Methodology

The Analysis of Real Accidents as a Didactic Tool: The Case of a Toxic Cloud

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Abstract: The interest in risk analysis and in the effects of chemical releases on the environment and people has steadily increased in recent years, both in the industry and academia. The classical approach in the related courses is essentially based on the teaching of the main theoretical aspects, and the subsequent application by the professor to a series of examples, among which there can be real cases involving major accidents. A somewhat different approach consists in organizing several sessions in such a way that it is a team of students who will analyse a case. The professor will give the required information to them, but they will have to manage to solve the case and to answer a set of questions, as if they were an expert team. Usually, the result is quite satisfactory and enriching for both the students and the professor.

Keywords: risk analysis; toxic clouds; environmental impact; teaching

1. Introduction

The accidents that occur from time to time in the process industry and in the transportation of hazardous materials can have a significant environmental impact. In many cases, the accidental release of toxic or polluting products has caused important damage to the environment: soil, water, air, and sometimes also to people. Examples are the well known case of Bhopal (1984), in which the release of methyl isocyanate killed approximately 4000 people; or the release from a process plant at Seveso in 1976 of a cloud containing dioxin, a material of extreme toxicity and persistence in the environment. Although initially perceived as having only minor immediate effects, the passage of the cloud caused acute symptoms among the local population—including nausea, headaches, and eye irritation—and led to the hospitalization of 19 children with skin lesions. In the following weeks, the area experienced significant environmental impact, with high mortality among plants and animals and nearly 200 reported cases of chloracne, mostly in children. The incident also resulted in severe and lasting contamination of vegetation and soil, with long-term ecological, economic, and health consequences, both physical and psychological [1]. Another noteworthy case involving the large-scale release of a toxic gas occurred in Graniteville, USA, in 2005, following a train collision that led to the release of 60 tons of chlorine. The accident resulted in 9 fatalities and 71 hospitalizations, caused extensive damage to the surrounding environment—including the death of hundreds of fish and animals—and left a visible impact on vegetation, which showed signs of bleaching within a radius of about one kilometre from the site [2].

Toxic clouds can also occur in processes involving green chemicals. For example, syngas—a mixture of carbon monoxide and hydrogen commonly used in methanol synthesis—can pose significant hazards in the event of an accidental release [3]. Similarly, ammonia, which plays a key role in sustainable energy systems such as green hydrogen storage and transport, is a toxic substance whose release can lead to severe health and environmental consequences [4]. Other green chemical processes, such as those involving bioethanol or Fischer–Tropsch fuels, may also entail the handling of flammable or toxic intermediates with the potential to form hazardous atmospheric plumes under accidental release conditions [5].

Besides the potential effects on people, toxic substances can have quite negative effects on the vegetation: necrosis of the plants leaves and needles, reduced photosynthesis, premature leaf drop, accumulation of toxic substances, etc. And these effects can persist for some time if the contaminant has entered the soil. In the

Graniteville accident the zone up to a distance of 1.6 km from the accident site required intensive work by the cleaning teams to be decontaminated [6].

Analysing these accidents is a very good way to understand why they occurred and to reach relevant conclusions to prevent their recurrence or significantly reduce their likelihood [7]. Moreover, such analyses can provide full-scale experimental data that can support the development or improvement of mathematical models describing the consequences of major accidents on both people and the environment.

Furthermore, it can also serve as a very effective didactic tool for teaching the main features of these accidents (origin, evolution, effects, consequences) and of quantitative risk analysis (probabilities and frequencies, risk maps). This tool can be used in safety and risk analysis courses, both at the university level—such as in chemical engineering degree or master's programmes—and in more specific courses for industry professionals.

The level of detail and depth in the analysis of these accidents will depend on the training and knowledge of the students that will attend these courses. It can be a simple explanation of the circumstances which originated them, a qualitative description of their effects, a description of their consequences on the affected area and some final conclusions; or can include a more in depth and detailed treatment including the evaluation of the effects associated to the accident (overpressure, thermal radiation, toxic dose) and the analysis of the corresponding consequences.

