Vinyl chloride leak in a chemical plant

February 3, 2004

TAVAUX (Jura - 39), France

Chemistry
Polymerisation
monomer
Autoclave
Batch
Valve
Manual operations
Organisation

THE INSTALLATIONS CONCERNED:

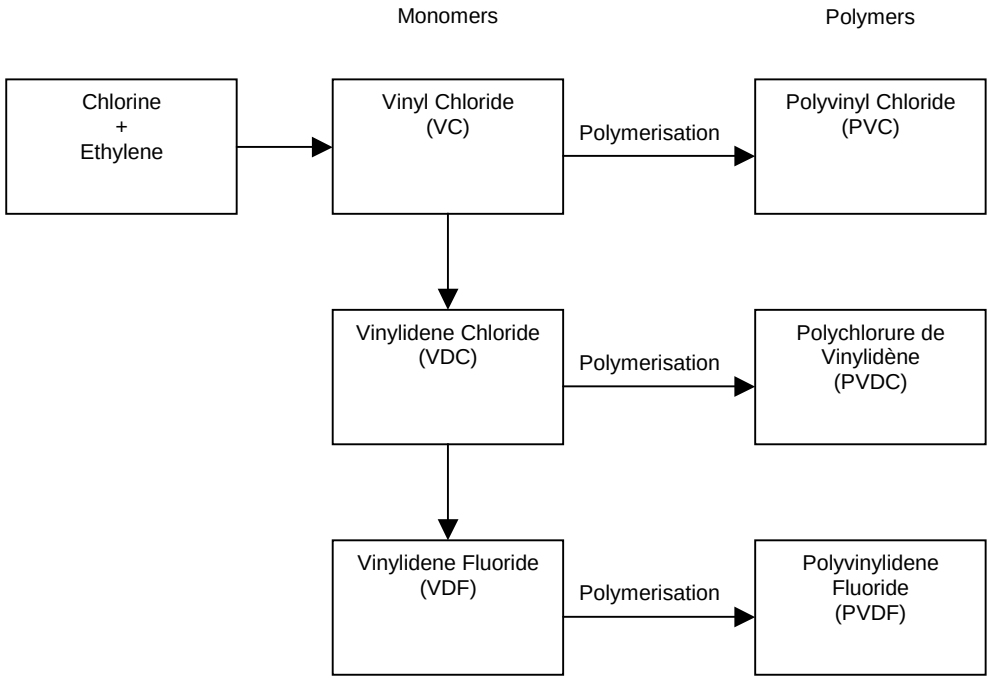
Located in Dole (Jura - 39) and created in 1930, the chemical platform is one of the largest in France and extends over 200 ha. The company employs 1,600 people at the site and approximately 700 people in external companies.

The establishment, which is governed by High Threshold Seveso regulatory requirements applicable to sites subject to authorization with public easement, includes 26 "AS" installations (for the use and storage of highly toxic and toxic liquids, manufacture, storage and use of chlorine, storage of liquefied flammable gases, and the manufacture and storage of flammable liquids…). The measures foreseen for urbanisation control around the plant apply to two circles measuring 1,000 and 1,500 m in diameter, centred on the chlorine storage facility.

For many years, the plant's activities, based on the processing and transformation of salt (essentially the production of sodium carbonate), had been developed toward high added-value productions with a strong emphasis on technology through specialisation in chemical products and plastic materials for industry.

Basic production operations are focused on polyvinyl chloride (PVC) and polyvinylidene chloride (PVDC); in 2004, the tonnage of the main products was in the order of 1,250,000 t/year all products considered, including 300,000 tons of miscellaneous plastic materials (PVC, PVDC and PVDF).

These plastic materials are produced from vinyl chloride monomer (VCM), which is itself derived from the reaction of chlorine and ethylene. The manufacturing sequence of the 3 plastic materials is as follows:



