Romania - Ministry of Environment, Water and Forests
National Environmental Guard
Cluj County Commissariat

Major elements of the SEVESO Directive and its development: "Hazard identification and a case study on accident scenarios for a Seveso installation" .

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Content of presentation

- HAZID and HAZOP
- Risk determination matrix
- Case study scenario and risk assessment for chemical accidents involving liquefied chlorine, also including elements of inspection report of the site

HAZOP –HAZID

Both related to study of Hazard identification and its safety measure, BUT:

HAZOP (hazard operability study)

- Is a structured and systematic technique for system examination and risk management.
- It is a systematic method of analysis of the operability parameters deviations using a specific vocabulary (key words - but other than HAZID).
- It is based on a theory that assumes risk events are caused by deviations from design or operating intentions.
- Hazop is done after the design reviews are completed and the P&IDs (piping and instrumentation diagram) are issued

HAZID (hazard identification Safety Equipment – State of the art / Operationphilosophy (Manning, Training, etc.).

- HAZID is done at a very early stage in identification)
- HAZID- is an utilized technique for the identification of the significant hazards related to an operational activity. The study is based on key-words such as Control philosophy / Flammable / toxic materials Hazards related to Electricity / Security hazards / Healthhazards / Hazards related to Height the project, at the scope and flowsheet stage
- Study is the process of identifying hazards in order to plan for, avoid, or mitigate their impacts
- Sources of external hazard, such as existing site infrastructure, weather, and geotechnical data, are also required.

RISK level

- RISK = FXC

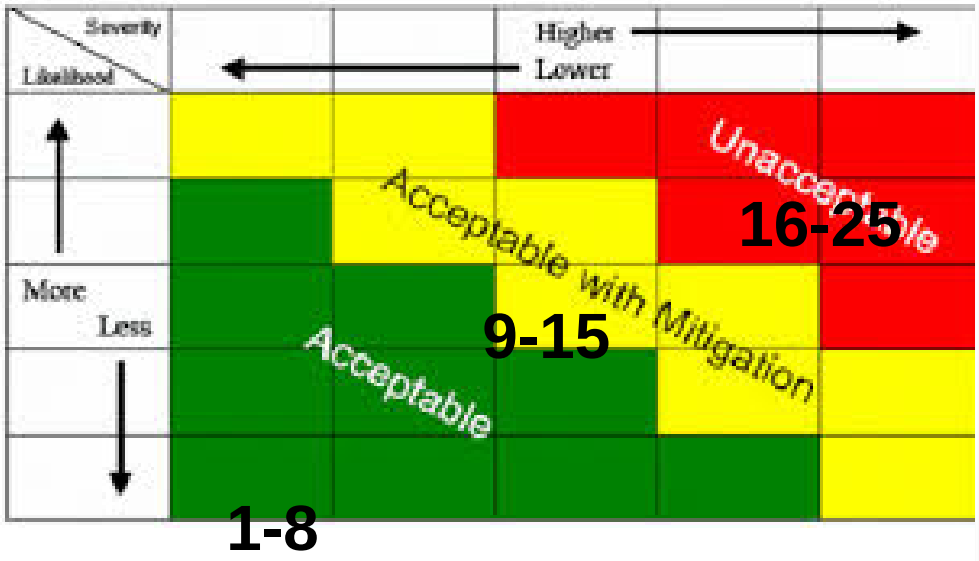
Where:

