Archives of Occupational Health | Volume 3 | Issue 1 | January 2019 | 299-306.

Original

Health risk Assessment of Exposure to Harmful Chemical Agents in a Refinery

Saber Moradi Hanifi[1], Fereydoon Laal[2]*, Zahra Panjali[1], Jamshid Khoubi[3]

[1] Department of occupational health, School of public health and safety, Shahid Beheshti University of Medical Sciences, Tehran, Iran• [2]Department of occupational Health, School of Public Health, Shahid Sadoughi University of Medical Sciences, Yazd, Iran• [3]Environmental health research center, Kurdestan University of Medical Sciences, Sanandaj, Iran•
*Corresponding Author: Fereydoon Laal, Email: fereydoonlaal@gmail.com Tel: +98-543-3295799

Abstract

Background: Process units, due to performance conditions at high pressure and high temperatures, are prone to many health risks that can lead to adverse effects during work. In order to identify health hazards, assess their risks and make appropriate decisions to control the risk and improve the health of individuals in this regard, the assessment of health risks is of particular importance. Therefore, the aim of this study is to assess and prioritize health risks in a refinery. **Methods:** This cross-sectional study was conducted in a refinery in 2012. In this study, 14 important chemical substances were identified and analyzed. Excel analysis was used to analyze the data. To assess the health risks due to chemical exposure the methodology proposed by the Department of Health Care in University of Singapore was used. First, important chemicals were identified and then the degree of risk and degree of exposure to chemicals were calculated and finally the level of health risk due to exposure to chemicals was determined. **Results:** The results showed that from 14 identified cases, exposure to diglycol diamine had a risk level of 4.47 (very high), hydrogen sulfide a risk level of 3.87 (high level), and molybdenum and nickel base catalysts a health risk of 3.87 (high), all of which were in a range of unacceptable risk. **Conclusion:** In this study exposure to diglycol diamine, hydrogen sulfide, and molybdenum and nickel based catalysts was in the range of unacceptable risk. Using management and engineering controls such as personnel training, shortening the work shift of individuals, pre-recruitment and periodical examinations, designing a ventilation system, and the use of detectors and discovery equipment are recommended to reduce the level of risk.

Key Words: Health risk assessment; Refinery; Catalysts; Hydrogen disulfide

Introduction

In the new era, with the advent of industry and technology, many concerns about the resulting adverse consequences threaten human life[1] It is clear that despite all the benefits that the development of industry has for human beings, it has been the origin of various hazards and failures, confirmed by the alarming numbers of small and big events that occur constantly in one corner of the world; on the other hand, although in recent years many countries in the world have succeeded, by applying appropriate control methods, provide the necessary training along with accurate monitoring and control of the incidence of accidents,[2] factors such as human error, excessive trust in the safety of installations, design defects, lack

Citation: Moradi Hanifi S, Laal F, Panjali Z, Khoubi J. **Health risk Assessment of exposure to harmful chemical agents in a refinery.** Archives of Occupational Health. 2019; 3(1): 299-306.
Article History: Received: 19 Agust 2018; Revised: 22 November 2018; Accepted: 5 December 2018

[DOI: 10.18502/aoh.v3i1.349]

of readiness in critical situations and in less developed countries, non-compliance with the principles of HSE in technology transfer are among the major causes of human and environmental catastrophes.[3]

One of the consequences of accidents, especially in process industries such as oil and gas and petrochemical industries, which deal with a wide range of contaminating and hazardous chemicals, is irreversible degradation of the environment and the resulting health effects, along with other environmental concerns such as global warming, ozone depletion, water pollution, and the extinction of animal species have become the most important global concern.[4] In view of the above, novel approaches to risk management, especially in the form of management systems such asISO14000, OHSAS18000 and HSE-MS, emphasize the prevention of accidents before they occur. For example, this issue has been highlighted as one of the main elements of the management system of safety, health, environment and quality, namely, risk assessment and risk management.

The first step in the process of managing and assessing the risks is identification and their effects.[5] There are several approaches in this regard, each of which can identify the risks and evaluate their effects with its own capabilities and limitations, These techniques include hazard and operation study (HAZOP), Fault Tree Analysis (FTA), and assessment of health risks of exposure to hazardous chemicals.[6] The present study was conducted to evaluate the health risks posed by exposures to chemical substances in the operating units of a refinery.

Operational units have a high risk of health hazards and therefore of great importance due to the continuous injection of chemicals as additives, and also charging and discharging of catalysts.[8] It is obvious that injection of these materials is highly sensitive in terms of health, and creates a hazard for workers of operational units.

