INTEGRATED MANAGEMENT SYSTEM FOR IN-HOUSE CONTROL OF ACCIDENTAL HYDROGEN SULFIDE LEAKS IN OIL REFINERIES

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1- INTRODUCTION

Also known as sour gas, stinkdamp or sulferetted hydrogen, hydrogen sulfide (H\textsubscript{2}S) is a colorless gas with a characteristic unpleasant smell that is extremely toxic and corrosive. Denser than air, it is partially soluble in water and soluble in certain polar organic solvents, such as: methanol, acetone, glycol, glycerol, gasoline, kerosene, and crude oil. It is fairly inflammable and its self-ignition temperature is 260°C, while its low explosivity threshold is around 4.3% (by volume) in air (Mainier, 2002).

The main source of hydrogen sulfide in the oil industry appears during the treatment of natural gas and crude processing in refineries, where the H\textsubscript{2}S is recovered as a substance deriving from these treatments and is generally turned into ultra-pure sulfur at Sulfur Units.

The concentrations of hydrogen sulfide found in natural gas and crude oil vary from 10 ppm to 100,000 ppm, depending directly on the geological sources. These concentrations prompt concern with the toxic effects of hydrogen sulfide on human beings as well as its corrosivity when in contact with materials and equipment, usually resulting in deterioration or fractures, with catastrophic consequences.

Due to its toxicity, hydrogen sulfide irritates the eyes and / or affects the human nervous and respiratory systems. Depending on its concentration, it can kill a human being in a matter of minutes. Thus, should an accident occur that involves a hydrogen sulfide leak, the consequences may reach massive proportions, endangering human lives, threatening the integrity of industrial assets and jeopardizing the environment.

The clinical signs of this type of intoxication include head-ache, dizziness, nausea, convulsions and coma. Acting as a respiratory depressant, H\textsubscript{2}S causes hypoventilation, hypoxia, cyanosis and metabolic acidosis. Pneumonia and pulmonary edema are frequent complications. Most deaths occur at the site of exposure to the lethal gas. It is important to stress that there is no laboratory test available for immediate diagnosis, meaning that information about the patient’s status is based on anamnesis and clinical assessments (Lovejoy & Linden, 1992).

According to research by Beauchamp et al. (1984), human beings may lose the ability to smell the odor of H\textsubscript{2}S at concentrations of higher than 100 to 150 ppm (140 – 210 mg/m\textsuperscript{3}), probably due to olfactory fatigue. This is a dangerous situation, as they are unaware of the dangers presented by the acute toxicity of hydrogen sulfide in the nervous system and lungs. Lethal intoxication by hydrogen sulfide occurs at concentrations of 1,000 to 2,000 ppm (1,390 to 2,780 mg/m\textsuperscript{3}), with paralysis of the respiratory system and the consequent stoppage of the cardio-respiratory system, resulting in death (ACGIH, 1992).

It is important to issue a warning about the severity and risks of this toxic gas, which may directly or indirectly affect everyone working in industrial plants generating this gas, in order to ensure that they are aware of the risks to which they are exposed in their daily tasks, should a leak occur. It is vital to establish a critical awareness of the need for workers to protect themselves and provide the necessary assistance to their work-mates, in case of any emergency.

Considering the extremely toxic aspects of H\textsubscript{2}S, it is important that everyone engaged in industrial processing is properly informed about the risks presented in Table 1, with all personnel being properly trained to render the necessary assistance in emergencies.

<table>
<thead>
<tr>
<th>Concentration H\textsubscript{2}S (ppm)</th>
<th>Exposure Time</th>
<th>Effects on Human Beings</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 - 5</td>
<td>1 min</td>
<td>Detection of characteristic odor</td>
</tr>
<tr>
<td>10 - 30</td>
<td>6 – 8 h</td>
<td>Eye irritation</td>
</tr>
<tr>
<td>50 – 100</td>
<td>30 min - 1h</td>
<td>Conjunctivitis, breathing difficulties</td>
</tr>
<tr>
<td>150 - 200</td>
<td>2 - 15 min</td>
<td>Loss of sense of smell</td>
</tr>
<tr>
<td>250 - 350</td>
<td>2 - 15 min</td>
<td>Eye irritation</td>
</tr>
<tr>
<td>350 - 450</td>
<td>2 - 15 min</td>
<td>Loss of consciousness, convulsions</td>
</tr>
<tr>
<td>500 - 600</td>
<td>2 - 15 min</td>
<td>Respiratory and circulatory disturbances</td>
</tr>
<tr>
<td>700 – 1500</td>
<td>0 - 2 min</td>
<td>Collapse, death</td>
</tr>
</tbody>
</table>