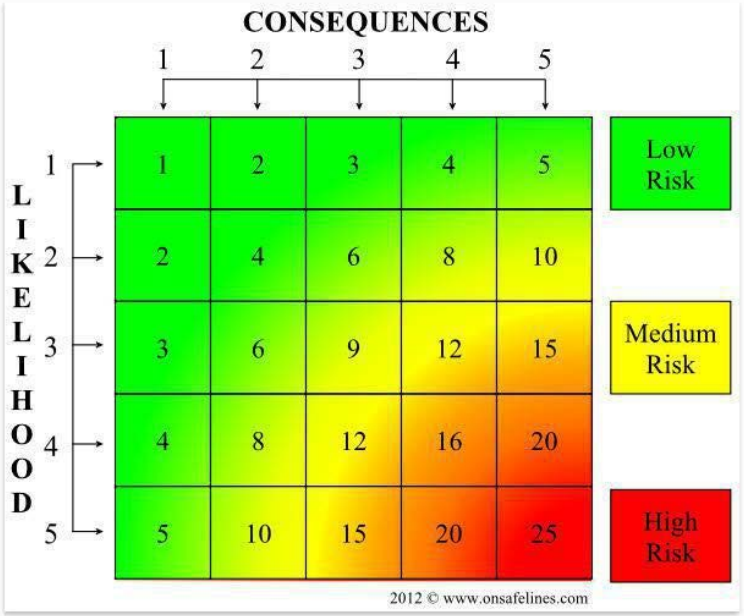
- F= frequency of scenarios (events/year)

- C = consequences of the accident (ex.no of death/event)

Risk determination matrix

Probability	Severity Level			
	Catastrophic	Serious	Moderate	Minor
Very Likely	High	High	High	Medium
Likely	High	High	Medium	Low
Unlikely	Medium	Medium	Low	Negligible
Remote	Low	Low	Negligible	Negligible





Risk ranking intervals

High risk equals 16 to 25.

These are the risks which can make the project completely unproductive and unfruitful. High Risks activities should cease immediately until further control measures to mitigate the risk are introduced. It must be a top priority during risk management.

Medium risk equals 9 to 15.

Medium Risks should only be tolerated for the short-term and then only whilst further control measures to mitigate the risk are being planned and introduced, within a defined time period. Medium risks can be an organizations greatest risk, due to the fact that they can be tolerated in the short-term.

Low risk equals 1 to 8.

Low Risks are largely acceptable,

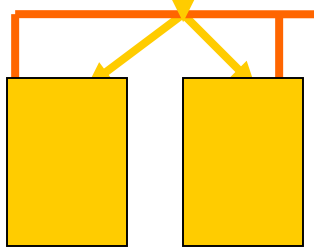
subject to reviews periodically, or after significant change etc

Case study – scenario and risk assessment for chemical accidents involving liquefied chlorine (Cl_2), at a Seveso chlorine storage located in Cluj county

Hungarian border

Main data

- Chlorine coming on railroad tanks
- Transport and deposited into 2 reservoirs (50 cubic meters maximum capacity each, with alternative use- pipe-18 m long)
- Transported (through pipes using dry comprimated air) to Chlorine bottling installation- where 50 kg, 500 kg si 900 kg recipients are loaded (maximum pressure – 10 bars, pipe -35 m)



Cl_2 reservoirs

Cl_2 cylinders

About Chlorine (Cl_2)

- Chlorine is a highly used substance in chemical industry, in organic and inorganic syntheses.
- There were several accidents involving chlorine release, generating human losses and affecting human health, due to its toxic and irritating properties.
- Chlorine is a dense gas, yellow-green and with an unpleasant, suffocating odour.
- Liquefied chlorine has the aspect of an oily liquid, green and with a chlorine content of min. 99.7 % vol. and a water content of max. 0.05 %.
- It is used in the chemical industry due to its high reactivity, as a strong oxidizing agent or chlorination agent.
- Also, chlorine is used for water disinfection, being a toxic substance for micro organisms and aquatic species.

Chlorine health effects

- Chlorine is a toxic gas that irritates the respiratory system. Because it is heavier than air, it tends to accumulate at the bottom of poorly ventilated spaces.

- Chlorine gas is a strong oxidizer, which may react with flammable materials.

- Chlorine is detectable with measuring devices in concentrations of as low as 0.2 parts per million (ppm), and by smell at 3 ppm. Coughing and vomiting may occur at 30 ppm and lung damage at 60 ppm. About 1000 ppm can be fatal after a few deep breaths of the gas.

- Breathing lower concentrations can aggravate the respiratory system, and exposure to the gas can irritate the eyes. The toxicity of chlorine comes from its oxidizing power. When chlorine is inhaled at concentrations above 30 ppm, it begins to react with water and cells, which change it into hydrochloric acid (HCl) and hypochlorous acid (HClO).