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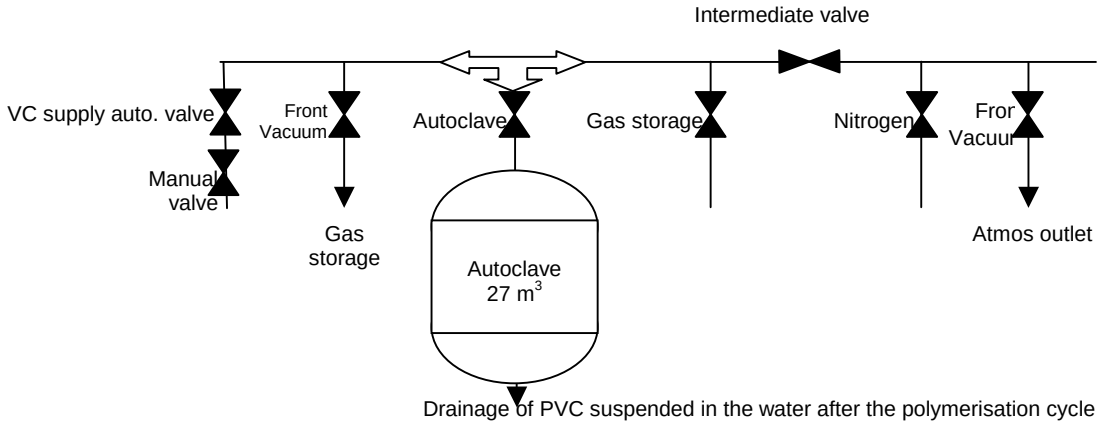
The accident took place in one of the PVC manufacturing installations (the polymerisation sector of the VCM).

The part of the installation concerned, which dates back to 1969, consists of a set of thirteen 27m³ autoclaves in which the polymerisation process is carried out according to a discontinuous "batch" process. This process requires that they be opened between 2 polymerisation operations. The installation is only slightly automated, notably in terms of the autoclave filling, drainage and cleanup processes. The accident took place between one of the VCM inlet/outlet pipes:

The system can be represented by the simplified diagram below:



Comment: The intermediate valve isolates the autoclave from any circuit not intended to convey VCM.

A series of preliminary operations are performed before the VCM is introduced:

- filling with water,
- dispersing agent and catalyst,
- degassing to the "Front Vacuum" network to remove traces of oxygen (the presence of air).

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These operations are manual. Prior to the modifications made following the accident, the following functions were automated at the installation:

- Filling of VCM,
- Monitoring of the polymerisation reaction.

The personnel were certified to perform the corresponding operations. Procedures were drawn up to describe these operations, although there are no accompanying record sheets of the various steps. The preliminary operations are not subject to formal qualification prior to the authorisation of the automatic VCM introduction sequence.

THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES

On February 3, 2004, during the preliminary VCM filling operations of autoclave No. 11, the operator was interrupted at 5.04 am by a PLC request to immediately intervene on autoclave No. 13. The interruption took place during the preliminary degassing phase of autoclave No. 11 on the "Front Vacuum" system.

Upon returning to autoclave No. 11 at around 5 am, the operator neglected to close the degassing valve on the "Front Vacuum" system and authorised the filling operation, which directed part of the VCM to the "Front Vacuum" and caused its loss of confinement through a 14 m stack.

At the same time, the increase in pressure on the "Front Vacuum", following this accidental operation, resulted in the release of VCM in the polymerisation hall though another open autoclave on the same system. The alarm, raised at 5.09 am by the air chromatography monitoring network (probe activation threshold: 10 ppm), allowed the operator to detect his error after 3 minutes time, during which 1.6 t of VCM were released to the atmosphere.

For the moment, the concern was essentially to have created an explosive cloud that could reach unprotected zones in which possible sources of ignition could be located.

Evaluation of the consequences:

EXTERIOR:

The outside emission point was located at the top of a 14 m stack having an outside diameter of 310 mm.

Considering the meteorological conditions, an evaluation of the cloud with the PHAST software indicated that:

- the LEL and UEL concentrations were within a parallelepiped H=3 m - W=3 m - L=17 m above the emission point located 14 m above the ground (a cloud there was no ignition source),
- the Lethal Effect Threshold (SEL) concentration is within a parallelepiped of H≤1 m - W≤1 m - L=2 m around the emission point, a zone in which the personnel cannot be exposed.

The Irreversible Effect Threshold zone (SEI) is not defined, as there is no longer a reference threshold for this substance since the last INERIS report on the subject published in 2000. Typically speaking, the zone corresponding to the No Effect Level (SER) of the VC: 8,000 ppm) was within the parallelepiped H=6 m - W=7 m - L=42 m above the emission point 14 m above the ground.

Finally, concentration measurements outside the platform were not conducted owing to the low levels reported on the chromatographic sensors nearest the VCM emission location following the rapid dissolution of the cloud.

MANUFACTURING WORKSHOP:

The chromatographic air-monitoring network detected the presence of VCM in the polymerisation hall. The maximum concentration recorded on a sensor was 2,763 ppm for less than 20 min. This network includes 10 sensors. Each of the sensors are read every 2 minutes, and for each of the 2 chromatographs.

