

CHEMICAL INDUSTRY RISK MANAGEMENT – RISK QUANTIFICATION

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ABSTRACT: This paper deals with problems in the metalworking industry concerning occupational health and safety, specifically chromium, and carbon monoxide poisoning. A subjective risk assessment is carried out, the data are quantified in a risk matrix suggesting the severity of the risk and control measures are offered to prevent the health of workers from being affected.
KEYWORDS: chemical industry, chemical risk, chromium toxicity, carbon monoxide toxicity, risk matrix.

1. INTRODUCTION

Toxicology is an interdisciplinary branch (biology, chemistry, medicine) that represents the study of adverse effects (these can occur at different levels of the body, segmental or total) caused by various chemical substances in contact with living organisms. It is imperative that any manufacturing institution, but especially the chemical industry, is concerned with the identification of risks that may occur during work processes to prevent unintentional accidents in the workplace, and providing employee safety to achieve the expected performance.

To know the chemical risks (dealt with in this article) it is necessary to know the type of substances that can come into contact with workers, the methods of dispersion, the intensity of their effect on the body, and the signs and symptoms that occur after contact. This paper deals with the reactivity of chromium and carbon monoxide in steelmaking with the body using data from literature, guidelines, and protocols on chemical hazards to subjectively determine their severity on employee health.

2. EFFECTS OF CHEMICALS ON THE BODY

The intensity of the effect of toxic substances on the body depends on the nature and quantity of the substance, as well as the particularities of the body, according to the formula:

$$I = f \cdot \left(D \cdot \frac{VA}{VE} \cdot P \cdot R\right) \quad (1)$$

In which :

I - is the intensity of the effect ;

D - dose;

VA - absorption velocity;

VE - disposal speed ;

P - physical-chemical properties of the toxic substance ;

R - general and organism-specific reactivity;

f - toxicity factor, variable depending on the substance.

Depending on their effect on the body, toxic substances can be classified as follows (pathophysiological classification)[1]:

- neuroparalytic toxicants, which act on the central nervous system and, in high concentrations, cause death (e.g. isopropyl and pinacolyl methyl fluorophosphonates, dimethylamino-thioethyl ethoxymethyl phosphonate);

- asphyxiating toxic substances, which mainly affect the respiratory system, preventing either the entry of oxygen in sufficient quantities into the lungs or its assimilation at the cellular level due to the blockage of blood circulation by the formation of a stable combination (carboxy-hemoglobin, cyanhemoglobin - example: carbon monoxide, cyanic compounds, hydrogen arsenate, chlorine, chloroacetates, phosgene, diphosgene ;

- toxic irritants, which cause inflammation and irritation of tissues and mucous membranes. Some compounds in this category have a tear-forming action (e.g. trichlor-nitromethane, acetophenone, ammonia), others irritate the airways, causing sneezing (e.g. adamista), and others produce a vomiting sensation.

- toxic narcotic substances which, on entering the body, act on the nervous system, causing narcosis (nitrous oxide, halogenated derivatives of hydrocarbons, alcohols, aldehydes, esters, aniline, nitrobenzene;

- various toxic substances which cannot be classified under any of the previous groups: volatile compounds of certain metals - mercury, lead, phosphorus, organic combinations of arsenic and stibium, etc.[2]

3. IDENTIFYING SIGNS AND SYMPTOMS OF CHROMIUM POISONING

Table 3.1. Practice guidelines for chromium

Agency	Transmission route	Reference values
American Conference of Governmental Industrial Hygienists	Air	10 μg/m³ 50 μg/m³ 500 μg/m³
National Institute for Occupational Safety and Health	Air	1 μg/m³ 500 μg/m³
Occupational Safety and Health Administration	Air	5 μg/m³ 500 μg/m³ 1,000 μg/m³
Environmental Protection Agency	Air	Not available

Table 3.2. Toxic effects of chromium

Transmission route	System affected	Toxic effects
Air	Respiratory system	Astm Chronic bronchitis Chronic pharyngitis Chronic rhinitis Ulcerations of the nasal mucosa Hyperemia and congestion Lung cancer
Tegument/skin	Skin	Dermatitis Erosive ulcerations
Oral	Digestive Breeder	Hepatomegaly Perforated gastric ulcer Hypertrophic gastritis Haemoptysis Miscarriage

According to the International Practice Guidelines, there are set values for the amount of chromium (in the air) allowed in employees' workplaces and these can be found in Table 3.1.