Source: Mainier & Rocha, 2003

In Brazil, several accidents have occurred with hydrogen sulfide leaking into the environment and consequently causing intoxications and deaths. According to Balbi (2001), a natural gas leak occurred, contaminated with hydrogen sulfide, on the P-37 rig operated by Petrobras in the Campos Basin in Rio de Janeiro State, Brazil, killing two outsourced workers employed by a company contracted by this mixed-ownership enterprise. Table 2 below lists a series of accidents that have occurred in various parts of the world resulting in intoxications and deaths.
Bearing in mind these specific aspects and the corrosive and toxic physical and chemical characteristics of H₂S, the application of this study is the maintenance of the safety, regarding the accidental H₂S leak to the atmosphere. It emphasizes the activities of emergency control, limited to the inner areas of the oil refineries, prioritizing the composition of the two most important protection actions: evacuation and sheltering. The principal strategy is related to the local sheltering. The results will be shown in a matrix.

### Table 2 – Accidents with Hydrogen Sulfide Leaks

<table>
<thead>
<tr>
<th>Place / Date</th>
<th>Brief Description of the Accidents</th>
<th>Intoxications</th>
<th>Deaths</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poza Rica, México, 1950</td>
<td>Plant stripping H₂S from natural gas</td>
<td>320</td>
<td>22</td>
</tr>
<tr>
<td>Texas, USA, 1969</td>
<td>Leak at oil refinery</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Maine, USA, April 2, 1971</td>
<td>H₂S formation in chromic acid tank</td>
<td>---</td>
<td>6</td>
</tr>
<tr>
<td>Chicago, USA, February 14, 1978</td>
<td>H₂S formation in chromic acid tank</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Texas, USA, 1979</td>
<td>Leak at oil refinery</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Texas, USA, February 20, 1989</td>
<td>Crude oil leak at tanker farm</td>
<td>30</td>
<td>---</td>
</tr>
<tr>
<td>Whitehall, USA, June 29, 1999</td>
<td>Outflow of chemical products</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Memphis, USA, October 26, 1999</td>
<td>Oil refinery</td>
<td>11</td>
<td>---</td>
</tr>
<tr>
<td>Dalian, China, December 29, 1999</td>
<td>Chemical products plant</td>
<td>11</td>
<td>4</td>
</tr>
<tr>
<td>Alberta, Canada, October 30, 2000</td>
<td>Maintenance of gas pipeline valve</td>
<td>13</td>
<td>---</td>
</tr>
<tr>
<td>Ufa, Russia, November 24, 2000</td>
<td>Sulfuric acid plant</td>
<td>9</td>
<td>3</td>
</tr>
<tr>
<td>Godorf, Alemanha, 1969</td>
<td>Mineral oil refinery</td>
<td>60</td>
<td>1</td>
</tr>
<tr>
<td>Ichihara City, Japão, 26/03/1974</td>
<td>Industrial process plant</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Gênova, Itália, 19/08/1978</td>
<td>Chemical products discharge</td>
<td>29</td>
<td>8</td>
</tr>
<tr>
<td>Rajasthan, India, 28/10/1984</td>
<td>Heavy water plant</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Montes Urais, Rússia, 05/1988</td>
<td>Oil refinery</td>
<td>51</td>
<td>---</td>
</tr>
</tbody>
</table>


#### 2 - EMERGENCY RESPONSE

The main purpose of mitigating the consequences of a hydrogen sulfide leak is to protect people who may be directly or indirectly affected by it. In order to ensure that this task is properly performed, in addition to rapid and efficient notification of the emergency situation, each worker must be aware of the actions to be performed, minimizing the chances of being affected by the leak, with the answers to some questions being decided in advance for the emergency situation in question:

- Is it necessary to halt the process?
- Is it better to remain in the shelter or attempt evacuation?
- What would be the most efficient respiratory protection?

Hence, the most efficient emergency response for accidental leaks of H₂S is the composition of the two protection actions: evacuation and sheltering, besides the use of adequate individual protection equipment and immediate medical assistance to the victims. The five most important actions to mitigate the consequences of a H₂S accidental leak are the following:

- **Emergency Procedures**

  Organizing the procedures requires drawing up a clear and systematic description of the actions that must be taken at the various stages of the accident. According to Souza Junior (2002), the main topics in this document are:

  - Identification of the purposes of each action;
  - Description of the appropriate techniques for performing each action;
  - The material resources to be used.

  Some of the emergency procedures adopted for toxic gas leaks forming vapor clouds encompass operating procedures that halt or divert the process flow. In addition to these procedures, consideration must be given to the equipment required to mitigate the effects of these leaks, such as: automatically shutting the air intake for the control room and switching off the ventilation system (CCPS, 2007).