The manufacturing shop was evacuated from 5.09 to 7.32 am.

OTHER WORKSHOPS:

The PVDC manufacturing workshop was evacuated at 5.20 am, for 58 minutes, after VCM had been detected by the chromatographic air-monitoring network. The maximum concentration was 22 ppm for less than 20 minutes.

Given the limited characteristics of the emission, only the risks resulting from short-term exposure (acute toxicity) should be retained. The carcinogen risks associated to chronic exposure were not considered.

There were no human consequences.

EUROPEAN SCALE OF INDUSTRIAL ACCIDENTS:

- Using the rules for scaling by the 18 parameters of the scale formalised in February 1994 by the Committee of Competent Authorities of the Member States in application of the 'SEVESO' directive and taking into account the available information, the Tavaux incident is characterised by the following indices:

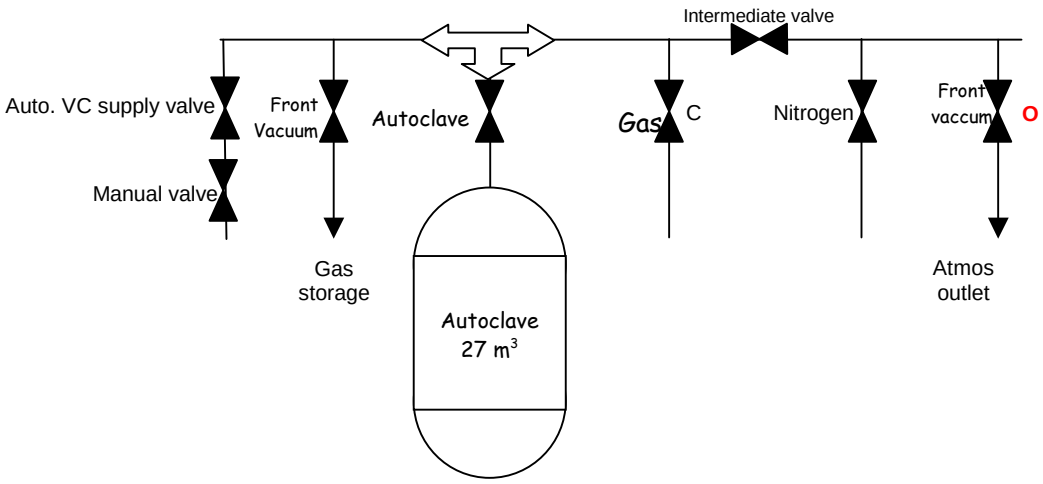
The accident caused the release of 1.6 t of VCM into the atmosphere. As the Seveso threshold for this substance is 200 tons, the quantity lost corresponds to 0.8 % of the threshold. The index relative to the dangerous materials released for this percentage is 2 (see parameter Q1). The operating losses associated with the shutdown of the shop modification work was 520,000 euros and explain the index relative to the economic consequences equal to 2 (see parameter €).

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT:

The autoclave VCM filling sequence is managed by a PLC that ensures the following points are accomplished before authorising the fill operation:

- all the VCM supply valves of the other autoclaves are closed,
- the autoclave agitator is in operation,
- the autoclave is in a vacuum (< 0.5 bar),
- no output on the VCM supply line.

There is thus no instrumentation on the shut-off valves of the other systems (Front Vacuum, Back Vacuum, Gas storage, nitrogen, …) that is taken into consideration in the VCM loading sequence. There are procedures to check the position of these valves prior to the VCM filling operation. These procedures require that the operator allow the automatic VCM filling valve to be controlled by the PLC. However, the interruption of the operator intervening on autoclave No. 13 caused the sequence of the preliminary manoeuvres of autoclave No. 11 to be lost and authorised the operation when the employee returned even though the "intermediate" manual valve and the "Front Vacuum" valve were not closed.



The diagram below shows the set of shut-off valves and their position at this moment:

Causes identified:

- Cause No. 1: poorly qualified preliminary manoeuvres prior to VCM supply authorisation,
- Cause No. 2: permanent monitoring fault of the "Front Vacuum" network.

Comment: the operator performing this manoeuvre has 33 years experience in the PVC sector, including 10 years at this installation. His experience and skill enabled him to become a member of the training team for newcomers at the installation.

MEASURES TAKEN:

The DRIRE requested that the operator propose a set of immediate actions to control the preliminary operations by eliminating the identified causes and by proving the efficiency of these actions.