On the other hand, waste of some of these valuable materials is economically unacceptable.

Health risk assessment is an analytical approach to risk assessment that seeks to identify the potential risks in the area in which the risk assessment is performed, as well as the exposure rate.[7] The use of health risk assessment method in assessing and managing risk and its position in improving the HSE management system has an effective role in identifying and measuring performance indicators in HSE management areas.[6,2] Therefore, the assessment of the health risks and the need to use preventive safety with respect to existing systems is very important.[8] Therefore, the present study aims to assess the health risks in a refinery that produces and stores a high volume of chemical substances.

Methods

The present study is an applied, cross-sectional research carried out in operational units of a refinery in 2012. To collect the required information, the information and consultation of the unit supervisor, employee representative, employer's representative, industrial health or safety experts, as well as work process analysis were used. Assessment of health risks of exposure to hazardous chemicals is a semi-quantitative method for identifying health hazards due to exposure to chemicals.[9] Because this technique is often used in chemical industries and in processes involving chemicals, we used this method to assess chemicals in a refinery that have potential for a wide range of hazards. It should be noted that the methodology has recommended by the Singapore Occupational Health Department.[10]

The procedures for assessing the health risks posed by exposure to chemicals are as follows: Stage One: Formation of the Working Group: The most important members of this group are the supervisor of the unit under study, the representative of the staff and industrial health and health experts. Stage Two: Work Process Analysis: At this stage, the employees are grouped according to their job responsibilities,

[DOI: 10.18502/aoh.v3i1.349]

during which the different parts of the site, the work processes of each part, as well as the occupational tasks of the employees are identified in each of the work processes. Process Flow Diagram and Process and Instrument Diagram maps can also be used to identify the exact tasks and processes. At this stage, all chemicals (raw materials, intermediates, primary and secondary products) that are consumed or produced during work processes should be identified. Chemical materials may include solids, liquids, gas, steam, dust, mist, or foam. For identification of chemicals, methods such as chemicals inventory review and material safety data sheet (MSDS) used to label chemical containers, as well as inspection of the site and all places where chemicals are consumed or stored, as well as chemical reactions during work processes to find intermediate materials can be used.

Step 3: Determining the hazard rate (HR): After identifying the chemicals present or used in the site, the next step is to determine the toxicity or risks posed by these materials.

The degree of chemical substances can be determined in two ways:

A) through the toxic or harmful effects of the chemical Table 1.

B) By acute toxicity of chemicals Table 2.

Table 1. Determining hazard rate using toxic or harmful effects of chemicals

Hazard rate	Description of the effects of chemicals for the classification of chemical hazards	Example(s)
1	Materials that do not have any known health effects and are not classified as toxic or harmful. The substances that ACGIH has classified as carcinogen A5.	Sodium chloride, Butane, Butyl acetate, Calcium carbonate
2	Materials that have reversible effects on the skin, eyes and mucous membranes, but their effects are not so severe that they can cause severe impairment. The substances that ACGIH has classified as carcinogen A4. Materials that cause skin sensitization and irritation.	Acetone, butane, acetic acid (10%), barium salts, etc.
3	Materials that are likely to be carcinogenic or mutagenic to humans or animals, but there is not enough information in this regard. The substances ACGIH has classified as carcinogens A3. The materials that IARC has classified as 2B. Corrosive materials (<PH <3 or 9 <PH <12) and respiratory sensitizers	Toluene, Xylene, Ammonia, Butanol, Staldehyde, Aniline, Antimony
4	Materials that can cause greater carcinogenic, mutagenic (gene mutation), and teratogenic (birth abnormalities) effects on animals than the previous class according to studies. The substances that ACGIH has classified as carcinogens A2. Group A2 in the IARC classification Very corrosive substances (2 <PH <0 or 14 <PH <5/11	Formaldehyde, cadmium, methylene chloride, acrylonitrile ethylene oxide
5	Materials that have known carcinogenic, mutagenic (gene mutation) and teratogenic (birth abnormalities) effects Substances that ACGIH has classified as carcinogens A1. Group 1 in the IARC classification Very toxic chemicals	Benzene, benzydine, lead, arsenic, beryllium, bromine, vinyl chloride, mercury