However, a quite interesting approach is not the description of all these points by the professor, but the investigation of a real case by the students. In other words, it must be the students whom, after receiving the required information about a given case, will perform its analysis by applying the adequate methodologies and mathematical models and tools to, finally, explain what happened and replicate and justify the effects and consequences and the risk associated to them.

It is therefore a creative exercise, which as well implies a challenge for those who must perform it. In fact, when presenting the case, the professor should emphasize this aspect: "Forget that you are students. You are now engineers and a company (or the Court) has commissioned you the task of analysing this accident: what exactly happened, why those were the consequences, what could have happened if some circumstances (as, for example, the meteorological conditions) had changed". Of course, the results of the analysis must be afterwards compared with the available information, and the existing differences should be commented and interpreted. In this last step the support and guide of the professor is required.

The accident analysed can be a famous and well known one, such as, for example, in the case of release and atmospheric dispersion of a toxic material, that of Bhopal; in this case, a lot of information and analyses can be found in the literature. Nevertheless, we think it might be more interesting, if possible, to use lesser known cases from which scarce information has been published or is available, but for which the professor has all the required data. The best option is to use an accident which analysis was performed in due time by the professor who poses the exercise. In this communication the analysis is applied to an accident involving the release and atmospheric dispersion of a toxic gas.

The aim of this paper is to illustrate how the analysis of a real accident involving the release and atmospheric dispersion of a toxic gas can be used as an effective didactic tool in safety and risk education. By guiding students through the structured investigation of the case, the exercise fosters the development of critical thinking, technical knowledge, and decision-making skills. The case presented here was selected not only for its relevance, but also because the authors had direct access to detailed data, allowing for a comprehensive and realistic analysis that can be replicated in educational settings.

2. Methodology

The exercise should not be performed by a single student or course attendee; solving it as a team will promote the discussion and results in a much more enriching experience. A group of four or five people is an appropriate size. A team leader should be appointed, as well as a scribe to document the work.

The trainer must stress to them that they are no longer students, but a team of engineers who have been commissioned to analyse the accident. It is likely that they will not have access to all the information that would be ideal from a technical standpoint, and they may have to make reasonable assumptions. This is one of the key differences between the analysis of a given lesser-known case and the academic study of a famous and well-known one, for which abundant information is available through reports, articles, and other sources. Moreover, even if some information is missing (though not the essential elements), the students will have to do an effort to explain what happened, why it happened and what could have happened under different conditions. Interestingly, it is this challenge what usually enhances the interest and creativity of the students, motivating them to take the exercise seriously. In addition, they are required to complete the task within a limited timeframe.

The introduction of the case is done by the trainer, who will also provide the essential information and data required to perform the necessary calculations: description of the plant or equipment where the accident occurred (photos, maps), amount of hazardous material involved, meteorological conditions, etc. The students should already be familiar with the mathematical models needed to solve the case, such as those related to atmospheric dispersion, thermal radiation from a fire, etc. Therefore, they should not use any additional documents or sources of information; for example, in the case presented here, references [7,8] are not provided to them. However, some specific information must be given, such as the chemical reactions involved in the decomposition of sodium hydrosulfite and the corresponding Material Safety Data Sheets (MSDS).

In principle, no specific data on the effects (e.g., thermal radiation or gas concentration at a given distance) should be given, as this is what the students are expected to calculate. However, supporting information necessary to perform the calculations—such as the relevant Probit equations—must be provided. It is acceptable to provide information on the observed consequences, such as the percentage of people affected by a toxic gas at a certain distance. This enables comparison between the calculated and actual data; if the two do not reasonably coincide, students should provide an explanation for the discrepancy. MSDS information should be used by students not only for safety considerations, but also for assessing the environmental aspects (e.g., biodegradability, bioaccumulation, etc.).

Then the students have a certain amount of time—between half an hour and one hour—to analyse the information supplied. Afterwards, there is a short debriefing session with the trainer to address any possible doubts. After this initial analysis, they receive the set of questions they must answer. They then proceed to work on solving the case. Finally, once the necessary calculations—possibly using dedicated software—and considerations have been completed, they are required to write a report.