Secondly, owing to the polymerisation shop's low level of automation, it was requested (and reiterated by the company's committee for hygiene, safety and working conditions - CHSCT), that a working group be set up to identify all risky manual operations that could have serious health and environmental consequences, then propose the corresponding safety barriers.

Finally, inspections were conducted jointly with the DDTEFP in March, June, and December 2004 and April 2005.

The operator immediately undertook the following action:

- the manual valve upline from the automatic VCM loading valve was closed and locked down with a chain and padlock (above photo). In this configuration, VCM filling is rendered impossible. In order to make this possible and enable this upline manual valve to be opened, a procedure uses this same chain to block and lock the manual "intermediate" valve closed (see previous diagram). In this configuration, the autoclave VCM filling sequence is authorised, with all expulsion rendered impossible. This control measure is limited in its objective to draw the operator's attention on the installation's configuration. It is active on all autoclaves as long as the measures taken to mitigate cause No. 2, presented below, are not implemented.

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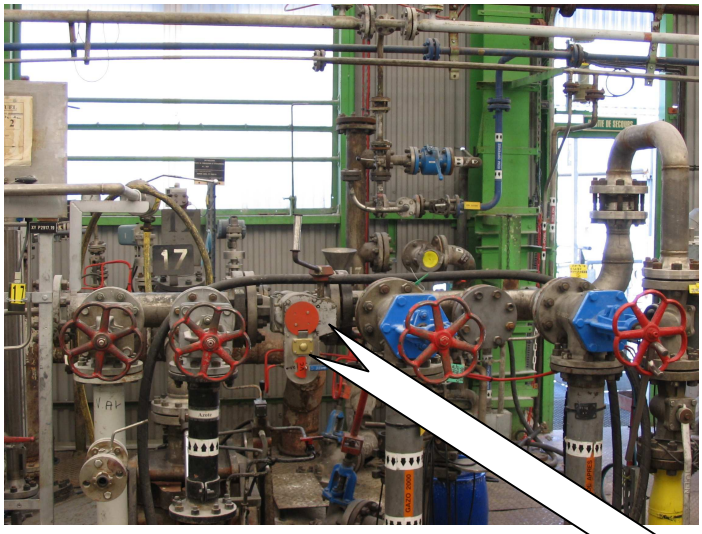
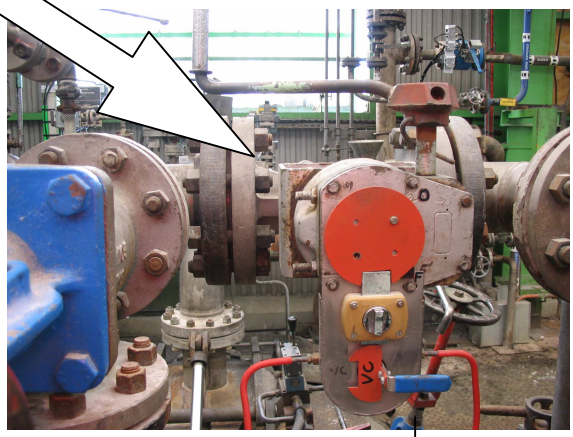
- And in the short term:

- corrective action on cause No. 1: Formal documentation and recording of the qualification of preliminary autoclave start-up operations before authorising VCM filling operations. Measure established 02/12/04.

- corrective action on cause No. 2: study of technical measures to reinforce monitoring of the Front Vacuum network. The results of this study were submitted 02/28/04 with a lead time proposal for the 13 autoclaves:

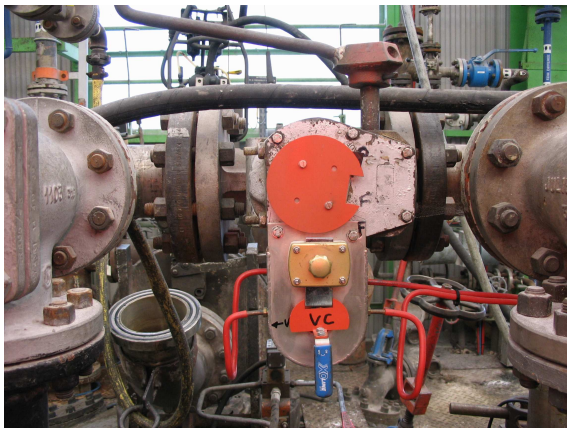
  - ❑ modification of the load control system for 04/05/04, by setting up a mechanical system which prohibits VCM from being loaded if the "intermediate" valve is not closed (see photo below):