Table 2. Determination of hazard rates by acute toxicity of chemicals

Degree of danger	LC50 of oral absorption (mg/kg rat body)	LC50 of skin absorption (mg/kg rat body)	LC50 of inhaled absorption (in mg/l of aerosols and suspended particles) for 4 h	LC50 of inhaled absorption in rat (in mg/l of aerosols and suspended particles) for 4 h
2	2000 >LD50	2000 >LD50	20 >LC50	5 >LC50
3	2000 ≤<LD50200	2000≤<LD50 400	20≤<LC50 2	5≤<LC50 1
4	200≤<LD50 25	400≤LD50<50	2≤<LC50 5/0	1≤<LC50 25/0
5	25≤LD50	50≤LD50	5/0≤ LC50	25/0≤LC50

[DOI: 10.18502/aoh.v3i1.349]

Stage 4. Determination of exposure rate (ER): The degree of exposure to chemicals is determined using the actual ER (pollutant measurement results), To this end, the average of weekly exposure is first determined using equation 1 and then by using Table 3, ER is determined:

(1) $E = \frac{F \times D \times M}{W}$

E: Weekly ER (ppm or mg/m3)

F: Number of exposures per week

M: ER (ppm or mg/m3)

W: Average working hours per week

D: The average time of each exposure (h)

PEL: Permissible exposure limit or time weighted average (TLV-TWA) (ppm or mg/m3)

In the case of short-term exposures (up to 15 min) ER should be compared with PEL or (short-term) TLV-STEL. When the results of the air monitoring (exposure estimation results) are not available (not measured), the ER can be determined using the exposure index (EI) or the use of equation 2:

(2) ER = [EI1 * EI2 * EI3 * ... * EIN] 1 / n

n: number of factors used

(2) ER = [EI1*EI2*EI3*…*EIn]1/n

The exposure index (EI) is calculated by using a 5-point grading scale (from 1 to 5) using Table 4, in which:

Grade 1=very low, grade 3=medium, and grade 5=very high.

Step Five: Risk level (RL) assessment: At this stage, the RL is determined by the use of equation 3 with regard to the HR of the chemical and the ER.

(3) $RL = \sqrt{HR \times ER}$

HR: Hazard rate based on 5-point scale

ER: Exposure rate based on 5-point scale

Step Six: Determination of risk level and rank: The risk of exposure to chemicals in each job is determined by Table 5.

Ultimately, the frequency distribution method has been used to calculate the HR. It is noteworthy that the ranges of risk ranks are determined by the equation (3) Table 6 ,10.

Table 3. Determination of exposure rate

E/PEL	ER
<0.1	1
0.1to 0.5	2
0.5 to 1	3
1 to 2	4
>2	5

Table 4. Determination of Exposure Index (EI)

Exposure index Factor	1	2	3	4	5
steam pressure Particle size (aerodynamic diameter)	<0.1mmHg (large, voluminous particles or wet materials)	0.1-1mmHg (large, dry materials)	1-10mmHg (small, dry particles larger than 100µm)	10-100mmHg (small, dry particles 10-100µm)	>100mmHg (powdery, dry, and tiny particles smaller than 10µm)
OT/PEL ratio	<0.1	0.1 to 0.5	0.5 to 1	1 to 2	>2
Control actions	Adequate control with regular maintenance	Adequate control with irregular maintenance	Adequate control without maintenance (moderate amount of dust)	Inadequate control (large amount of dust)	No control (very large amounts of dust)
The rate of use/week	The rate of use is negligible (less than 1kg or l)	The rate of use is small (1-10kg or l)	The rate of use is moderate-Workers have been trained in the transportation of chemicals (10-100kg or l)	The rate of use is high-Workers have been trained in working with chemicals (100-1000kg or l)	The rate of use is high-Workers have been trained in working with chemicals (>1000kg or l)
Duration of work per week	Less than 8 hours	8 to 16 hours	16 to 25 hours	24 to 32 hours	32 to 40 hours

[DOI: 10.18502/aoh.v3i1.349]

Table 5. Risk Ranking

Risk ranking	Risk level
Slight-negligible	1
Low	2
Moderate	3
High	4
Very high	5

Table 6. The degree of risk taking

The cumulative frequency	Relative abundance	Rank abundance	Rows	Risk level
0.17	0.17	2	1.0 - 1.6	1
0.67	0.50	6	1.7 - 2.7	2
0.75	0.08	1	2.8 - 3.2	3
0.92	0.17	2	3.3 – 4.0	4
1.00	0.08	1	4.1 – 5.0	5

