

## A perspective on Seveso accident based on cause-consequences analysis by three different methods

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### ABSTRACT

Seveso incident happened on Saturday 10<sup>th</sup> July 1976 within the production plant of 2,4,5-trichlorophenol at the ICMESA factory represents a watershed because it gave off a specific legislation in the field of safety regarding activities subjected to Major Accident Hazards (MAH) and the handling of dangerous substances. Although the severity of the mishap, still nowadays the real cause of the accident remains, at least partially, shrouded in uncertainty and different mechanism hypotheses were proposed. These doubts could lead considering Seveso mishap as a “black swan” incident, i.e. an improbable event characterized by three peculiarities: it is not expected; it has an extreme impact; it is explainable and predictable after the fact. Further investigation appears to be essential, analyzing the available material and processing a deep analysis towards several methods, which provide different views and interpretations of the fact. To this purpose, three methods were selected: AcciMap approach; the Energy Barrier Model; the System-Theoretic Accident Model & Processes (STAMP) coupled with a dynamic approach. The last part of this work is dedicated to a specific modelling of the incident through system dynamics technique using a customized framework covering technical, human and organizational aspects.

KEYWORDS: AcciMap; Black swan; Energy barrier; Seveso accident; System dynamics

### 1. INTRODUCTION

A large part of current process safety management systems are a consequence of root cause identified and shared within the scientific and industrial community after high profile accidents like Seveso one. With no doubts, as revealed by accident statistics both on the process side (e.g. Fabiano and Currò, 2012) and the personnel side of safety (Fabiano et al., 1995), human error still represents the larger contribution to accidents, notwithstanding the attention given to human factors in process/plant design, structuring organizations and drafting procedures. This paper has been developed starting from the historical interest viewpoint and aims at investigating additional lessons that could be learned, with the benefit of hindsight and new theoretical approaches. In the following paragraph, we firstly provide an overview of the accident, subsequently we critically discuss known facts and competing theories on root accident causes.

## 1.1 Overview

The ICMESA Company (Industrie Chimiche Meda Società Azionaria) was engaged in the production of 2,4,5-trichlorophenol (TCP) by a process designed by Givaudan, a parent company of Hoffman-La Roche. The plant was located in Meda, at 20 km North of Milan, in Italy, and the TCP production unit included two 10,000 litre reactors and various columns, condensers, pumps and equipment set out over an area of 230 m<sup>2</sup>. Subsequently, the produced TCP was transported to another site of the same company to produce herbicides such as hexachlorophene and antiseptics (Mazza and Scatturin, 1976). The Meda plant used a discontinuous batch process starting from the reactants fed at the beginning of the operation summarized in Table 1 (Cardillo and Girelli, 1981).

The process consisted of two steps:

Step 1: TCP and NaOH, the reactants, were introduced in the alkaline hydrolysis reactor along with the solvents EG and xylene, for the reaction:

### FIGURE 1

The reactor was equipped with a condenser to eliminate the water and to feedback xylene into the reactor. The choice of the solvents lay in the fact that NaOH is soluble in glycol, while the TCB and the product of the first step (sodium trichlorophenate) are soluble in xylene. Furthermore, xylene eliminates water by azeotropic distillation promoting the reaction with a high conversion rate. According to the Givaudan patent, TCP was heated at about 160 °C, using steam at 12 bar for 6-8 hours. The entire xylene and part of glycol were then vacuum distilled in order to recover solvents; then, about 3000 l of water was added to cool to 50-60 °C.

Step 2: the product of stage 1, sodium trichlorophenate, was hydrolyzed with an aqueous solution of hydrochloric acid, in order to obtain the TCP through the reaction:

### FIGURE 2

The end product was then washed with water purified by vacuum distillation (Ferraiolo, 1979). Traces of dioxin can be produced as an unwanted by-product through an exothermal condensation reaction between two molecules of sodium trichlorophenate:

### FIGURE 3

While dioxine concentration would not exceed 1 ppm at T < 180°C, it could reach 1,600 ppm at higher temperatures (Marshall, 1980). A simplified scheme of the Cr-Mo-Ni alloy alkaline hydrolysis reactor is depicted in Figure 4.