VCM filling authorised

Valve allowing the pneumatic supply of the automatic valve of completion of CVM



VCM filling prohibited

- pressure measurement on the "front vacuum line for 03/17/04, in order to confirm the presence of VCM in the "front vacuum" network,
- fractioning of the VCM load into 2 steps: initially 200 kg, followed by a 2-minute delay before continuing the loading operation if no leak is detected. The loading operation is continued upon PLC authorisation (after the 2 min. time delay) accompanied by operator acknowledgement in the control room. The modification on the 13 autoclaves was deployed as of 04/01/04.

Cost of these corrective actions: 20,000 €, half of which was required to modify the PLC VCM load management program.

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At present, several automated functions have been added to the installation:

- closing of all VCM valves on the other autoclaves,
- fractioning of the VCM filling operation: 200 kg then the remaining 10 t upon operator authorisation,
- checking that the intermediate valve is closed.

Medium and long term:

- Organization of a 7-person task force made up of workshop personnel, members of the CHSCT (committee for hygiene, safety and working conditions) and another neighbouring workshop, with the group being run by the shop supervisor. The task force's objective is to initially list all the manual operations that could create an accidental situation in which VCM is released through all possible systems, then, secondly, implement the corresponding barriers to mitigate human error on the operations identified.

The task force, which meets 2 times per month for 2½ hours, structures its approach through the AMDEC method. In its analysis, at the request of the manager, the task force also included transitory phases, particularly maintenance steps that include many manual operations.

An initial report regarding the implementation of this recurring action plan was carried out with the DRIRE on April 5, 2004, followed by 3 meetings held in conjunction with the labour inspector. In addition, the CHSCTs were kept informed of the task force's work. The inspectors of the DRIRE and the DDTEFP, recipients of the CHSCT reports, were also informed.

In all, the task force identified 39 manual sequences that could result in loss of VCM confinement. The sequences were the subject of proposals for technical barriers, possibly declared as being safety-related, and completed by organizational barriers in certain cases.

The group met 15 times and established the action plan based on the proposals retained during the AMDEC analysis. These proposals will cost approximately 150 k€ and are scheduled for 2005.

Joint Labour Inspectorate / Classified Installations Inspectorate intervention:

A joint Labour Inspectorate / Classified Installations Inspectorate study was conducted:

- owing to the nature of the accident involving a new VCM leak, categorized as carcinogen (R45), on an installation of the Tavaux platform. The previous leak, which occurred in 2002 on a different installation, had already been subject to a joint inspection operation.
- due to the operator being put aside.
- because the CHSCT rapidly requested a special meeting about this incident.

Action of the CHSCT:

A special meeting was held 03/03/04, in which the presence of the Labour Inspectorate and the DRIRE was requested. According to the members of the CHSCT, this installation had the following characteristics:

- a former job site, the shut-down of which had been announced several times,
- a significant workload for the personnel, workshop P69 had a high production load.
- personnel understaffed (with, according to management, many individuals on long-term sick leave).
- A high level of stress among the personnel, working with the fear of making a mistake,

- insufficient security, the control of the operations was based on procedure logs in which the operator must check off the operations performed one by one successively during a production cycle. The studies showed that this procedure did not guarantee the site a sufficient level of safety and, to a certain degree, places the responsibility on the personnel in case of an incident.

The CHSCT was instructed to conduct an internal assessment with the personnel in order to:

- analyse all tasks performed at P69 (start-up, shut-down, normal and downgraded operation),
- record all operating methods,
- identify the risks involved in the VCM atmosphere,
- analyse the impact of the workplace organization on the order in which tasks are performed,
- identify the factors which could have an influence on the personnel's working conditions.

This decision was in addition to that taken by the operator on 02/16/04 during the meeting with the DRIRE for the presentation of the short-term, medium and long-term action plan, namely, for the latter:

- record all operations in which there is a risk of VCM to the atmosphere (during operation, maintenance, downgraded operation),
- find and implement technical and organizational barriers.

➢ An internal task force was created with the participation of the personnel concerned and certain members of the CHSCT who were particularly familiar with the P69 installation.

This task force, defined during the CHSCT meeting of 03/11/04, included:

- 1 person in charge: the PVC Suspension (PVC S) manufacturing supervisor
- 2 PVC S personnel: the P69 / P79 production manager and the P57 autoclave operator
- 4 members of the CHSCT.