  The prepared procedures must be applied as parameters, becoming an integral part of the safety training program and providing input for assessing behavior during the investigations of any accidents that may occur.
**Plant Evacuation**

Plant evacuation is a procedure that must be adopted in case of gas leaks, particularly inflammable gases such as Liquid Petroleum Gas (LPG). According to CCPS (2007), all personnel located outdoors and downwind of toxic or toxic-inflammable gases must leave the area immediately, moving towards the safety shelters and avoiding any movement in the same direction as the cloud.

For H₂S, which is a toxic-inflammable gas that is colorless and affects the human olfactory system at harmful concentrations, avoiding the direction of the toxic cloud while moving towards the shelters becomes an impossible task without the presence of devices indicating its direction, such as windmills, windsocks and telltales. These devices must be installed in sufficient numbers to ensure that they can be seen from all over the facility, and also must be properly lit so that they are visible at night.

**Sheltering**

The Chemical Shelters or Safety Units (SU), are designed to protect people from high gas concentrations found in toxic clouds that form during accidental leaks (Lees, 1996, Souza Junior 2002).

The SU are dual-purpose facilities that will be used normally as meeting rooms, but are specially designed and equipped for conversion into emergency shelters in case of any accidental H₂S leaks. They are thus endowed with specific characteristics, designed mainly to block inflows of air contaminated by the toxic cloud, as soon as the accident is notified. The architectural designs of rooms in a building must be adapted, in order to convert them into Safety Units.

These SU must be specially sealed with rubber or silicon blocking all cracks and gaps in windows, doors, etc., with autonomous breathing equipment, oxygen cylinders, escape masks with faceplates, first-aid and emergency equipment bags, H₂S sensors in the pipelines and in the rooms, and an emergency system blocking air inflow that consists of: an airlock; a positive pressure system; filters able to remove the contaminant; an automatic air control shut-off system, exhaust and ventilation mechanisms, and a manual system for handling all these operations.

**Individual Protection Equipment**

Individual Protection Equipment (IPE) offers yet another protective barrier between an accident and the process operators exposed to its effects. Depending on the severity of the occurrence, the correct use of IPE makes a difference. Because they may help operators to escape unharmed from a serious accident, or with only minor injuries, IPE sets are mitigatory measures of the utmost importance and efficacy in emergency situations.

In order to provide protection against the risk of toxic substance leaks, the IPE offers respiratory protection, allowing its wearer to get away unscathed. Depending on the chemical substance and the protection level desired, there is a variety of respiratory protection equipment.

For the specific case of H₂S, which is highly toxic and also irritates the eyes (from 10 ppm upwards) the IPE to be used by the operators must be able to withstand high concentrations of this gas and provide protection for the eyes. In this context, the following options are available on the market:

- Full face masks with absorbent filters: the concentrations handled by the filters must be ascertained, ensuring that users are aware of this constraint.
- Compressed air cylinder escape sets, which are more effective as they can withstand higher toxic gas concentrations, but are heavier, and users require training to use them, although the procedure is simple.

Compressed air breathing equipment consists of stand-alone masks, which are independent respirators providing their users with oxygen from steel or composite cylinders, for up to 45 minutes. They are used during rescue operations or for emergency response actions. They must be placed in the control rooms and at strategic locations that have been studied and established previously in order to provide support for the operations.

**Medical Care**

As already shown previously in this Paper, hydrogen sulfide is an extremely toxic gas, meaning that immediate medical care or first aid measures may mean the difference between life and death for the victims of an H₂S leak. Rescue crews must be very well trained in this type of action, particularly revival by heart massage. In addition to training, the rescue crews must be equipped with respiration equipment and defibrillators (automatic revival equipment).

The first-aid room or medical centre at the refinery must be fitted with all necessary items of equipment and medications, including antidotes for this type of emergency.
3 - METHODOLOGY

As parameters for the SU project design, and in order to prove that sheltering must be the main strategy used as the emergency response action in case of accidental leaks of H$_2$S at Oil Refineries, the study examined the following factors through potential accident scenarios:

- **Dispersal of toxic hydrogen sulfide cloud**
  The speed at which a toxic H$_2$S cloud builds up, taking its concentration into account, meaning its dispersal, as well as the length of time it remains within the inner boundaries of the industrial site (radius of 3 kms) are key factors for defining shelter requirements and the SU project parameters.
  The dispersal of a toxic gas cloud varies according to its heat source, meaning the quantity of toxic substances discharged into the atmosphere, in addition to local meteorological conditions at the time of the accident. In order to study this phenomenon, the PHAST 6.53.1 accident scenario mathematical modeling software was used as a tool, developed by *Det Norske Veritas* (DNV, 2007).

