

CHEMICAL INDUSTRY RISK MANAGEMENT

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ABSTRACT: The main objective of this work is represented by the identification of the necessary tools for the estimation of the acute toxicity of a chemical based on mathematical models and chemical databases. The first part of this paper contains draft practice guidelines for preventive measures for exposure to chemical hazards and an example calculation for acute toxicity estimation for a mixture of substances with unknown toxicity of less than 10%.

KEYWORDS: risk factors, preventive measures, chemical agent, chromium toxicity, ATE, hazardous

1. INTRODUCTION

The work aims to quantify the risk factors of chemical etiology and their influence on workers, the environment, and production.

The first is to identify the possible chemical factors to which industrial workers may be exposed, the pathways by which they enter the body, and methods of protection for the safety and health of the employee at work.

The existence of risk factors in the industrial sector manifests itself in economic losses, environmental pollution, and the occurrence of minor or major accidents that can have serious consequences including worker illness, injury, or death. According to statistics, at least one employee in ten suffers from an occupational disease, and employees have become victims of their own workplaces through daily exposure to noxious fumes, noise, high temperatures, electric fields, electromagnetic radiation, stress, and more. Hundreds of millions of employees around the world are exposed to harmful risk factors: physical, chemical, biological, psychosocial, and ergonomic, and often risk factors are combined in the same workplace.

Economic operators are ethically, morally, and legally obliged to assess the level of risk to which their employees are exposed, thus improving working and environmental conditions to move from high-level risks to the lower, acceptable step. The environmental component of a company's risk management is a key element in ensuring the company's good image, ensuring that industrial activities are carried out without harming the health of staff, the public, and the quality of the environment. The health of employees in any country

has serious consequences for the national economy and internationally.

2. CHEMICALS AND TOXICITY

According to EU-OSHA (represents the European Agency for Safety and Health at Work), the employer is obliged to take the necessary measures to minimize exposure to hazardous substances with the aim of reducing or eliminating the risk, taking into account the order of priority of the measures:

Table 2.1. Preventive measures for exposure to chemicals

EU-OSHA approved term	The term translated and adopted in Romania
Substitution (substance or process)	Înlocuire (substanță sau proces)
Technical controls	Controale tehnice
Organizational measures	Măsurile organizatorice
Personal Protective Equipment (PPE)	Echipament individual de protecție (EIP)

A chemical agent represents any chemical element product as a result of activity in the form of a finished or waste product, irrespective of the final purpose (product intended for placing on the market or not), and a hazardous chemical agent is defined as any chemical agent which is identified in the classification criteria as a hazardous substance and belongs to a class provided in (EC) No 1272/2008 (Regulation of the European Parliament) and of the Council of 16.12.2008 (L353)[1], as amended by its amendments, hereinafter referred to as Regulation No 1272/2008.[2]

Table 2.2. Hazardous substances identified in the industrial sector and their exposure risk classification - according to ECHA [3]

Substance	Classification of exposure to the substance
Steelmaking - chemicals	Acute toxicity 3 Skin irritation 2 Eye irritation 2 Skin sensitivity 1
2- bromobenzyl alcohol	Acute toxicity 4 Eye irritation 2
Distillates (petroleum), solvent-refined light naphthenic	Carcinogen 1 B
BENZENE, 1,1'-METHYLENEBIS[ISOCYANATE-, HOMOPOLYMER	Respiratory sensitivity 1
Petrol, natural	Toxic by inhalation or if swallowed 1 Mutagen 1B Carcinogen 1B
Ethylbenzene	Acute toxicity 4 Inhalation or swallowing toxicity 1
Sludges and slurries, copper electrolyte refining	Respiratory sensitivity 1 Skin sensitivity 1 Mutagen 2
(Methylthio)acetic acid	Respiratory sensitivity 2 Skin sensitivity 2
Silicic acid, barium salt	Acute toxicity 4
Lubricating oils (petroleum)	Carcinogen 1B
Glass, oxide, chemicals	Carcinogen 1B