In the event of exposure to a quantity of chromium exceeding the permissible reference values for worker safety, effects can be identified according to the route of transmission of the toxic substance in the body.

Acute effects of chromium in contact with the body are identified at the digestive (epigastric pain, diarrhea, emesis, liver damage, gastric ulceration, and erosions), muscular (myalgia), neurological (fever, chills, dizziness) levels.

If contact with the toxic substance is not interrupted and urgent treatment measures are not taken, these symptoms may degenerate into damage to the renal and circulatory systems through intravascular hemolysis, organ failure, coma, and death.[3]

4. RISK MATRIX, RISK PREVENTION, AND MITIGATION SOLUTIONS

To exemplify the methodology for identifying risks and their impact on the health of workers in the chemical sector, the safety data sheet for hot-rolled or cold-rolled steel, a product sold by ArcelorMittal to steel-consuming industries (automotive, construction, mechanical, etc.) is used. [4]

Thanks to a wide range of high physical, mechanical, chemical and technological properties, alloy steels have experienced a particular development since the end of the 19th century. To increase one or more properties, they are frequently alloyed with Mn, Cr, Ni, Si, W, Mo, Ti, V, Co, Nb, Zr, Hf, Ta. [5]

Chromium is an alpha-age element, unlimited soluble in iron, which easily forms simple, and complex carbides (Cr4C; Cr7C3; (FeCr)4C; (FeCr)3C etc) It refines the structure, increases mechanical strength properties, wears resistance, and elasticity, and over 12% Cr makes steel stainless.

Chromium can occur in three distinct forms in diffuse emissions from the steel industry:

- Cr metal is present in ferrochromium, used in the manufacture of stainless steel;
- Cr(lll) results mainly from the secondary treatment of steel and further processing of stainless steels (welding);
- Cr(lV) is characteristic of emissions generated during the pickling of stainless steels and passivation of coated steels,

Chromium occurs mainly in the production of stainless steel brands and is a typical pollutant in steel plants. Chromium-containing refractory materials and dust collected from gas collection facilities can be sources of Cr lll and lV.

The potential effects of chromium metal on human health vary according to the form in which the chromium is found. Exposure to chromium metal-containing dust can lead to eye and respiratory tract irritation. In the body, metallic chromium can partially oxidize to Cr (lll), but even this form has low toxicity and is absorbed by the body.

Cr(lV) is the most dangerous form, however, short-term exposure to high levels can lead to irritation of the nasal mucosa, and gastrointestinal tract, perforation of the nasal septum, and skin ulceration.

Ulceration is the most common chromium injury in the occupational environment, caused by its abrasive properties. Dermatoses (erythematous, papular, eczematous) are another form of chromium damage. Ulceration of the nasal septum is a form of aggression, due to the accumulation of chromates. Inhalation of Cr (lV) dust can have irritative effects of the asthmatic type - dyspnoea, coughing and retrosternal pain.

Long-term exposure to moderate levels of chromium can damage the nose and lungs, increasing the risk of lung disease. Long-term exposures can also lead to adverse effects on the liver and kidneys. Cr(lV) is recognized as a carcinogenic pollutant, which can affect the lung, oesophagus, prostate and sinuses. Individuals allergic to chromium may suffer asthma attacks after inhaling high concentrations of Cr(lll) and respectively Cr(lV). [6]

The maximum permitted atmospheric concentrations are 0.55 mg/m^3 and 0.5 mg/m^3 for soluble chromium and chromium salts. STAS 12574-87 stipulates 0.15 μg/m^3 , averaged over 24 hours.

Control measures: compliance with the limits laid down in the Occupational Protection Regulations; Cr (Vl) is limited to 0.05 mg/m^3 and Cr (lll) to 0.5 mg/m^3 . Reduction of chromium emissions in work areas by sealing machinery, local exhaust ventilation, protective equipment, etc.

NB: For the subjective estimation of the impact of chromium on workers' health, a scaled score from 1-5 was used where 1 represents the highest impact and 5 is the highest impact.

Continuous gaseous emissions from stacks, containing particulate matter, CO, NO_x , have a high impact on humans and the environment. It is noted that environmental factors, water and soil are less affected by activity-related pollution. A high risk for the personnel involved in the activity on the platform is the methane gas distribution network and the combustion installations, which under improper operating conditions can lead to accidents.