- **Benchmark Accident Scenarios**
  These scenarios were modeled after an extensive survey of Oil Refinery Risk Analysis documents involving accident scenarios encompassing hypothetical H$_2$S leaks from Sulfide Plant equipment. Two distinct types of heat sources were taken into consideration: those released instantaneously, and continuous leaks.

- **Weather Conditions**
  The movement of the toxic cloud through the environment depends basically on local topography, wind speeds and atmospheric turbulence levels at the time of the accident. In order to conduct this study and in order to assess the same accident under different weather conditions, the following meteorological parameters were taken into consideration:

<table>
<thead>
<tr>
<th>Table 3: Meteorological Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Meteorological Conditions Used in the Vulnerability Analysis</strong></td>
<td></td>
</tr>
<tr>
<td>Air Temperature</td>
<td>20°C</td>
</tr>
<tr>
<td>Relative air humidity</td>
<td>70%</td>
</tr>
<tr>
<td>Surface temperature for dispersal calculation</td>
<td>20°C</td>
</tr>
<tr>
<td>Solar radiation flow</td>
<td>0.5 Kw/m²</td>
</tr>
</tbody>
</table>

  Stability classes used in the Vulnerability Analysis

<table>
<thead>
<tr>
<th>Class</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>Very stable -- possibility of fog</td>
</tr>
<tr>
<td>D</td>
<td>Neutral – little sun and wind, or cloudy night with wind</td>
</tr>
</tbody>
</table>


- **Toxicity Threshold**
  For the preparation and sizing of the SU, it was assumed that the concentration around the SU would allow individuals to reach them after hearing the alarm siren. In order to attain this goal, the threshold concentration was established at a level rated as Immediately Dangerous to Life and Health (IDLH), with the IDLH value of the H$_2$S equal to 100 ppm (150 mg/m$^3$).

- **Worker Movement Speed**
  This was one of the parameters taken into consideration for the decision on the safe distance limit for deciding between the use of the SU or evacuation. The figure used was 5 km/h, corresponding to 1.39 m/s, meaning that under adverse conditions caused by an incident, a worker would require 1.2 minutes to cover 100 meters, which proves to be a conservative figure.

- **Emergency Response Time (RT)**
  The emergency response time in this case corresponds to the time needed for an H$_2$S leak to be identified, modified and notified. The shorter the response time to an incident, the more time is available for implementing the emergency response actions. In this study, three response times were taken into consideration: 2; 3 and 4 minutes.
• Physical Characteristics of Industrial Sites
  Each industrial plant has its own physical characteristics and particular layout, as well as different numbers of workers. Thus, an assessment is required for each of them in order to locate, quantify and size the SUs.

  The hypothetical accident scenarios that were modeled and researched were drawn up on the bases of all the parameters mentioned above.

  After completing this stage, the worst case scenario was selected and an even more specific study was conducted, taking into account all the parameters presented above, in addition to the following factors:
  • Inventory varying from 10 kg to 300 kg;
  • Time required for the toxic cloud to reach its maximum concentration at places where workers are clustered;
  • Maximum range of the toxic H₂S cloud;
  • Total dispersal time of the toxic H₂S cloud.

  This more specific study showed that no matter how short the response time to the incidents involved in an H₂S leak, when the emergency response actions are launched, the toxic cloud is already some distance away from the source of the leak (approximately 250 m). Sheltering is thus the most appropriate protection action for workers in nearby areas, up to 500 m from the source of the accidental leak.

  All these factors are taken into consideration in the matrix underpinning the emergency response planning that was drawn up on the basis of this study, presenting the composition of the response actions that must be taken in each case.

4 - EMERGENCY RESPONSE PLANNING SUPPORT MATRIX

  The practical purpose of the matrix is to present a detailed ranking of the expected efficiency of the various protection measures pertinent to the technical scenarios taken as a benchmark. The determining factors for the maximum efficiency of the protection measures are: the dispersal characteristics of the toxic H₂S cloud; the spatial distribution of groups of workers in areas vulnerable to leaks; and the quantitative details of each group within the inner boundaries of the refinery.