Objectives

- The objectives of the study were the estimation of risks associated to chlorine storage, calculation of dangerous areas for the populations and finding practical, efficient solutions for LUP (Land Use Planning) and chemical EP(emergency planning).

- 2 specific software used:
  - SLAB view (2 D model)
  - SEVEX view (3 D model)

SLAB View

- SLAB View – toxic dispersion simulation software, using the bi-dimensional SLAB model (Lakes Environmental 2009)

- SLAB View is a graphical user interface for the SLAB model - an atmospheric dispersion model for denser-than-air releases. Chlorine (Cl_2) =71, air =28.9

- SLAB View is a tool to predict hazardous zones and potential impacts of accidental releases.

SEVEX

- SEVEX view is an Integrated Software to be used for your emergency response PLANNING preparedness.
- 1. SEVEX View – major chemical accidents simulation software, using a complex meteorological model, terrain topography and 3D Lagrangian dispersion model (ATM-Pro 2009).
- Assuming conservative assumptions, but using state-of-the-art modeling tools SEVEX View increases the efficiency in producing realistic & ready-to-use risk zones mapping.

- SEVEX View is based on state-of-the-art modeling tools such as :
  - Leakage rate, jet, rainout, pool evaporation, heavy dispersion,
  - Complex terrain - topography and land use
  - 3D meteorology & 3D passive dispersion,
  - VCE (vapor cloud explosion)& BLEVE (Boiling liquid expanding vapor explosion)
  - Explosives
  - The danger zones calculated by SEVEX take into account toxicity, radiation & overpressure effects.

Scenarios of Chlorine release

- Based on the study of the tank, the critical points of chlorine accidental releases were identified. According to these critical points, 3 main scenarios of chlorine release were elaborated, namely:
- ***A. From the storage tank:***
- **Scenario 1 –A1. Catastrophic releases of the total stored chlorine (56 tons) – considered the *worst case scenario*;**

- **Scenario 2- A2** . **Continuous chlorine release through the R7A flange coupling, in a 10 minutes period** (considered the necessary period of time for stopping the release).

- ***B. From a 1000 kg cylinder:***
- **Scenario** 3 (B1). **Catastrophic release scenario – considered the *worst case scenario* with cylinders.**

All scenarios were evaluated taking into consideration that the Chlorine release may take place during day or night

Considering the three identified scenarios, the following installation failure frequencies were estimated: for failure of flanges at coupling a frequency of $3.1*10^{-3}$ events/year was considered (according to probabilistic calculations) and $3*10^{-6}$ events/year for the total failure of the storage tank (Mannan 2005). There were several accidents of chlorine release from the cylinders on site, thus a high frequency for this scenario was considered (between 10^{-2} and 10^{-4} events/year).

The risk assessment matrix for the relevant accident scenarios is presented in Table 5.

