pump. The excess of steam flow rate from the boiler to de-aerator (S6-2) can increase the temperature, following the deterioration of P10 pump.

Two main reasons may lead to high pressure in absorber towers (S7-1), elevating the risk of explosion in them. These include the failure or improper operation of the hydrogen output of each tower to open the control valve in the service and failure to timely close the control valve of inlet hydrogen path.

With the application of independent protection

layers, a puncture at compressor transducer (S1-2) and the blockage of natural gas flow in the reformer furnace tubes (S2-1) will have the minimum likelihood of 2. The blockage of natural gas flow in the tubes of reformer furnace reverses the direction of the flow in the furnace. This may lead to an increase in pressure from desulphurization reactor to compressor and the natural gas return through steam pipes which may end up with boiler explosion.

The application of the proposed IPLs is expected to have the maximum reduction of 60% at the likelihood of scenario S2-1(blockage of natural gas flow in the reformer furnace tubes). The likelihood of failure in S7-3 will not change with IPLs applied. In this scenario, if lightning deals with purge gas buffer then temperature

**Fig 5.** The risk priority numbers of failures with and without IPLs

will increase. The presence of methane and hydrogen gas can end up with a fire and explosion then. The maximum, average and minimum reduction in the likelihood of failures due to the application of the proposed IPLs are expected to be 60%, $33.3\% \pm 16.49\%$ and 0% respectively.

The RPN determined from Fig 2 considering the likelihood of the failure and the severity of its consequence showed that without IPLs applied, poor performance of 21434 control valve (S3-1) and high pressure in absorber towers (S7-1) have the highest RPN of 12 (Fig 5). In both scenarios, high likelihood of the failure (e.g. 7) and a relatively high severity of the consequence (e.g. 4) ended up with such a high RPN. The consequences of both scenarios were explained before. In a quantitative risk assessment applied to the same hydrogen unit, Jafari and Zarei showed that the reformer and heat exchanger have the highest individual risk which is consistent to the present study [18, 19].

Without IPLs, a puncture at compressor transducer (S1-2) had the lowest risk priority number of 7. A low likelihood of the failure (e.g. 4) led to such a low RPN although it had a relatively high severity of consequence (e.g. 4). The consequence of a puncture at the compressor transducer was explained earlier. The average risk priority numbers of all scenarios without IPLs applied were 9.75 ± 1.61 .

With the application of proposed IPLs, The risk priority number of S7-3 (lightning at purge gas buffer) will not change its RPN of 10. Constant likelihood of this failure (with and without IPLs) led to a constant RPN. The consequences of this failure were described earlier. The statistical paired t-test showed that the application of proposed IPLs are expected to significantly ($P\text{value} = 0.000013$) reduce the average RPN of all scenarios by 28.2% from 9.75 ± 1.61 to 7.00 ± 1.67 .

If the proposed IPLs were applied, S7-1 (high pressure in absorber towers) will still have the highest RPN of 11. In this case, S1-2 (a puncture at compressor transducer) and S2-1 (the blockage of natural gas flow in the reformer furnace tubes) would have the lowest risk priority numbers of 5. The consequences of both scenarios were described earlier.

The maximum, average and minimum reduction of RPN due to the application of the proposed IPLs are expected to be 50%, $27.6\% \pm 14.74\%$ and 0% respectively. The application of proposed IPLs at scenario S2-1 (the blockage of natural gas flow in the reformer furnace tubes) is expected to have the maximum reduction of 50%.

The assessment of the risks showed that without IPLs applied, all risks were unacceptable. A quantitative risk assessment conducted by Rosyid in 2006 showed that individual risk is unacceptable in all stages of the hydrogen generation cycle which is consistent with the present study [20]. Without IPLs applied, 12.5% of risks required immediate action, 56% required action at next

opportunity and 31.5% were operational but required to evaluate alternatives. With the application of the proposed IPLs, the risk numbers were significantly reduced so that, 12.5% of the risks required action at next opportunity, 75% required to evaluate alternatives and 12.5% required no further action (Table 4) after the application of the proposed IPLs.

In 2011, Li Zhiyong and Jianxin showed that a leakage from the compressor of a hydrogen station has unacceptable risk value which is consistent with the present study [21].

The results of an overall risk assessment of the studied scenarios for two cases of with and without IPLs are tabulated in Table 4. The cells are colored based on the recommended colors in Fig 2.

The following control measures were adopted by LOPA team to reduce the risks of the unit. In order to reduce the risks of S4-2 (e.g. Gas leakage from flanges), it was recommended to collect all emitted gasses from the process, exhaust them through a common duct to the outdoor environment and apply a flare at the outlet stack. This will reduce the accumulation of flammable gases in the process unit. Using gas sensors and display gages will help to alarm the gas leakage and improperly operating equipment. The application of lightning arrester will help to reduce the risks of S7-3 (Lightning at purge gas buffer). Testing the earth system and the electrical equipment of the unit will help to reduce the electrical risks. The thickness of the tanks and safety valves need to be tested. Catalyst and adsorbent beds need to be replaced on time. It is recommended to replace all filters of the compressors on time according to the local haze.