4.1 - Matrix Entry Parameters and Application Limits
  • Inventory (varies from 10 kg to 300 kg of pure H₂S)
  • Minimum flow rate (0.5 kg/s of pure H₂S)
  • Occupancy of area around the source of the leak
  • Emergency Response Time
  • Number of people in the vulnerable area (up to 10; up to 50; more than 50)
  • Buildings located in the refinery
  • Distance from the source of the leak (varies from 50 m to 1,350 m)

4.2 - Recommendations

A – Area fitted with a short sensor circuit and specific alarms. Access only for personnel with specific regular training. IPE must be carried at all times, with an estimated placement time of up to 15 seconds;
B – Area fitted with specific alarms. Access only for personnel with brief instruction on safety procedures. IPE must be carried at all times, with an estimated placement time of up to 30 seconds;
B1 – Area with access only for personnel with brief instruction on safety procedures.
C – Adopt local sheltering as a protection measure, using an appropriate SU compliant with the specifications of each refinery, in order to shorten access times to areas rated as safe.
D – Adopt an evacuation strategy for the contaminated area, identifying evacuation routes and their respective meeting points in areas rated as safe.
E – Conduct medical examinations of groups leaving contaminated areas.
F – Block traffic flows towards contaminated areas from this boundary distance.
G – Reassess the location of groups of workers in the area, due to the low efficiency in any protection measure to be adopted at the site.
H – The area must be subject to rigid access control with mandatory monitoring of human presence.
I – The toxic cloud does not reach this boundary distance.
J – Safe boundary distance for establishing the escape route meeting points.
### Table 4: Quick Check Summary Matrix

<table>
<thead>
<tr>
<th>POPULATION</th>
<th>Up to 10</th>
<th>Up to 30</th>
<th>Up to 50</th>
<th>More than 50</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>INVENTORY</strong></td>
<td>10 kg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 m – 100 m</td>
<td>A-C-E-H(^1)</td>
<td>A-C-E-H</td>
<td>G-H</td>
<td>G-H</td>
</tr>
<tr>
<td>150 m</td>
<td>B-C/D-E-H</td>
<td>B-C/D-E-H</td>
<td>G-H</td>
<td>G-H</td>
</tr>
<tr>
<td>250 m</td>
<td>B1-D-E</td>
<td>B1-D-E</td>
<td>B1-D-E</td>
<td>B1-D-E</td>
</tr>
<tr>
<td>300 m – 450 m</td>
<td>B1-D</td>
<td>B1-D</td>
<td>B1-D</td>
<td>B1-D</td>
</tr>
<tr>
<td>500 m</td>
<td>I-J-F</td>
<td>I-J-F</td>
<td>I-J-F</td>
<td>I-J-F</td>
</tr>
<tr>
<td><strong>INVENTORY</strong></td>
<td>50 kg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 m</td>
<td>A-C-E-H</td>
<td>G-H</td>
<td>G-H</td>
<td>G-H</td>
</tr>
<tr>
<td>100 m</td>
<td>A-C-E-H</td>
<td>A-C-E-H</td>
<td>G-H</td>
<td>G-H</td>
</tr>
<tr>
<td>150 m</td>
<td>B-C/D-E-H</td>
<td>B-C/D-E-H</td>
<td>B-C/D-E-H</td>
<td>G-H</td>
</tr>
<tr>
<td>200 m</td>
<td>B-C/D-E-H</td>
<td>B-C/D-E-H</td>
<td>B-C/D-E-H</td>
<td>G-H</td>
</tr>
<tr>
<td>250 m – 300 m</td>
<td>B1-C/D-E</td>
<td>B1-C/D-E</td>
<td>B1-C/D-E</td>
<td>B1-D-E</td>
</tr>
<tr>
<td>350 m – 450 m</td>
<td>B1-D-E</td>
<td>B1-D-E</td>
<td>B1-D-E</td>
<td>B1-D-E</td>
</tr>
<tr>
<td>500 m – 700 m</td>
<td>B1-D</td>
<td>B1-D</td>
<td>B1-D</td>
<td>B1-D</td>
</tr>
<tr>
<td>800 m</td>
<td>I-J-F</td>
<td>I-J-F</td>
<td>I-J-F</td>
<td>I-J-F</td>
</tr>
<tr>
<td><strong>INVENTORY</strong></td>
<td>100 kg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 m</td>
<td>A-C-E-H</td>
<td>G-H</td>
<td>G-H</td>
<td>G-H</td>
</tr>
<tr>
<td>100 m – 200 m</td>
<td>A-C-E-H</td>
<td>A-C-E-H</td>
<td>G-H</td>
<td>G-H</td>
</tr>
<tr>
<td>250 m – 300 m</td>
<td>A-C-E-H</td>
<td>A-C-E-H</td>
<td>G-H</td>
<td>G-H</td>
</tr>
<tr>
<td>350 m – 500 m</td>
<td>B1-D-E</td>
<td>B1-D-E</td>
<td>B1-D-E</td>
<td>B1-D-E</td>
</tr>
<tr>
<td>600 m – 900 m</td>
<td>B1-D</td>
<td>B1-D</td>
<td>B1-D</td>
<td>B1-D</td>
</tr>
<tr>
<td>1000 m</td>
<td>I-J-F</td>
<td>I-J-F</td>
<td>I-J-F</td>
<td>I-J-F</td>
</tr>
<tr>
<td><strong>INVENTORY</strong></td>
<td>200 kg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 m</td>
<td>A-C-E-H</td>
<td>G-H</td>
<td>G-H</td>
<td>G-H</td>
</tr>
<tr>
<td>100 m – 250 m</td>
<td>A-C-E-H</td>
<td>A-C-E-H</td>
<td>G-H</td>
<td>G-H</td>
</tr>
<tr>
<td>300 m</td>
<td>B-C/E-H</td>
<td>B-C/E-H</td>
<td>B-C/D-E-H</td>
<td>B-D-E-H</td>
</tr>
<tr>
<td>350 m – 600 m</td>
<td>B1-D-E</td>
<td>B1-D-E</td>
<td>B1-D-E</td>
<td>B1-D-E</td>
</tr>
<tr>
<td>700 m – 1100 m</td>
<td>B1-D</td>
<td>B1-D</td>
<td>B1-D</td>
<td>B1-D</td>
</tr>
<tr>
<td>1150 m</td>
<td>I-J-F</td>
<td>I-J-F</td>
<td>I-J-F</td>
<td>I-J-F</td>
</tr>
<tr>
<td><strong>INVENTORY</strong></td>
<td>300 kg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 m</td>
<td>A-C-E-H</td>
<td>G-H</td>
<td>G-H</td>
<td>G-H</td>
</tr>
<tr>
<td>100 m – 300 m</td>
<td>A-C-E-H</td>
<td>A-C-E-H</td>
<td>G-H</td>
<td>G-H</td>
</tr>
<tr>
<td>350 m – 450 m</td>
<td>B-C/E-H</td>
<td>B-C/D-E-H</td>
<td>B-D-E-H</td>
<td>G-H</td>
</tr>
<tr>
<td>600 m – 700 m</td>
<td>B1-D-E</td>
<td>B1-D-E</td>
<td>B1-D-E</td>
<td>B1-D-E</td>
</tr>
<tr>
<td>800 m – 1300 m</td>
<td>B1-D</td>
<td>B1-D</td>
<td>B1-D</td>
<td>B1-D</td>
</tr>
<tr>
<td>1,350 m</td>
<td>I-J-F</td>
<td>I-J-F</td>
<td>I-J-F</td>
<td>I-J-F</td>
</tr>
</tbody>
</table>