As for the time allocated to the exercise, five hours (half a day) is usually practical and sufficient. During this time, the professor will not follow their progress closely, although he should be available to clarify specific questions if needed. In certain cases, the exercise may be extended to a full day, depending on its complexity.

The special case proposed here, related to a Natech (Natural-technological) accident followed by a domino effect involving various chemical reactions, a fire, explosions followed by fireballs, and the formation of a large toxic cloud, is also useful for illustrating the challenges that sometimes arise in quantitative risk analysis. These include the lack of accuracy in some of the mathematical models and expressions that must be used. More specifically, the answer to the main question posed to students in the proposed case will depend on the Probit equation used—in particular, on the value assumed for the exponent n in the dose expression. This serves as a valuable opportunity for the trainer to emphasize the fact that, in this field, experience and sound judgement are essential.

3. Case: A Fire Originating a Toxic Cloud

In January 1996 a ship with a cargo of diverse chemicals was approaching the harbor of Barcelona [7,8]. At 10.45 h in the morning the captain informed the harbor that there was a smoke release from a container. Due to the bad weather and to the fact that fighting a fire was easier if the ship was moored, it was decided to allow the ship to enter the harbor. 40 min later, at 11.25 h a.m., it moored in such a position that the wind blew the smoke towards the sea and away from the town.

The fire was in a container containing sodium hydrosulfite, also known as sodium dithionite (CAS number 7775-14-6, UN Number 1384), a substance reactive with water. Probably the container had cracked due to the bad weather the ship had endured in the Gulf of Lion, which had violently moved some containers, and some water (it was raining) had leaked inside it, reacting with the chemical. However, when the ship moored in the harbor, there was also a fire in another container containing hexane drums (the ship did not comply with the International Maritime Dangerous Goods (IMDG) code [9] concerning the segregation between dangerous goods).

At 11.32 h the firefighters arrived. At 11.45 h they started to throw water to disperse the smoke and to extinguish the fire. At 11.55 h water was thrown on the containers also from another ship. At 12.15 h three ships were throwing water on the containers. A zone of the port was evacuated due to the toxic smoke.

At 13.18 h there was a first explosion (a BLEVE) caused by the bursting of a hexane drum; it was followed by more explosions. All these explosions were immediately followed by a short duration fireball. At 16 h the release of smoke from the sodium hydrosulfite container stopped. At 16.04 h one of the explosions opened the door of the hexane container, with the consequent enlargement of the flames. At 19.30 h the fire was finally extinguished.

The event generated an important smoke plume until 19.30 h. This plume was a mixture of gases produced by the decomposition of sodium hydrosulfite and the combustion of hexane. It travelled to the harbor inlet along the evacuated pier and dispersed over the sea, as there was essentially NE (40°–49°) wind during all the time. The smoke did not affect either the harbor buildings or the town, being just dispersed over the sea.

Eleven people (seven workers, three crew members and two policemen) received medical attention due to the effects of the smoke. Nobody was injured by the explosions (no fragments were ejected, as they were trapped by the hexane container) or the thermal radiation, which effects reached a rather short distance.

The event had an important impact in the newspapers, as many people in the town saw the smoke plume and, furthermore, there had been another accident in the harbor two weeks before. Therefore, the decision to allow the ship to enter the harbor was criticized by several journalists and local politicians, who believed that the toxic smoke released could have been dangerous for the population.

The exercise will therefore address the dispersion of the toxic plume containing SO_2 and the possibility that a change in wind direction could have posed a danger to the population.

3.1. Information Available

Although in the plume there were also several gases from the hexane combustion, the main toxic component was SO_2; the modeling of the atmospheric dispersion will therefore be based on this gas. Its toxicity parameters are those in Table 1.

Table 1. SO_2 toxicity parameters.

Toxicity parameter	Value $^{(*)}$	Reference
IDLH	100 ppm, 262 mg·m^{-3}	NIOSH [10]
ERPG-2	3 ppm, 7.8 mg·m^{-3}	AIHA [11]

$^{(*)}$ For toxicity evaluation of effects, concentration is measured at 1 atm and 25 °C.