Table 5

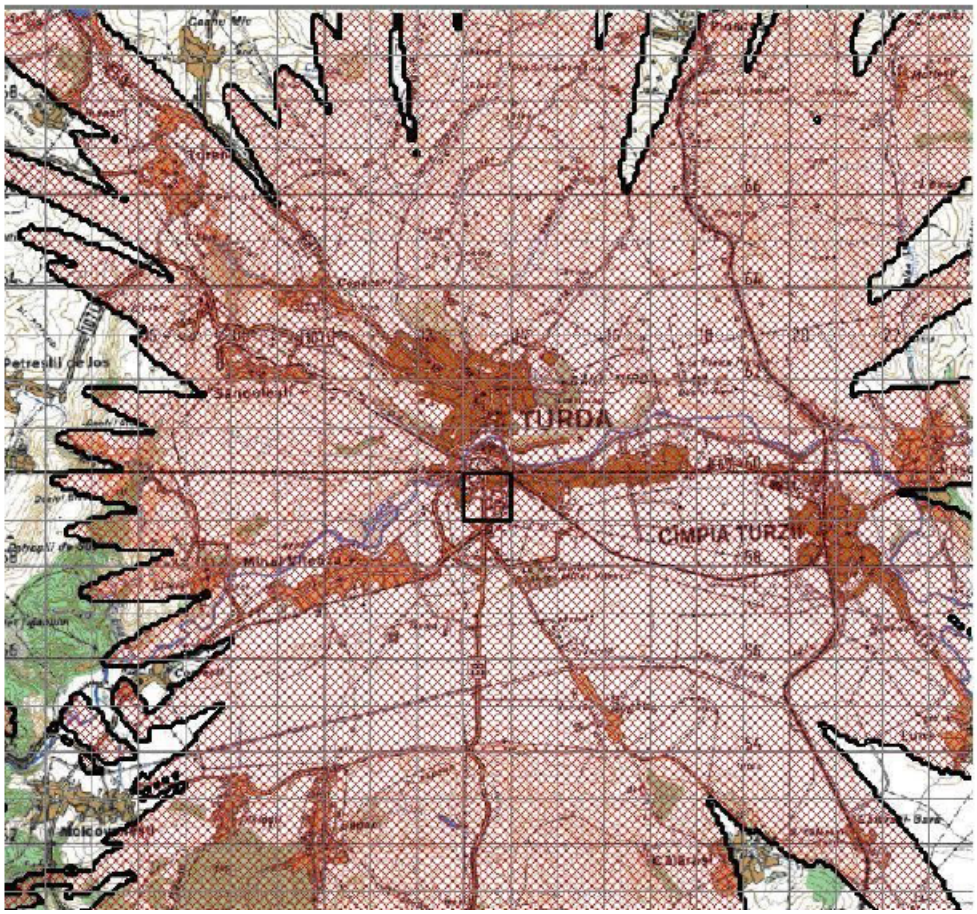
Risk Matrix: Risks associated to studied accident scenarios

No.	*Danger*	*Frequency*	*Consequences*	*Risk*
	A. Accident at the storage tank			
1	Instantaneous release of the total chlorine quantity from the storage tank	3	5	**15**
2	Liquid chlorine release for 10 minutes from the input pipe	4	4	**16**
	B. Accident at the chlorine cylinders			
1	Instantaneous release of the total chlorine quantity (1 t) from a cylinder	4	2	**8**

Frequency ranking on scale 1-5, where 1 = Improbable ($F \leq 10^{-8}$ events/year); 5 = Very frequent ($F \geq 10^{-2}$ [8] events/year); Consequence ranking on scale 1-5, where 1 = Insignificant (without health effects), 5 = Catastrophic (lethal effects, off-site toxic dispersions).