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### 5 - PREPARATION OF THE SAFETY UNIT PROJECT DESIGN

From the operating use standpoint, the SUs are divided into two groups:

A. Safety units that are not allow people to enter once the door has been closed, due to the risk of undermining the efficiency of the life support system.

B. Safety units fitted with a sealed chamber at the main entrance, allowing people to enter during the critical dispersal time of the toxic H₂S cloud.

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\(^1\) O hifén (-) entre as letras que representam as recomendações significa “e”.

\(^2\) A barra (/) entre as letras que representam as recomendações significa “ou”. Nesses casos, recomenda-se selecionar a opção mais adequada ao local da refinaria.
5.1 - Benchmark Parameters

- The oxygen concentration may not be less than 19.5% by volume (DRAEGER SAFETY, 2007);
- The CO₂ concentration may not exceed 0.5% (DRAEGER SAFETY, 2007);
- The temperature in the SU must be kept at 25ºC and may rise to 35ºC when people are standing still, with no physical effort (ACGIH, 1986; DRAEGER SAFETY, 2007);
- The module representing the human body must be a cylinder with a volume equal to 85 liters (base diameter: 80 cm; height: 1.70 m);
- The SU must be designed to shelter people for five hours, as a safety margin. The capacity to renew the air and maintain habitable conditions in the SU must be overestimated, in terms of the duration of the toxic H₂S cloud at critical concentrations, within the critical limits considered as being those of an oil refinery.

The B Group SUs are fitted with secondary injection systems equipped with one-way retention valves and secondary release systems for the entrance chamber. After admitting people to the entrance chamber and closing the door, which is in direct contact with the outside air, this secondary system runs through a purge-type recirculation stage that is designed to eliminate contaminants let in through opening the door.

In addition to the secondary release system and also in order to eliminate contaminants allowed in through opening the door, the entrance chamber must also be fitted with a sprinkler system that is triggered automatically when people enter and the door is closed. This system contains a decontaminating agent consisting of sodium carbonate with sodium peroxide (Sandres, 2009).