Other toxicity threshold values can be used, such as the Acute Exposure Guidelines Levels (AEGL) [12] or Protective Action Criteria (PAC) datasets [13] (formerly known as the Temporary Emergency Exposure Limit, TEEL), but the exercise proposed is focused on the Immediately Dangerous to Life or Health (IDLH) concentration and the Emergency Response Planning Guidelines (ERPG-2). The chosen values can be dependent on local or governmental rules; i.e., actual Risk Management Program rule in US uses ERPG-2 as end point for hazardous substances [14]. Discussion about alternative toxicity thresholds can be part of the exercise as an option. See the cited literature for sources of information about these toxicity thresholds or end points available. Additionally, some teaching opportunities about potential for persistent and ecotoxicity hazards can be developed using the information included in the MSDS section about ecological information.

Several Probit equations have been proposed for the SO_2, such as for example:

$$Y = -15.67 + 1 \cdot ln\ (C^1 \cdot t) \text{ [15,16]} \quad (1)$$

$$Y = -19.2 + 1 \cdot ln\ (C^{2.4} \cdot t) \text{ [17,18]} \quad (2)$$

In Equation (1) C is the concentration in ppm, in Equation (2) C is the concentration in mg·m^{-3}; in both equations, t is the time in min.

SO_2 was produced by the thermal decomposition of sodium hydrosulfite exposed to heat or flames:

$$2\ Na_2S_2O_4 \rightarrow SO_2 + Na_2SO_3 + Na_2S_2O_3 \quad (3)$$

or by its reaction with water:

$$2\ Na_2S_2O_4 \rightarrow 4\ Na^+ + 2\ S_2O_4^{2-} \quad (4)$$

$$2\ S_2O_4^{2-} + H_2O \rightarrow S_2O_3^{2-} + 2\ HSO_3^- \quad (5)$$

$$2\ HSO_3^- + 2\ H^+ \rightarrow 2\ SO_2 + 2\ H_2O \quad (6)$$

Due to the impossibility of establishing the contribution of each one of these mechanisms, two limiting situations can be assumed: a) all SO_2 was generated by the reaction (3) (smallest possible emission rate), and b) all SO_2 was generated by the reactions (4), (5) and (6) (largest possible emission rate); a constant release velocity can be also assumed. The amount of sodium hydrosulfite in the container when the ship moored in the wharf can be assumed to be approximately 18,000 kg and the smoke was released at the harbor from 11.25 h up to 16 h.

Due to the variation of wind velocity during the accident, two different atmospheric situations must be taken (Table 2), corresponding to the limit values of wind speed (the meteorological data were taken from the harbor station). Even though it experienced light changes during the event, wind direction can be assumed to have been constant from NE.

Table 2. Meteorological conditions for the two situations studied.

	Condition A	**Condition B**
Wind speed	2.5 $m \cdot s^{-1}$	8.5 $m \cdot s^{-1}$
Wind direction	NE (45°)	NE (45°)
Stability class	B	C
Temperature	10 °C	10 °C
Relative humidity	90%	90%
Cloud cover	50%	50%
Roughness coefficient (open sea)	0.0001 m	0.0001 m

According to the accident videos, the smoke did not undergo buoyant rise or gravity lowering, its behavior being that of a neutral gas.

3.2. Tasks and Questions to Be Answered

The following tasks and questions are asked to the team:

- Write a description of the accident.
- Simulate the toxic dispersion for the two limiting SO_2 release rates and for the two atmospheric situations defined in Table 2.
- Estimate the evolution of SO_2 concentration as a function of distance. Compare it with the values of IDLH and ERPG-2.
- Where the SO_2 concentrations dangerous for the population? If the answer is yes, up to which distance?
- Would the SO_2 concentrations have been dangerous for the population if the wind direction had changed and the smoke plume had been directed towards the town?
- Write the main conclusions.