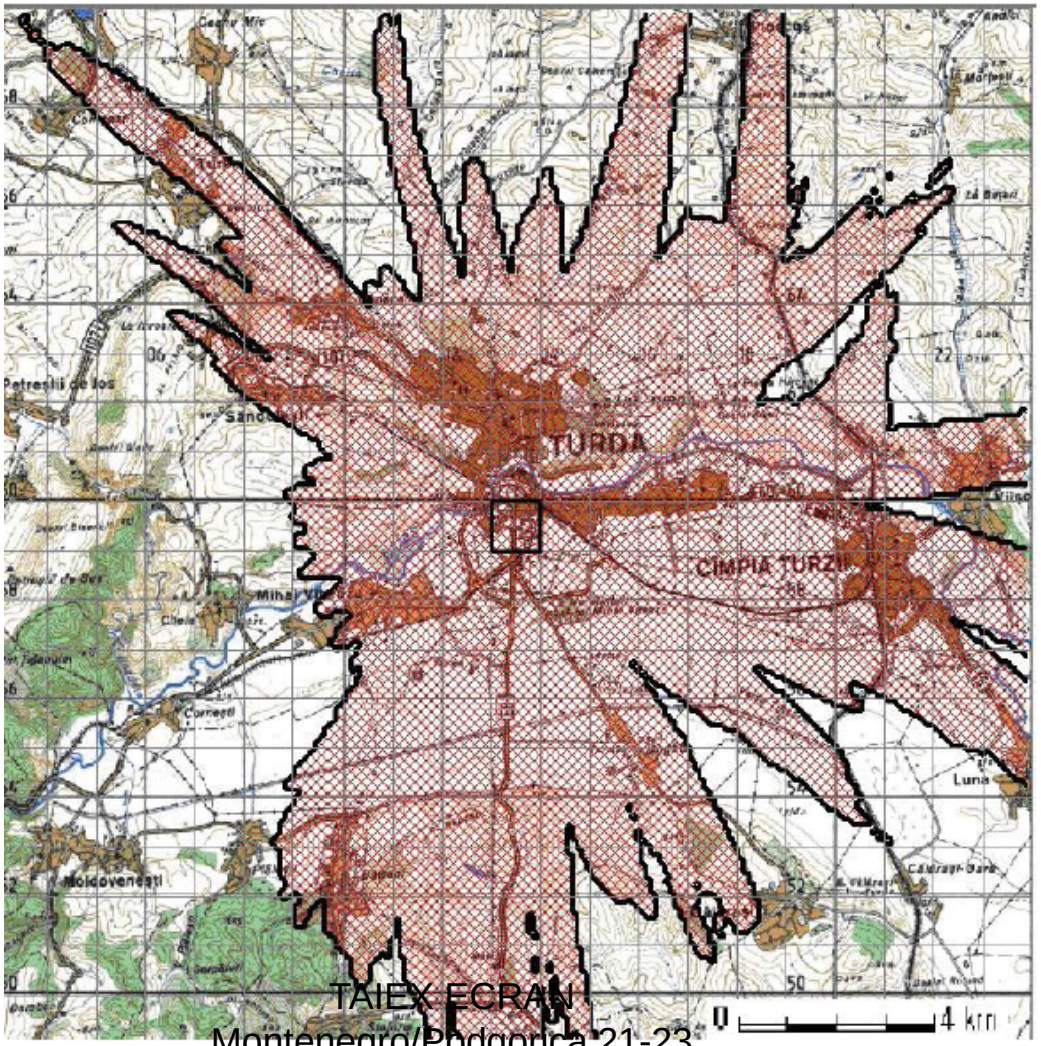
Scenario 1

Figure 3. Risk map: total possible area affected by dangerous concentrations (10.0 < C < 430.0 ppm) outside buildings – Scenario A.1.