Results

In this study, the health aspects resulting from the activity of process units at the time of injection of additives, and charging and discharging of catalyst and materials were identified during the process and their health risks were analyzed. Table 7 lists the HR, risk rank, and the ER for various chemicals. The use of diglycol amines due to its stimulatory effects has a an HR of 4.7 which is above the permissible level (1.4).The resulting consequence from this health aspect of the inappropriateness of the workplace due to stimulatory effects can cause respiratory stimulation of the staff. The control measures in this area are taken in units, i.e., the use of paper masks by individuals, are not very effective and more effective corrective and control measures are required, which will be discussed in the discussion and conclusion. At the time of major repairs, the replacement of nickel and molybdenum based catalysts results in the release of these metals. This aspect with a risk level of 3.8 is higher than the permissible risk level of 1.4. The consequence of this health aspect is the systemic effects of heavy metals in the human body. Workers use process units to replace catalysts from dimethyl sulfide (DMDS) to sulfurize the catalysts to recover them. This activity is considered to be a health aspect with a risk level of 2.4 and above the minimum permissible risk level of 1.4.

The consequence of this health aspect is the inappropriateness of the work environment due to the pungent smell of sulfur, which can weaken the smell of the employees. Working with a variety of oils leads to effects on the skin that have a risk level of 1.8 which is above the permissible level of 1.4. The consequence of this health aspect is different types of skin dermatitis, the control measure that is carried out in this regard in the SRP unit, is wearing tarpaulin gloves. SRP unit workers are exposed to hydrogen sulfide. This gas has an extremely unpleasant odor and highly stimulating due to its very unpleasant odor, and has a risk level of 3.87 that is above the permissible risk level of 1.4.The consequence of this health aspect is the dysfunction of the olfactory, respiratory stimulation, and in the critical conditions, suffocation.

Table 7. Hazard rate, risk rating, and exposure rate for chemicals

F	E	D	W	HR	EI	ER	RL	TLV -TWA	Chemicals	
Twice a day	0.72	15 minutes		2	1	2	2	5mg/m3	SAE30	
Six times a day	1	-	72	2	--	2	2	5mg/m3	SAE40	Oils
Six times a day		15 minutes	72	2	1	1	1	5mg/m3	HB100	
On maintenance	1	38 Hours	72	3	2	2	2	0.1 ppm	DMDS	
Six times a day	1	-	72	5	4	4	4	-----	DGA	
Once a day	0.005	0.05 minutes	72	2	2	2	2	8 ppm	Fine Amine 06	
Seven times a day	1	35 minutes	72	-	2	2	2	-	E - 807	Additives
Once per 3 months	0.000016	5 min per month 45 min per month	72	4	2	2	1	0/002 ppm	E101	
-	1	35 minutes	72	3	-	-	1	50 ppm	EDC	
According to reactor's conditions	1	According to reactor's conditions	72	3	--	--	1	----	Ceramic Ball	
-	1	24 Hours	72	2	2	2	2	5mg/m3	ICI	Catalysts
-	1	84 Hours	72	3	-	-	5	0/5mg/m3	KF-1015	
Once per 3 months	0.000035	0.02 Hours	72	---	3	3	--	1.5 ppm	MP - 704	
Constantly	56	always	72	3	-	-	5	10 ppm	H_2S	Products

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Conclusion

According to the results, it was observed that employees were exposed to 14 different types of chemicals. These materials are classified as oils, additives, catalysts and process-produced materials. Among the above-mentioned materials, exposure to diglycol amine and H_2S had the highest risk level and exposure to the EDC catalyst and ceramic the lowest risk level. Regarding exposure, nickel and molybdenum-based catalysts had the highest levels of exposure and the E101 additive the lowest exposure. Diglycol amine is used in hydrogen tower as Co and Co2 adsorbent. The health aspect of this chemical is the emissions of diglycol amine in air and the stimulatory effects on the respiratory system. Control measures to prevent the emission or dropout of this chemical during injection are the precise implementation of operation, cleaning in accordance with the instructions and the use of appropriate barrels whose lids are not torn out while being opened, and personnel training and proper use of personal protective equipment (PPE).

Dimethyl disulfide (DMDS), used to sulfurize the catalysts and prepare them for charging reactors, is a health aspect of this activity that releases sulfading chemicals in the atmosphere and produces an unpleasant odor when DMDS is being used, which has a high risk level. Odor pollution is one of the environmental pollution that is most of industrial origin It is an unpleasant odor. The odor contamination is an important issue and largely due to the presence of certain elements, such as sulfur, in various compounds. Most of the odorous compounds are toxic and hazardous, and therefore protection against these types of substances is essential. A number of epidemiological studies have indicated that the comparatively higher prevalence of neurobehavioral disorders among those exposed to solvents at work and the petroleum industry is among the industries whose work involves exposure to solvents, and these disorders are more obvious among those who are more exposed,[12] so it is important to pay attention to this issue.