3.3. The Exercise

The first step is the calculation of the sulfur dioxide release rates (200 g/s and 400 g/s, respectively) corresponding to the two mechanisms assumed.

Then the simulations by using the ALOHA software (Version 5.4.7) [19] must be done (Gaussian model). The students must already know this software, having used it previously. Four simulations must be performed, covering the two release rates and the two meteorological conditions. If the team progresses too slowly, then they should work only with condition A. A typical plot showing the shape of the smoke plume can be seen in Figure 1.

From the simulations, the variation of the SO_2 concentration as a function of the distance should be plotted, compared with certain parameters such as IDLH and ERPG-2. Such a plot has been represented in Figure 2. It can be seen that the concentration decreases quickly, reaching values lower than the IDLH which certainly should not be considered dangerous in the frame of a short event.

One interesting point of the exercise is that concerning the question "What would have happened if the wind direction had changed (same speed), sending the smoke towards the town?". Here the team may need the help of the trainer. In this second scenario, the exposure time would have been much larger and even concentrations significantly smaller than the IDLH could have implied a danger. The following approach can be suggested to the students: in the Probit analysis, the dose is a function of the concentration (affected by a certain exponent) and the time; therefore, the same dose can be reached with very low concentration if the exposure time is sufficiently high:

$$SO_2 \text{ dose} = C_1^n \cdot t_1 = C_2^n \cdot t_2 \tag{7}$$

This expression is in fact a modification of the Haber's rule [17], which assumes n = constant = 1.

Therefore, this expression can be applied to the IDLH concentration and time (C_1 = 100 ppm or 262 $mg \cdot m^{-3}$, and t = 30 min) and to the situation that would imply the same dose for an exposure time of 275 min (from 11: 25 h up to 16 h) and a concentration C_2. However, a problem appears here: the n exponent can have different values, according to the selected source (see Equations (1) and (2)):

$$100^1 \cdot 30 = C_2^1 \cdot 275 \tag{8}$$

$$262^{2.4} \cdot 30 = C_2^{2.4} \cdot 275 \tag{9}$$

According to Equation (8), C_2 = 10.9 ppm (i.e., C_2 = 28.6 mg/m^3); and according to Equation (9), C_2 = 104 mg/m^3. This is a good example of the lack of accuracy that can appear in certain calculations—which sometimes should rather be called estimations—in the field of risk analysis. This point should be emphasized by the professor in the discussion and comments once the exercise is finished.