From a legal point of view, a chemical substance (substance, mixture) is highly toxic if it meets the CLP (C is for Classification, L is for Labelling and P is for Packaging of Substances) criteria certifying

acute toxicity through the existence of adverse reactions occurring immediately after contact (oral or dermal) with a single dose of a chemical. Multiple doses are taken over 24 hours and inhalation exposure over 4 hours are also valid (dermal, oral, or inhalation toxicity).[4]

Exposure involves the presence of a substances in a worker's environment that can be inhaled or picked up through skin contact (including through the eyes and ears) or ingestion. Exposure is quantified by the amount of agent that is found at the body's metabolic exchange barriers (e.g. skin, lungs, intestines) and is available for absorption. Chemicals can have a sensitizing effect on organic structures, thus sensitizing substances are identified for the airways which will generate an airway hypersensitivity after inhalation of the substance, and for the skin which will generate an allergic response.

Preventive measures

Risk management is the process of identifying, assessing, managing (including treating), and establishing a plan of risk mitigation measures, periodic review, monitoring, and establishing responsibilities [5], while informing employees about :

- results of the risk assessment;
- the dangers to which they are exposed;
- how they may be affected by the substances to which they are exposed;
- the actions they must take for their safety and that of other workers;
- procedures to be followed to check and detect possible problems;
- the delegated person to whom they should bring to the notice any issues;
- preventive methodology and measures to prevent workplace hazards;
- first aid procedures;
- emergency procedures;
- the results of all exposure monitoring actions

Replacement of the substance or process generating chemicals affecting the health of workers is necessary. Each chemical substance used in the industry is accompanied by a technical data sheet describing the characteristics of the product and its usefulness and a safety data sheet containing first aid measures in case of direct contact with the substance.[6]

The security data sheet contains

- Composition
- Transport information
- Personal protection

- Substance identification (relevant uses, contra-indicated uses, supplier details, contact details)
- Physical and chemical properties
- Hazard identification (substance classification, additional information)
- First-aid measures
- Measures to be taken in case of accidental spillage
- Storage
- Handling
- Stability and responsiveness
- Toxicological and ecological information
- Regulatory information
- Fire-fighting measures

The product safety data sheet also includes an acute toxicity assessment (acute toxicity refers to undesirable effects that may occur following exposure to a substance within 24 hours). To mixture or substances that have been classified as a toxic substance, it is necessary to estimate the ATE (acute toxicity estimate) of the mixture. Further is compared with the classification criteria to determine the acute toxicity rank. Source (chemsafety.com) mentions the existence of two types of equations used to choose whether the total concentration (all substances of unknown toxicity) represents 10% or not.[7]

a) A mixture with unknown toxicity is $\leq 10\%$.

$$\frac{100}{ATE_{mix}} = \sum_n \frac{C_i}{ATE_i} \quad (1)$$

C_i - is the concentration of substance i

i - take value 1-n

n - substances

ATE_i - acute toxicity assessment for a substance i

b) A mixture of unknown toxicity is $> 10\%$.

$$\frac{100 - (\sum C_{necunoscut\ dac\ a > 10\%})}{ATE_{mix}} = \sum_n \frac{C_i}{ATE_i} \quad (2)$$

C_i - is the concentration of substance i

i take value 1-n

n - substances

ATE_i - acute toxicity assessment for a substance i

To calculate the acute toxicity estimate for a product, the known ATE and the concentration of all substances must first be obtained. The acute toxicity estimate is:

- An actual value for LD50 or LC50
- A converted value- this value can be found in the GHS acute toxicity rank (category)

LD 50 (lethal dose) is a method of estimating poisoning with a dose that proves to be lethal to half the batch of animals tested in a species, for a relatively short time after exposure (determination of acute toxicity). Toxicology specialists use different animals for laboratory tests but most often these tests are performed on rats or mice because it is admitted that the organism is closest to the human body in activity and reactivity.