Figure 1 below shows the entrance chamber of the B Group SU, while Figures 3 and 4 present details of the sprinkler system and the concentration meters.

Figures 1, 2 and 3: Entrance chamber of the B Group SU, and details of the sprinkler system and concentration meters.

From the standpoint of their physical configurations and life support systems, the SU are rated as:
1. Safety Units with outside air intake.
2. Safety Units with air renewal based on compressed air stores.
3. Safety Units with air renewal based on liquefied gas (O₂) stores.

5.2 - Safety Units with Outside Air Intake

These chemical shelters take in outside air, using forced ventilation with H₂S removal and purification filtering systems and blow valves that keep their inside pressure slightly positive in order to ensure that no outside air seeps in.
5.2.1 - Life Support System Efficiency Controllers

The life support system efficiency controllers consist of items of equipment that must be installed in the SU in order to meter conditions and intervene for re-establishing their habitability conditions. For SU with outside air intake systems, they are:

- Contaminant concentration meters at the point where air is injected into the SU, indicating the efficiency of the filter system; and at the air intake point, showing the \( \text{H}_2\text{S} \) concentration in the outside air. The display of the contaminant concentration meter at the point where air is injected into the SU must be located inside it, so that people being sheltered can read it.
- Oxygen (\( \text{O}_2 \)) and carbon dioxide (\( \text{CO}_2 \)) concentration meters.
- Internal temperature and moisture control system that must consist of split-type air conditioning equipment adapted to block any inflow of outside air through the drainage system.
- Shelter sealing system: set of devices designed to seal gaps and cracks in the building structure that might allow contaminants to seep into the shelter. They must be applied to all structural openings, including electrical conduits, wastewater drainage systems, air conditioning equipment and exhaust fans.

5.2.2 - Operating Constraints

For this type of SU, critical faults are:

- Loss of the air injection system due to mechanical defects in the equipment or power outages.
- Expiry of the useful life of the \( \text{CO}_2 \) filter system.
- Blockage of the positive pressure control and release valve.
- Breach in the physical integrity of structural elements and sealing systems.

5.3 - Safety Units with Air Renewal based on Compressed Air Stores.

These chemical shelters do not take in outside air, but are based on compressed air stocks injected intermittently or continuously into the shelter in order to maintain the air quality. This set of equipment is supplemented by blow valves calibrated to release amounts of air corresponding to the injected compressed air, keeping their inside pressure slightly positive in order to ensure that no outside air seeps in.

Figure 6 below shows the SU model with air renewal based on compressed air stocks, and Figure 7 shows a detail of the compartment holding the compressed air cylinders and \( \text{CO}_2 \) filters.
5.3.1 - Life Support System Efficiency Controllers

- Contaminant concentration meters located inside and outside the shelter in order to control the efficiency of the sealing system and the outside H₂S concentration respectively.
- Oxygen (O₂) and carbon dioxide (CO₂) concentration meters.
- Internal filter system with forced circulation that limits any increase in the carbon dioxide concentration in the shelter.
- Internal temperature and moisture control system that must consist of split-type air conditioning equipment adapted to block any inflow of outside air through the drainage system.
- Shelter sealing system: set of devices designed to seal gaps and cracks in the building structure that might allow contaminants to seep into the shelter. They must be applied to all structural openings, including electrical conduits, wastewater drainage systems, air conditioning equipment and exhaust fans.

5.3.2 - Operating Constraints

For this type of SU, critical faults are:

- Blockage of the injection valve or rupture of the liquefied gas (O₂) transfer line supplying the shelter.
- Expiry of the useful life of the CO₂ filter system.
- Loss of the forced ventilation system for the CO₂ filters due to mechanical defects in the equipment or power outages.
- Breach in the physical integrity of structural elements and sealing systems.

5.4 - Safety Units with Air Renewal based on Liquefied Gas (O₂) Stores

These chemical shelters do not take in outside air, but instead maintains the oxygen (O₂) levels of the air n the SU. This system is supplemented by blow valves calibrated to release amounts of air corresponding to the injected compressed air, keeping their inside pressure slightly positive in order to ensure that no outside air seeps in.