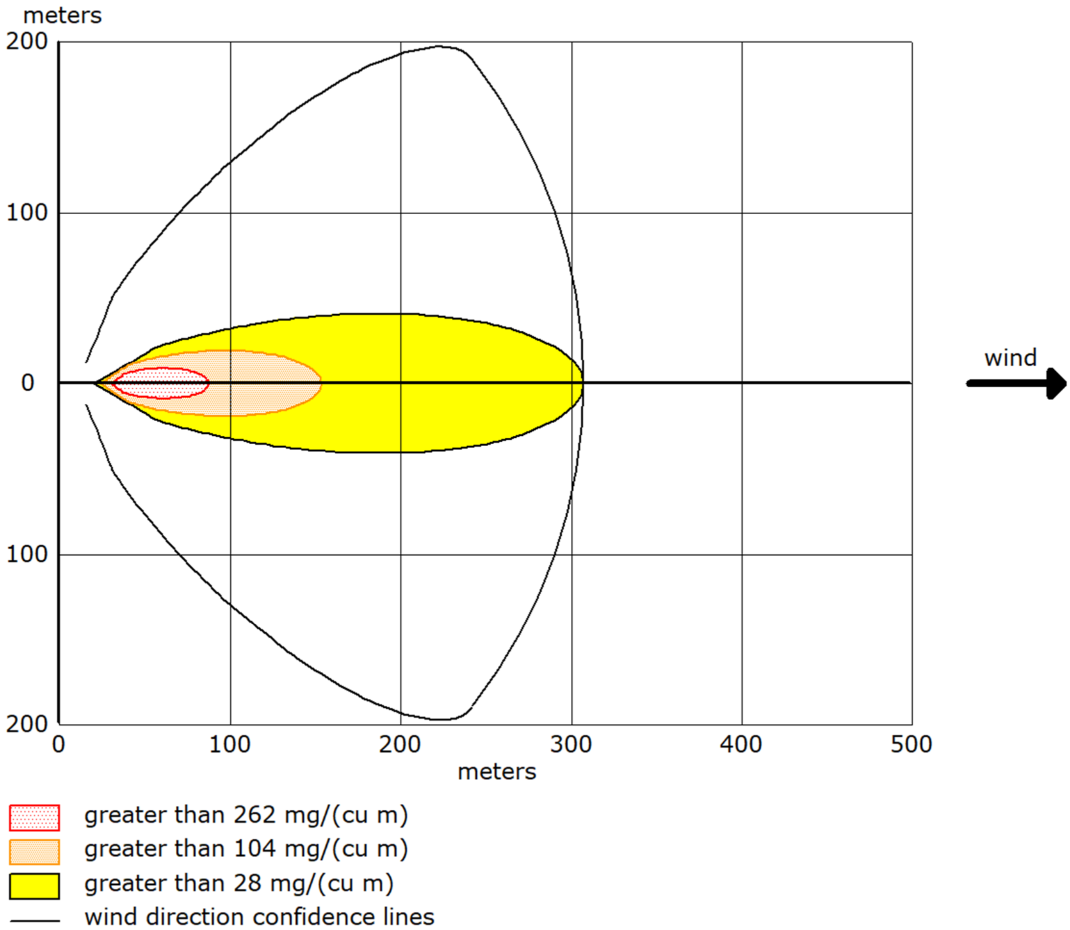

Figure 1. Image of the plume for case A, release rate = 400 g/s. Profiles for the concentrations corresponding to IDLH and those predicted by Equations (8) and (9).

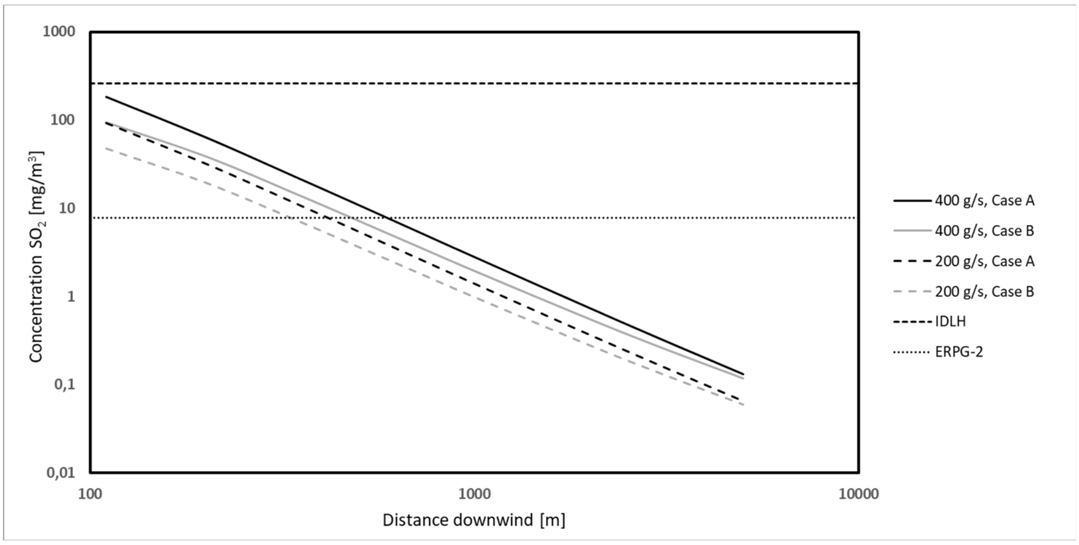

Figure 2. Variation of SO_2 concentration as a function of the distance from the source, for the four situations analyzed.