Table 4.1. Estimation of the impact of chromium transport pathways on target elements

TRANSPORT ROUTE	**AIR**	**SKIN**
score	3	
TARGET	**HUMAN**	
score	3	
GRAVITY	Very big	
score	4	
FREQUENCY	Continuous	
score	1	

Carbon monoxide

Carbon monoxide is a colorless, indoor, tasteless gas produced by the incomplete combustion of carbon in fuels. CO is specific to combustion and metallurgical processes, and its release in high concentrations is favored by insufficient control of combustion and technological processes, as well as inadequate maintenance of installations.

CO enters the body via the lungs, crosses the pulmonary alveolar-arteriolar barrier, and blocks hemoglobin in the blood by forming carboxy-hemoglobin (1 mg/m^3 of CO leads to blockage of 0.16% of haemoglobin), which leads to hypoxia or even cellular anoxia.

In muscle CO forms carboxyhemoglobin, disrupting muscle metabolism, especially in the heart. In addition to this, there are other enzyme blockages e.g. cytochrome oxidase. By binding carbon monoxide to hemoglobin, carboxyhemoglobin is formed, the affinity of CO to hemoglobin being 200 times greater than that of oxygen.

Determination of serum carboxyhemoglobin is used in suspected CO poisoning. In smokers the levels are higher than in non-smokers. The organs most sensitive to COHb (carboxyhemoglobin) are the brain and the heart.

CO begins to be harmful at concentrations of 0.06% in air.

In short-term exposures, symptoms of poisoning begin with headaches, irritability, abdominal pain, dizziness, and vomiting. Sometimes these symptoms are combined with the nervous syndrome. When CO concentrations are high, death can occur. After poisoning, a series of sequelae (neuropsychic disorders due to organic damage to the nervous system) may remain, manifesting themselves over a long period. [7]

Long-term exposure, even at low concentrations, may result in anemia,and nutritional and nervous disorders - headaches, amnesia, personality changes, paresis, and inattention (the latter may cause accidents at work).

Permanent symptoms include asthenia, headache, vertigo, intraventricular conduction disturbances, sinus bradycardia, and ventricular extrasystoles.

According to WHO data, the following exposures are acceptable: 100 mg/m^3 per 15 minutes, 60 mg/m^3 per 30 minutes, 30 mg/m^3 per 1 hour, provided these exposures are not repeated within 8 hours. For a duration of 8 hours a concentration of 10 mg/m^3 is acceptable. At concentrations of 2500 mg/m^3 very severe symptoms may occur after 1 hour.

STAS 12574-87 provides the following limits:

- 6000 µg/m^3 average for 30 minutes;
- 2000 µg/m^3 average for 24 hours;

CO_2 is not considered a hazardous pollutant to human health, it is found in virtually all steelmaking streams and is the result of combustion and metallurgical processes. According to the WHO, a concentration of 9800 mg/m^3 is allowed for an 8-hour average.

Control measures: control of the CO concentration to keep it below the permitted limit in the workplace atmosphere of 30 mg/m^3 , folowing the Occupational Protection Regulations.

Operations, where CO is released must be carried out with certain precautions, with personnel being warned of the risk and adequately trained. Where necessary, alarm devices (CO detectors) and personal protective equipment (masks with specific filters, fresh air supply) should be used.

It is also recommended that CO-containing gaseous emissions be captured locally and discharged to the atmosphere at higher elevations for dilution. Exhaust vents from enclosed spaces should be coupled with outdoor exhaust ducts. It should be taken into account that it diffuses easily into the surrounding atmosphere and enters spaces where it has not occurred.

Although the matrix assessment method is subjective, it can give a picture of the importance of the risks according to the severity of the consequences and frequency, as well as the prevention-remediation solutions that are required.

Table 4.2. Estimation of the impact of carbon monoxide transport pathways on target elements

TRANSPORT ROUTE	AIR
score	3
TARGET	**HUMAN**
score	3
GRAVITY	Very big
score	4
FREQUENCY	continuous
score	1

Based on Table 4.3, risks that may occur due to exposure of personnel to diffuse emissions of chromium or carbon monoxide in a steel manufacturing company are identified and the likelihood of occurrence and impact is determined.

For the calculation of the risk index I_R the scaling from 1 to 5 is used for both probability and impact.