The task force's specifications, defined on 03/11/04, include the complete analysis of the polymerisation operations from the start-up of the autoclave to the transfer to the final slurry tanks (obtaining of the PVC to be dried, after treatment of the excess gaseous VC), by including the operating and maintenance operations:

- to define the barriers concerning the possibilities of venting the VC to the atmosphere,
- to check that the procedures and manoeuvres are adequate with the workplace organization.

In the end, the task force held fifteen 2½-hour meetings over a period of 8 months, with:

- meeting minutes,
- regular presentations of the work to the manager and to the members of the management of the P69,

- task force progress reports during the quarterly meeting of the sector's CHSCT,
- regular presentation of the current work to the personnel of the 5 stations,
- validation of the technical solutions proposed by the STI Manager ("Sécurité Technique et Intervention", technical safety and intervention department).

➢ This demonstrates the involvement at all levels.

The STI Manager stipulated that the objective of all the technical barriers set up or to be implemented is to create new alarms designed to assist in controlling the installations. They should provide the operators a certain level of assistance and prevent them from being apprehensive about possible errors.

Furthermore, the PVC Manager, in charge of the P69 site, decided not to launch a cycle during the 15 minutes preceding a shit change (which was not the case prior to the incident).

In the end, the task force work was considered to be satisfactory with:

- operations conducted by the production foreman,
- constructive presence of the members of the CHSCT,
- the use of a finite and systematic analysis method (AMDEC),
- discussions with the sector's personnel and regular meeting with these individuals,
- implementation of solutions on an autoclave used as a prototype, prior to widespread use,
- review of procedures and rewriting of procedures, including the clarification of the shift change phase (2 people were designated in each shift to make the link, written instructions, record sheet, no batches started less than 15 minutes prior to a shift change).

Interest and success conditions of such an approach (task force + AMDEC):

- participative approach, with discussions with the personnel ⇨ involvement of the personnel, notably with regard to the respect of new procedures and new operating methods,
- finite and systematic analysis of tasks and risks (AMDEC method),
- internally-designed solutions:
    - the personnel now have a sense of security, the barriers implemented have done away with the possibility of making a mistake and the procedures were completely reworked. The personnel is now reassured.
    - a large psychological impact on the personnel from which a reduction stress and feelings of insecurity can be expected by the employees of workshop P69.

During discussions with the personnel representatives about the interest of this task force, it appears that the conditions for its success were based significantly on a particular condition. The task force was created following an incident and its work was followed very closely by members of the CHSCT, DRIRE and the Labour Inspectorate.

This context allowed the operator to become aware of the risks presented by these manual operations and to rapidly implement technical and organisational solutions.

Finally, it appears that the opinion of the Labour Inspectorate, the collaboration of DRIRE/Labour Inspectorate allows the members of the CHSCT and all employees of workshop P69, to learn more about the missions performed by DRIRE inspectors who were previously perceived as being an authority in charge of handing out sanctions.

THE LESSONS LEARNED:

The human factor:

- A procedure and, more generally, the organisational barriers do not by any means prevent the risk of human error and cannot alone be considered reliable safety barriers with regard to the stakes involved for both man and the environment,

- The certification of the personnel is not an end in itself and is thus a safety barrier with a low level of reliability (the operator was also a trainer),

- The task force's results show that it is advantageous to conduct a risk analysis that includes the field personnel, notably when the installation have little automation and includes manual operations that could lead to significant accidents. The involvement of the field personnel demonstrated the efficiency and complementarity in the risk analysis for the "VCM loss of confinement" event. The work will be included in the danger study that is scheduled to be updated in late 2005.

- Involving the field personnel in this project allowed the operator to tap previously unknown skills among the personnel and, as a result, was able to put them to good use. In fact, it is a company employee and not a technical department employee who deployed the modifications to be made on all the autoclaves. Finally, the operator will promote this example to spearhead a company innovation program.

Concerning the installation:

- When an installation's level of automation is low and includes risky manual operations, this experience shows that an installation can be secured by simple and efficient technical measures (physical or positive security measures without systematic automation). This project, which is essentially based on the implementation of technical barriers instead of organisational barriers, showed that it is possible to automate the management of safety measures without automating the operation of the installation.

Given the satisfactory results obtained, the head of the PVC department will present the platform managers the approach (advantages and drawbacks) and the solutions implemented (scheduled for late June 2005). The operator has set an objective to deploy this method on the installations where this approach is pertinent.