To answer to the question concerning the toxic plume moving towards the town, two radial distances should be determined for each case by the team: those corresponding to (a) the distance at which an exposure of about 30 min would imply toxic effects requiring medical assistance, but without any danger for the life of a person (IDLH), and (b) the distance implying the same effects after an exposure of 4:35 h (Figure 3). It can be observed that the different values of the concentration C_2 obtained from Equations (8) and (9) have a significant influence on the corresponding maximum distances (307 m and 153 m, respectively) reached.

Figure 3. Distances reached by the different concentrations (IDLH and the ones implying the equivalent toxic effects on population according to Equations (8) and (9) (case A, release rate 400 g/s).

Taking into account the distances obtained (87 m for 262 mg/m^3, 153 m for 104 mg/m^3 and 307 for 28 mg/m^3), the team should reach the conclusion that even in the worse case—wind and smoke plume moving towards the town—there should not have been any serious danger for the population, as the affected area would have remained clearly inside the harbor and far from the inhabited zones. Therefore, the decision to allow the ship to enter into the harbor did not really imply a risk for the town.

3.4. Evaluation

The evaluation of the exercise is based on several components: the final report submitted by the students, the simulation of the toxic cloud, their responses to the assigned questions, and the conclusions they draw. In addition to assessing the written work, it is often useful to hold a follow-up meeting with the students to discuss the report. This discussion can provide further insight into their understanding of the case and contribute meaningfully to the overall evaluation.

4. Conclusions

This example has been used in courses at the Universitat Politècnica de Catalunya (UPC), both at the graduate and master's levels in chemical engineering, as well as in other training programs delivered in institutions in Chile, Argentina, and Mexico. The outcomes have always been very positive. Although no formal surveys have been conducted specifically to assess this exercise, general course evaluations are carried out every semester, and many students spontaneously mention this type of case study as one of the most engaging and enriching components of the course. Participants consistently show strong interest and embrace the challenge that such exercise implies with a highly positive attitude. For many, it is their first opportunity to take on the role of "experts" in the context of an engineering problem, which makes the exercise particularly motivating. This type of activity requires a creative effort, which also contributes to the team's sense of achievement once the final report is completed. For this reason, trainers should consider providing only the bare minimum of additional information or hints, just enough to help students overcome specific difficulties or doubts without compromising the open-ended nature of the task.

Moreover, these exercises offer a valuable way to learn from real accidents—events for which society has often paid a high price. Other case studies could also be used, potentially introducing different phenomena such as fires (including wildfires) or explosions. However, the toxic cloud scenario presents a particularly high potential for environmental impact, which makes it especially interesting and instructive from the students' point of view.

This approach aligns with the growing emphasis on experiential and problem-based learning in engineering education, and it proves particularly effective in safety and risk training, where the ability to analyse complex real-world scenarios is essential for developing professional competence and sound judgement.

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Nomenclature (Acronyms)

AEGLs, Acute Exposure Guideline Levels: airborne concentration at which most people-including sensitive individuals such as old, sick or very young people, will begin to experience health effects if they are exposed to a hazardous chemical for a specific length of time (duration). ERPG-2, Emergency Response Planning Guidelines tier 2: the maximum concentration in air below which it is believed nearly all individuals could be exposed for up to 60 min without experiencing or developing irreversible or other serious health effects or symptoms that could impair their abilities to take protective action (ppm, mg/m^3). IDLH, Immediately Dangerous to Life and Health: the maximum airborne concentration of a substance to which a healthy male worker can be exposed for up to 30 min and still be able to escape without loss of life or irreversible organ system damage (ppm, mg/m^3). MSDS, Material Safety Data Sheet: document that provides comprehensive information about the composition, physical and chemical properties, health effects and environmental impacts of a substance or mixture. It also contains guidance on the safe handling, use, storage and disposal of the product. PAC, Protective Action Criteria values for emergency planning for chemical release events are based on the following exposure limit values: AEGLs, ERPGs, TEELs. TEELs, Temporary Emergency Exposure Limits: airborne concentrations at which the general population, including susceptible individuals, could experience health effects if they are exposed for more than one hour.

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