LC 50 (lethal concentration) represents the concentration of a chemical substance determined in air or water (for some studies the value determined in water is relevant). To determine this, experiments are carried out on a batch of animals exposed to a concentration.[8]

GHS stands for Globally Harmonised System (GHS) for hazard communication and is an internationally accepted standard for identifying health, physical and environmental hazards in the workplace. The GHS defines and classifies chemical hazards and lists health and safety information on labels and safety data sheets.[9]

3. ACUTE TOXICITY ESTIMATION FOR CHROMIUM

Chromium is classified as medium toxicity with an LD50 between 50-500 mg kg⁻¹ and these values change depending on the compounds added. One study reports the LD50 of chromium changing with compounds for oral administration in batches of rats.

For the determination of the degree of toxicity of the compounds a specific table is used which contains color schemes suggestive of LD 50.

Table 3.1. Acute toxicity comparison for chromium compounds [10]

Chemical compound	LD50 - oral, mg×kg ⁻¹ (rats)
CrO ₃	52
CrCl ₃	440
CrCl ₂	1870
Cr ₂ O ₃	> 15 000

Table 3.2 Toxicity classification

Toxicity grade description	LD 50, mg×kg ⁻¹
Extreme toxicity	≤ 1
Increased toxicity	1-50
Medium toxicity	50-500
Relatively low toxicity	500-5000
Non-toxic	5000- 15 000
Harmless	> 15 000

Using the data in the table and formula (1) the calculation method for the mixture with unknown toxicity $\leq 10\%$ is exemplified.

$$\frac{100}{ATE} = \frac{40}{52} + \frac{10}{50}$$

$$ATE = \frac{100}{\frac{100}{0.76+0.2}} = \frac{100}{0.96} = 104.16 \text{ mg/kg (3)}$$

The data obtained in relation (3) will be interpreted (risk category determined) using a table containing data for the acute toxicity rank.

Table 3.3. Example database for ATE calculation

name	concentration	LD 50(mg/kg)	ETA
CrO ₃	40%	52	400
Substance A	10%	50	40
Other ingredients - known toxicity	50%		

For ATE = 104.16 mg/kg the model chemical compound falls into rank 3 for oral toxicity and rank 2 for dermal toxicity.

The chemical substances resulting from the processing process are regularly monitored based on the study of the technological process, the purpose of the determinations to be able to determine the quantity emitted or released in the workplace, with the aim of employee safety. The hazardous substances to be investigated will be fixed, since their nature will also depend on the equipment and working methods to be used in the process.

In the event of the simultaneous presence of several pollutants in the air, an account will be taken of their mode of action and interaction both from an analytical point of view (chemical reaction, interference in the determination of one or other of the pollutants by the chemical analysis methods used) and, in particular, of their mode of action on the body (synergism by addition or potentiation, antagonism).[13]

Table 3.4. Acute toxicity categories [11][12]

ETA	RANK 1	RANK 2	RANK 3	RANK 4
Oral (mg/kg)	ATE ≤ 5	5 < ATE ≤ 50	50 < ATE ≤ 300	300 < ATE $\leq 2\ 000$
Tegument (mg/kg)	ATE ≤ 50	50 < ATE ≤ 200	200 < ATE ≤ 1000	1000 < ATE $\leq 2\ 000$
Gases (ppm)	ATE ≤ 100	100 < ATE ≤ 500	500 < ATE $\leq 2\ 500$	2500 < ATE $\leq 20\ 000$
Vapors (mg/l)	ATE $\leq 0,5$	0,5 < ATE $\leq 2,0$	2,0 < ATE $\leq 10,0$	10,0 < ATE $\leq 20,0$
Dust and mist (mg/l)	ATE $\leq 0,05$	0,05 < ATE $\leq 0,5$	0,5 < ATE $\leq 1,0$	1,0 < ATE $\leq 5,0$

To identify the substances, either a sampling will be carried out by specialists at fixed points or a report will be issued on the background pollution of the whole room based on the determinations made at the elective points or by mobile points.

The purpose of this process is to draw up the professional logbook, which is the time photography, the minute-by-minute timing of the entire worker's activity of a given profile to reveal the actual time of exposure of the worker to the pollutants in the different phases of the technological process, while also determining the nature of the process (continuous or discontinuous).