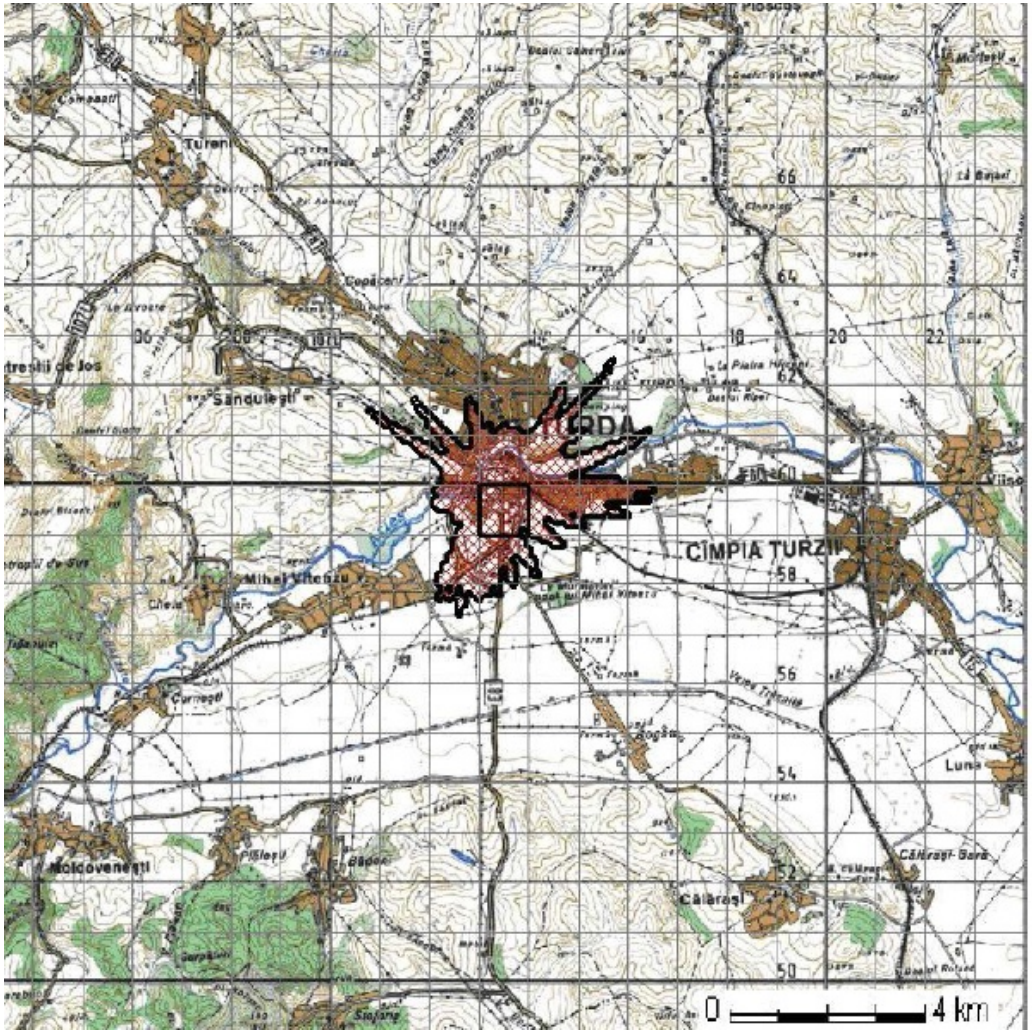
Scenario A2

Risk map: total possible area affected by dangerous concentrations (10.0 < C < 430.0 ppm) outside buildings – Scenario A.2.



Scenario 3 (B1)

Risk map: total possible area affected by dangerous concentrations (10.0 < C < 430.0 ppm) outside buildings – Scenario B.1.



Conclusions

- Chlorine storage in large quantities pose high risks for the population in Turda town;
- the consequences of the studied accidents can be catastrophic, except the scenario of chlorine release from the cylinder;
- in case of a chlorine accident, the affected areas must be immediately evacuated;
- the three accidental scenarios must be analyzed in a quantitative manner, too, in order to quantify the accidents effects and consequences.

Considering a chemical accident involving the entire chlorine quantity spilling at the Turda storehouse, in the worst meteorological conditions, an area equal to or larger than 56.93 km^2 should be evacuated. This area partially affects Turda, Câmpia Turzii towns and Mihai Viteazu and Sănduleşti villages, affecting more than 10,000 inhabitants.

Among the scenarios calculated with SEVEX software, the largest affected areas (in a period of 240 minutes) were obtained in cases A.1. and A.2., for night-time dispersion, when the wind is blowing from South-East, with a speed of 2 m/s. These results emphasize that the night-time scenarios are more dangerous, the atmosphere being stable and thus, the cloud dispersion is weaker. The situation is worsened by the fact that the population is more difficult to warn and evacuate during night-time. Scenario B.1 with 1 t chlorine release from a cylinder has a lower risk than the other two scenarios, but the simulations show that the affected areas are significant and evacuation measures from the neighbouring areas must be taken.

Key facts regarding the Seveso inspection of this site

- **The management and organization of the lens to prevent accidents**

  - Is provided trained personnel for safe operation and intervention (intervention mode, an alarm in case of accident) in case of emergencies - 9 employees who provide permanent shift and maintenance; their training in emergency situations is done through monthly trainings recorded in the records of training for emergency situations.

- - Visual check of the installation is performed by the shift; any aspect conformity is registered in contract damages / shift register and call management repository.
- - Security objective is assured by company staff and also using electronic surveillance with recording

- - Simulation exercises are done monthly

Seveso inspection -2

- Routes chlorine unloading of tank (compressed air route, route Cl2) chlorine length of the route until the deposit is about 18 m, with small portions segmentation (cca.5m) and has 5 Valves

- Cl2 route from warehouse to plant load (length approx. 35 m – also segmented into smaller safety portions) and is equipped with safety valves 6; If a fault finding one of bottles, they are dipped in a neutralization basin.