Table 4.3. Risk matrix[8]

SOURCE	POLLUTING AGENT	DANGER	TRANSPORT ROUTE	TARGET
Electric oven basket	Chromium powders in suspension	- air purification - respiratory disorders - intoxications	air	- environment (air) - staff - the neighbouring population
Exhaust gas chimney	Sedimentable dust	Heavy metal contamination (**Cr**, Ni, Zn, Mn)	air	- environment - staff
Deep and propeller kilns	CO	- air purification - respiratory diseases, poisoning	air	- environment (air) - staff - the neighboring population
Deep and propelled furnace hall	Diffuse CO	- air purification - respiratory diseases, poisoning, dehydration, burns	air	- environment - staff
Electric furnace hall	Diffuse emissions of heavy metal dust, CO	- air purification - Respiratory tract diseases, poisoning, ENT diseases, dehydration, burns	air	- environment - staff

Table 4.4. Risk ranking and risk index determination

RISK	P	I	$I_R = P \times I$
Air pollution	4	4	**16**
Respiratory system damage	2	4	**8**
ENT conditions	1	3	**3**
Poisons	3	4	**12**
Dehydration	1	2	**2**
Burns	2	5	**10**

P - probability

I - impact

Table 4.5. Risk ranking according to the subjectively identified risk index

Sorting in ascending order	Risk index	Risk identified
1	16	Air pollution
2	12	Poisons
3	10	Burns
4	8	Respiratory system damage
5	3	ENT conditions
6	2	Dehydration

According to the risk index calculated subjectively based on experience, we have identified and ranked the possible risks in a company belonging to the chemical industry, that deals with steel manufacturing. According to Table 4.3, the greatest impact on workers' health is caused by air pollution, (respiratory) poisoning, and burns. In order to schematically illustrate the impact of the risks it is decided to use a risk matrix approach based on the risk index determined above.

To highlight the severity of a hazard in the chemical industry, a color scheme is used (shown in Table 4.7), where light green expresses very low severity and red is specific for extreme severity.

The scales used for likelihood and impact usually have five levels although these may vary and the colors used may also be assigned differently depending on individual perceptions of risk.

The risk matrix can be used at all stages of risk assessment (for current, future, or/and emerging risks, risks, and major risks with a low probability of occurrence and major impact).[9]

According to the risk matrix, extreme severity is identified in the case of air pollution and poisoning, risks arising from diffuse emissions of heavy metals, chromium dust, and carbon monoxide. For prevention, regular technical inspections for air testing, checks according to the rules in force and the manufacturer for machinery (electric, deep and propelled furnaces, exhaust stacks, etc.), the provision of personal protective equipment for employees, and their regular retraining are recommended.

High severity is identified in the case of burns but also in the case of damage to the respiratory system and the factors favoring it are the same as mentioned above. A notable impact is also ENT damage although there is a low probability for it to occur because assuming there is a risk of exposure to toxic substances the employee, will show immediate symptoms, report the incident, and action can be taken before these substances affect his sensory organs (we exclude in this case an accident that may occur near the employee).

In case of contact with chromium, first aid measures and immediate referral to a hospital for care and evaluation are recommended.

Table 4.6. Risk matrix by risk index

	PROBABILITY				
IMPACT	very low	low	average	raised	very high
minor					
low	dehydration				
notable	ENT conditions		poisoning		
major		respiratory system damage		air purification	
extreme		burns			

Table 4.7. Meaning of colors in the matrix

COLOUR	SIGNAGE
	very low severity
	low severity
	severity
	high severity
	extreme severity

Table 3.8. First aid measures[10]

Method	First aid procedures
Inhalation	Moving to an uncontaminated area Artificial respiration if not breathing Emergency medical support
Skin contact	Wash the pile with soap and water for at least 15 minutes Covering burned skin with sterile compresses after decontamination Removal of clothing that has come into contact with the substance
Eye contact	Wash your eyes with clean water for at least 15 minutes. Emergency medical support
Ingestion	Administration of clean water to dilute the solution. Emergency medical support

5. CONCLUSIONS

In the steel industry, steel producers use chromium to create alloys, and during the transformation process, workers are exposed to toxic factors such as chromium and carbon monoxide in different sectors/workshops.

In this paper, risks to which employees may be exposed have been identified and a subjective assessment of these risks has been carried out, resulting in a risk matrix that can be used for risk management to optimize working methods in the metal industry. Of course, this method is estimated, being limited to 2 determinants and 6 identified risks, but it represents an outline that can be further adapted for a complex chemical risk assessment methodology and with the help of a database, we can digitalize the process of obtaining a form adaptable to the requirements of today's society.

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