Following the analytical determination of the emissions, a report is drawn up expressing the occupational toxic concentrations (expressed in mg/m³ or ppm - parts per million) and the results are examined. In the event of increased background pollution being detected, it is indicated that the process or substances used should be replaced.

During sampling, the Sampling Report is filled in and the values for temperature and pressure are noted. The weighted average concentration for 8 hours is calculated with the formula:

$$CMPT = \frac{\sum C_i \cdot t_i}{\sum t_i} = \frac{C_1 \cdot t_1 + C_2 \cdot t_2 + \dots + C_n \cdot t_n}{8} \quad (4)$$

In which

$C_1, C_2 \dots C_n$ are the concentrations measured in technological phases 1,2...n

$t_1, t_2 \dots t_n$ is the duration of work operations with emissions $C_1, C_2 \dots C_n$ [14]

Technical controls

The frequency of technical inspections is determined according to the industrial area and the equipment used in the technological process. The inspectors draw up reports which are then forwarded to the management area to establish the following measures for maintaining the health of employees and the

safety of the place where they carry out their activities in the job description.

4. ORGANISATIONAL MEASURES

According to the Working Conditions, Labour Protection, and PSI, to maintain and improve working conditions, the employer is obliged to adopt the following measures:

- a) ergonomic design of workplaces;
- b) ensuring environmental conditions (microclimate, noise, lighting, ventilation, temperature, ventilation, humidity);
- c) the fitting out of the social annexes of workplaces (changing rooms, toilets, bathrooms, restrooms, canteen-restaurant);
- (d) the reduction until the gradual elimination of polluting emissions. [15]

PPE - Personal Protective Equipment

Depending on the industry in which the employee works, he/she is obliged by the Internal Rules of Order and by the terms mentioned in the job description to use the necessary protective materials according to the guidance and instruction received, and the employer is obliged to provide all employees with the necessary protective materials. In the EU Directive 89/656/EEC, under Article 2, the section on protective equipment states that PPE is any equipment designed to protect the worker who uses it against any factor which may endanger his health or safety. This category also includes accessories used in conjunction with basic protective equipment, depending on the field of activity. [16]

The employer is advised to adopt the following recommendations on protective equipment:

- elimination of hazards
- replacement of the cause of the hazard
- implementation of engineering controls
- monitoring administrative controls
- choice according to risks, specifications, conditions of use and product endorsements
- offering free PPE to employees
- ensuring storage, cleaning, and disinfection according to the manufacturer's instructions
- organizing training sessions for trainees on the correct use of the PPE

Types of PPE [17]

- skin protection
- eye and face protection
- foot protection
- protection for hand and arm
- protection for head

- hearing protection

5. CONCLUSIONS

Any chemical, physical or biological factor present in the work environment (also called the work environment or occupational environment) that may constitute a hazard to the health of employees is defined as a harmful agent or noxious substance.

Therefore, the occupational environment, which comprises the totality of the physical, chemical, biological, and psychosocial conditions in which employees work, must be monitored to assess the exposures present (determination of the amount, degree, and significance of a particular type of exposure).

In this respect, we try to highlight some of the harmful chemical and physicochemical agents identifiable in the work environment and the circumstances of occupational exposure to these agents.

Most of the noxious substances are complex mixtures generated in *thermal* processes (welding, combustion of coal, wood, coke, pyrolysis of plastics, rubber, etc.), *mechanical processes* (mechanical processing of steels, refractory materials, composite materials, mining, insulation activities, mechanical processing of textiles, etc.), *electrochemical processes* (metal coatings), *chemical processes* (synthesis of organic and inorganic compounds, paints, polymers, fuels, preservation of wood, leather, etc.) and other work processes.

In the concrete conditions of professional activity, sometimes the processes are particularly complicated and their evolution depends on many local and random factors.

The paper is not exhaustive but only covers a relatively small number of harmful agents that are frequently encountered in the working environment (e.g. acids, solvents, paints, etc.) or which are more aggressive to the body (carcinogenic compounds), or whose composition is less well known (extenders, refractory materials, abrasive powders, fumes from pyrolysis of plastics, composite materials, liquid or solid fuels, etc.).

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