DMDS odor is due to the presence of sulfur in the chemical, and it is a toxic substance and a chemical solvent,[13] so its steady smell and its toxicity in the long term may weaken the olfactory sensation and also affect the nervous system of the individual. The release of sulfur compounds in the air in the present study is due to leakage and dropout when opening the barrel lid that can create an unpleasant odor and respiratory and pulmonary disorders in the staff. When operating personnel use this material for a short time, the likelihood that the work environment and the disruption of smell understanding are overestimated is high.

According to studies, if the duration of contact with this substance increases, due to the high probability of occurrence and toxicity, it can affect the perception of odor and also the nervous system,[13] which requires stronger corrective and control actions to prevent the diseases.[7] First action: If smell was released in the area, the paper mask could not be responsive.

In this case, a fresh air mask or a cartridge mask could be used, but because of its heavy weight, its use is difficult; therefore, in order to prevent the adverse effects of exposure to this chemical, rotational work shift is recommended.[14] Second action: Replacement of substances is one of the basic principles of prevention, and it is intended not to use pathogens and to replace them with non-pathogenic substances or with less pathogenicity, that have the same industrial properties or efficiency.[13] It is recommended that the storage temperature of DMDS (dimethyl dysulfate) be stored. According to the MSDS conditioning warehouse to be good. Although the level of diglycol amine is almost twice as high as DMDS, the duration of exposure to diglycol amine has not been determined. The results showed that exposure to nickel and molybdenum-based catalytic dust, including KF1015, had the highest ER, and during overhaul, had a risk level of 3.8.Exposure to this dust occurs during charging and discharging of reactors, the problems caused by exposure to these dusts are chronic systemic

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complications that cause a substantial risk to humans.[4] Corrective actions in this area include: reducing the duration exposure by implementing management procedures such as rotational work shift for the personnel involved in essential repairs and replacement of catalysts, and the use of standard safety devices recommended by the safety unit. The H_2S gas has a risk level of 3.87. Exposure to this substance is constant due to operational conditions and possible leakage. In a study by Si et al. (2012), the risk level of residents' exposure to H_2S was high, [16] which is consistent with the current study. In the processes related to the sulfur unit, reservoirs, distillation and drainage systems of reservoirs, and in granule units, acute exposure to this gas in process units can lead to death. In low concentrations, it can also cause headaches, drowsiness, lethargy, nausea, vomiting, and eye irritation.[15] The corrective measures in this area are as follows:

First action: management controls, i.e., personnel training, shortening the duration of the shift work of exposed persons to H_2S gas, performing pre-recruitment examinations and periodical examinations with special attention to the respiratory tract, cardiovascular system, and eyes. Second action: Engineering controls, the use of proper ventilation and reducing pollutant emissions, modifying the working process, using the equipment for the detection and declaration of hydrogen sulfide gas. Third Action: Using PPE: If engineering and management technical controls cannot reduce the level of exposure to hydrogen sulfide, using PPE such as full face mask with a special hydrogen peroxide canister at the workplace is essential. Many studies have been done in this regard, e.g., the study of Jahangiri et al.[8] Jahangiri et al. conducted a study to assess the health risks in petrochemistry. They concluded that the highest risk rank was exposure to epichlorohydrin in two job positions, namely, utility operation and utilities and maintenance. In addition, exposure to epichlorohydrin in technical inspection and methylethyl ketone in utility operation and utilities were found to cause the highest risk level of exposure.

The final analysis suggests that the long-term health risks may interfere with the sensation of the odor (resulting from the sulfur pungent smell) and systemic disorders (due to exposure to the catalysts dust) and the respiratory tract problems (caused by exposure to diglycol amine).The use of appropriate PPE, management controls such as rotational work shift and the replacement of low risk chemicals are recommended as control strategies. Risk assessment studies show that one of the limitations of the study is the judgment of individuals about risk assessment that can be very effective in risk consequences,

as Nouri et al. have pointed out that one of the most important problems with this relationship in risk assessment is the effect of assessment judgments on risk consequences.[17] Other limitation of the study is that the time of exposure to materials such as dichloroamine was not known. In the present study, with the formation of a technical, engineering, and research team and a survey of experienced people, we tried to control these limitations as much as possible.

Conflict of interest

The authors did not report any contradiction of interests.

Acknowledgments

The research team tank to the cooperation of Mrs. Fatemeh Jafarinia with the respected personnel of the Tehran Refinery who helped us to carry out this study.

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[DOI: 10.18502/aoh.v3i1.349]