Figure 8 below shows the SU model with air renewal based on liquefied gas stocks, and Figure 9 shows a detail of the set of equipment storing the liquid oxygen and the compartment holding the vaporizing unit and the CO₂ filters.
5.4.1 - Life Support System Efficiency Controllers

- Contaminant concentration meters located inside and outside the shelter in order to control the efficiency of the sealing system and the outside H₂S concentration respectively.
- Oxygen (O₂) and carbon dioxide (CO₂) concentration meters.
- Internal filter system with forced circulation that limits any increase in the carbon dioxide concentration in the shelter.
- Internal temperature and moisture control system that must consist of split-type air conditioning equipment adapted to block any inflow of outside air through the drainage system.
- Shelter sealing system: set of devices designed to seal gaps and cracks in the building structure that might allow contaminants to seep into the shelter. They must be applied to all structural openings, including electrical conduits, wastewater drainage systems, air conditioning equipment and exhaust fans.
- Humidification Unit at the pure oxygen (O₂) injection point.

5.4.2 - Operating Constraints

For this type of SU, critical faults are:

- Blockage of the injection valve or rupture of the liquefied gas (O₂) transfer line supplying the shelter.
- Expiry of the useful life of the CO₂ filter system.
- Loss of the forced ventilation system for the CO₂ filters due to mechanical defects in the equipment or power outages.
- Breach in the physical integrity of structural elements and sealing systems.
- Defect in the oxygen (O₂) meter.
Bearing in mind these classifications, specific SU models designed for a variety of contexts may be formatted for project design purposes, blending a variety of specifications, provided that they comply with safety requirements and present positive characteristics in a cost x benefit analysis.

The following combinations are presented as examples:

1A – Fixed Safety Unit with outside air intake that does not allow anyone to enter once the door has been sealed.

1B – Fixed Safety Unit with outside air intake with isolation chamber at the main entrance.

2A – Fixed Safety Unit with air renewal based on compressed air stocks that does not allow anyone to enter once the door has been sealed.

2B – Fixed Safety Unit with air renewal based on compressed air stocks with isolation chamber at the main entrance.

3A – Fixed Safety Unit with air renewal based on liquefied gas stocks that does not allow anyone to enter once the door has been sealed.

3B – Fixed Safety Unit with air renewal based on liquefied gas stocks with isolation chamber at the main entrance.

6 - CONCLUSIONS

- It is important to stress that H_{2}S leaks cause effects that extend beyond their sites and the times of their occurrences.
- The maximum efficiency of an emergency planning system that encompasses processing hazardous substances – such as H_{2}S – is grounded on the effectiveness of the Accident Prevention Program as well as the efficiency of the Emergency Plan itself.
- The most efficient response to a H_{2}S leak lies in the composition of the protective actions (evacuation and sheltering), using appropriate IPEs and providing immediate medical care for the victims.
- Distances of 50 m and 100 m from the sources of the H_{2}S leak are critical. According to the toxic H_{2}S cloud dispersal study, in the briefest Response Time taken as a reference (RT = 2 minutes), these areas are already contaminated by hazardous concentrations of H_{2}S. This is why Recommendation A includes mandatory carrying of IPEs, with regular specific training in their use, and the existence of a fast warning circuit consisting of H_{2}S detectors connected to alarms in the area. These two elements allow movements to take place after being reached by the toxic cloud, prior to launching the protective measures.
- Within critical distances (50 m and 100 m) of the sources of the H_{2}S leak, it is strongly recommended that groups of more than thirty workers should be forbidden. In larger numbers, moving the groups hampers the synchrony of the protective actions, increasing the risks to which these workers are exposed, in addition to making the installation of multiple SU non-economic.
- The Emergency Response Planning Support Matrix recommends the use of Safety Units by workers located within 300 m of the source of the H_{2}S leak, for inventories of up to 200 kg of pure H_{2}S; for larger inventories, their use is recommended by workers located within 500 m of the source of the H_{2}S leak.
- For the area evacuation and sheltering recommendations, it must be stressed that signposting the area in order to guide worker movements is a vital step. The most common signs are wind direction indicators and escape routes arrows leading to the SU and/or the meeting points.
- Ideally, only facilities sheltering workers linked directly to oil and gas processing should be located close to oil refinery processing plants. Buildings with offices, canteens, restaurants, first aid posts etc must be placed at safe distances, meaning outside the H_{2}S leak impact area. Should this not be possible, it is recommended that these buildings be equipped with SUs that can shelter all their employees.
- These SUs must be designed to meet the needs of a small number of workers (no more than 30) at fixed locations. Their main purpose is to block inflows of air contaminated with H_{2}S, thus protecting the people sheltering there. They are essentially places of refuge designed as completely sealed areas, with no exchanges of air with their surroundings. Their designs must be based on safety parameters and environmental comfort, in order to ensure that their habitability conditions are adequate for the lengths of time estimated as necessary for worker safety.

References available upon request. E-mail: gisele@garta.coppe.ufrj.br