CONCLUSIONS

1. LOPA is a credible tool for risk assessment of hydrogen generation units.
2. The risks of all scenarios studied in present work were unacceptable.
3. The application of the proposed IPLs will significantly reduce both the likelihood and the RPN of the failures.

ACKNOWLEDGEMENT

This paper was extracted from Shimasadat Lajevardi thesis supervised by Dr Mohammad Javad Jafari. The authors wish to greatly thank the Shahid Beheshti University of Medical Sciences as well as Behshahr Industrial Complex for their technical support. The authors announce no conflicts of interests.

REFERENCES

1. US Department of Energy. Hydrogen Incident Reporting and Lessons Learned. Available online in: <http://www.h2incident.org>, (2011).
2. Center for Chemical Process Safety (CCPS). Layer of Protection Analysis-Simplified Process Risk Assessment, American Institute of Chemical Engineers (AIChE), New York, US, (2001)

3. Shojaei S. Analysis of the protective layer (LOPA) for nitroglycerin production units. MA thesis, Chemical Engineering Process Design trends, Sharif University of Technology, Tehran, Iran, 2009, Pages: 68-54 and 95-100.
4. Shirzadian K. Smart Event tree modeling and genetic algorithm for risk assessment in the boiler, desalination unit, Cheshmekhosh (oil and gas companies to exploit west). 2010, <http://www.betsa.ir>
5. Dowell AM, Dennis C. Simplified risk analysis-Layer of protection analysis (LOPA). National Meeting of AIChE, 2002, Indianapolis
6. Sanders RE. Practicing chemical process safety: a look at the layers of protection, *Journal of Hazardous Material* 2004; 115: 141-147
7. Schupp BA, Hale AN, Pasman HA, Lemkovitz BS, Goossens LO. Design support for the systematic integration of risk reduction into early chemical process design. *Safety Science* 2006; 44: 34-54.
8. Fang JS, Mannan MS, Ford DM, Logan J, Summers A. Value at risk perspective on Layers of Protection Analysis. *Trans IChem E, Part B* 2007; Vol 85 (B1): 81-87.
9. Wei C, William J, Mannan S.M. Layer of Protection Analysis for reactive chemical risk assessment. *Journal of Hazardous Material*, 2008; 159: 19-24.
10. Markowski A, Mannan S. Fuzzy logic for piping risk assessment (pfLOPA). *Journal of Loss Prevention in the Process Industries* 2009; 22: 921-927.
11. Markowski A, Mannan S. ExSys-LOPA for the chemical process industry. *Journal of Loss Prevention in the Process Industries* 2010; 23: 688-696.
12. Markowski A, Kotynia A. Bow-tie model in layer of protection analysis. *Journal of Process Safety and Environmental Protection* 2011; 89 (4): 205-213.
13. Markowski A, Mannan S, Kotynia A, Pawlak H. Application of fuzzy logic to explosion risk assessment. *Journal of Loss Prevention in the Process Industries* 2011, 11: 1-11.
14. Gowland R. The accident risk assessment methodology for industries (ARAMIS) / LOPA methodology: A step forward towards convergent practices in risk assessment? *Journal of Hazardous Material* 2006; 130: 307-310.
15. Mohammad Fam I. Safety Techniques (PrHA). Fanavaran publisher, 2003, Pages: 10-3. Tehran
16. Frederickson A. The Layers of Protection Analysis (LOPA) method. Look for best practices and guidelines on how to use the LOPA method as an alternative to mitigate risks. Safety Users Group Network, 2002
17. Jafari MJ, Gharari N, Sheikhi HR. The Reliability of a Tunnel Boring Machine, *IJOH* 2009; 1: 19-24.
18. Zarei E. Quantitative Risk Assessment of a Hydrogen Plant in Tehran. MSc thesis, supervised by MJ Jafari, Occupational Health Eng Dept, Faculty of Health, Shahid Beheshti University of Medical Sciences, Tehran, Iran, 2012.
19. Jafari MJ, Zarei E, Badri N. Quantitative Risk Assessment of a Hydrogen Generation Unit. *International Journal of Hydrogen Energy* 2012., Oct, (in Press)
20. Rosyid O. System-analytic Safety Evaluation of the Hydrogen Cycle for Energetic Utilization [thesis]: Germany: university of Magdeburg; 2006.
21. Li Zhiyong PX, Jianxin MA. Quantitative risk assessment on 2010 Expo hydrogen station, *International Journal of Hydrogen Energy* 2011; 36: 4079- 4086.

Archive