- If damage is charging cylinder valve is a valve safety act, Cl being sent in order to neutralize the NaOH reserve tank. There is a stock of caustic soda for preparation in case of faults

- Emergency equipment in case of fire are functional:
  - 4 hydrants, warehouse annex building perimeter mount Cl
  powder extinguishers and nitrogen - 9 pieces.
  Fixed a splash of chlorine tanks;
  a water supply is provided in case of fire - 2 tanks of 17 cubic meters and semi-buried pool of about 5 cubic meters retention tank running weaned CF-28.4 cubic meters cm
  - There are 12 fully self-contained breathing equipment consisting of respirators, oxygen tube, oxygen dispenser and nine complete protection Anti-Chemical; Chlorine filter cartridges with expiry date in 2015;
  - Intervention kit (metal clips, rubber sleeves, plugs wood, wrenches) is present

Seveso inspection -3

- Under the rules ISCIR tanks are inspected every two years by conducting proof hydraulic pressure checks, checking thickness with ultrasonic and penetrating liquids checks, if applicable. The last review was conducted in 2012, according to the minutes of the technical verification no.166 / 437-28.08.2012. valid until August of 2014.

- Air exhaust system inside the tank, with the introduction thereof in the column by neutralization with NaOH (in the event of failure) and the circulation pump of neutralizing solution absorption tower.

- Transport pipelines (from deposit to bottling installation) are above ground, are segmented into sections of max. 20 m to limit emissions of chlorine in disaster. Daily checking is performed to check if there are corrosion protection problems. Conventional painted is ensured. The routes are marked with the type of vehicular substance and meaning

Seveso inspection -4

- **Safety Measures**
  Fencing deposit with protective wall is intact; is equipped with motion detection systems (infrared motion sensor) are connected to the acoustic alarm. Also, the platform unit is equipped with video surveillance system.

- Warehouse is equipped with 3 sensors for detecting accidental leakage of Cl, mounted in warehouse loading ramp bottles and hypochlorite production facility. Electronic records are displayed sensors, exceeding 20 ppm concentration of putting into operation acoustic alarm system, part of the detection system.

- The two liquid chlorine storage tanks: retention tanks mounted in concrete; sprinkling system of tanks and reservoirs in emergency enclosure is functional.

Seveso inspection - Other findings

- Transport of mobile chlorine containers (with neutralizing solutions in case of intervention) is provided by an authorized company - in terms of environmental protection for performing these operations.

- When checking stock ready for filling containers to ascertain the type of a total of 12 containers conforming cylinder (degraded) and a total of eight recipients barrel type,

Testing

- On April 2014 there was an ISU (Inspectorate for Emergency Situations) test exercise, for internal emergency plan and external emergency plan

- It was verified the operation of the intervention forces in case of a chemical accident (scenario: accident resulting in cracking a mobile container with chlorine, the chlorine escaping into the atmosphere).

- It was analyzed how the company representatives have applied the internal emergency plan to limit the toxic cloud created, removing chlorine leak checking reaction times of rapid intervention operational groups, how to be notified of the accident, the use logistics of communication, alarm and evacuation of the civilian population out of the contaminated area.

- At the same time and to check back during the intervention / response and intervention formations how professional fire brigade at the request of economic operator in emergency phone - 112 - in response to the external emergency plan.

References

- AES Bioflux - Zoltan Torok, Alexandru Ozunu “Chemical risk assessment forn storage of hazardous materials in the context of land use planning” Used with prior permission.
- Directive 2012/18/EU of the European Parliament and of the Council of 4 July 2012 on the control of major-accident hazards involving dangerous substances
- http://www.atmpro.be/product.php?item=sevex_view&onglet=general visiting date january 24th 2015
- http://www.environmental-expert.com/software/slab-view-emergency-release-dense-gas-model-156198 visiting date january 24th 2015
- Chlorine – Safety Data Sheet

Thank you for your attention

Questions?