### FIGURE 4

On Saturday 10<sup>th</sup> July 1976, the alkaline hydrolysis reactor, switched off without completing its cycle, released a huge amount of 2,4,7,8-TCDD at 12:37 p.m., because of the rupture of the bursting disc, which was set at 3.5 atm. It should be noted that on Friday 9<sup>th</sup> July, the production cycle started at 4 p.m., ten hours later than usually. The distillation of xylene was completed before the shutdown,

but the same could not occur for EG, whose distillation was accomplished just for the 15% in spite of the 50%. On Saturday morning, at 5 a.m., the reactor was shut-down, the stirring stopped 15 minutes later and any cooling operation was performed. At 12:37 p.m., the maintenance staff heard a whistling noise and for 20 minutes a cloud of vapour, dense and reddish was seen to blow off from a vent on the roof, forming a cloud of considerable altitude (Marshall, 1980). A shift foreman entered the plant and, by applying cooling water, stopped the emission. The toxic cloud was carried by the wind (4 m/s) to the southwest of the plant, towards a farming area. Within a few hours, many small animals died, but no deaths occurred among humans. In the following days, some children showed intestinal problems and burns appeared on their skins. 27 hours after the fact, the company told that “a cloud of herbicides had been released”, but any word was spent about dioxin. Six days later, 15 children were hospitalized, four of which in serious conditions; because the dioxin presence was ignored, the doctors were not aware of the therapy to be followed. Just nine days later, the presence of dioxin in the release was made public; only fourteen days after the most affected areas were officially identified and at last eleven towns were declared impacted. The authorities classified the contamination zones on the basis of dioxine concentration measured in the ground:

- Zone A: about 110 hectares around the towns of Meda and Seveso with dioxin concentrations averaging  $240 \mu\text{g}/\text{m}^2$  and rising to over  $5,000 \mu\text{g}/\text{m}^2$ ; about 733 inhabitants were evacuated in July 1976.
- Zone B: about 269 hectares with dioxin concentrations averaging  $3 \mu\text{g}/\text{m}^2$  with a maximum of  $43 \mu\text{g}/\text{m}^2$ ; resident population 4,613 people, children below 12 years and pregnant women were evacuated.
- Zone R: about 1430 hectares of zone of Respect, with traces of dioxin and maximum concentration  $5 \mu\text{g}/\text{m}^2$ ; resident population 30,774 people, farming activities were prohibited.

This approach however did not allow evaluating the actual exposition dose of residents, as revealed in the follow-up clinical studies; an estimation considered a TCDD concentration of 3,500 p.p.m. in the release and an approximate total TCDD amount of 2 kg (Gustin, 2002). A more accurate evaluation of the source term should consider experimental ground data and solve the inverse modelling problem by applying advanced regularization techniques (e.g. Revereberi et al., 2013). Health and social consequences: as discussed by Bertazzi et al. (1998), early health investigations including liver function, immune function, neurologic impairment and reproductive effects yielded inconclusive results, while chloracne (nearly 200 cases with a definite exposure dependence) was the only acute effect established with certainty. An excess mortality connected to cardiovascular and respiratory diseases was uncovered, possibly related to the psychosocial consequences of the accident. Results of cancer incidence and mortality follow-up showed an increased occurrence of cancer of the gastrointestinal sites and of the lymphatic and hematopoietic tissue even if the results do not provide conclusive evidence of long-term effects on the exposed subjects of the Seveso accident (Bertazzi et al., 1998). Environmental consequences: about 81,000 animals died and nearly 2,000 hectares were contaminated. Short-term economic consequences: because of the prohibition of activities, 2 companies, 37 cottage industries, 61 farms, 4,000 kitchen gardens were affected (Warner et al., 2002; Gustin, 2002).

## 2. Origins and Causes: an ongoing discussion

In this chapter, first we review the underlying prequel of Seveso accident and the relevant hazardous attitudes associated with components of process safety management. Then, we provide a theoretical insight into the complex phenomena leading to the runaway scenario.

### 2.1 Prequel

Before 1976, five other incidents occurred in plants aimed at producing TCP. Four of them (Monsanto, USA, 1949; BASF, Germany, 1953; Dow, USA, 1960; Philips-Duphar, The Netherlands, 1963) used methanol processes, while the last one, happened at Coalite industry in Great Britain in 1968, used an ethylene glycol process, similar to the Seveso one (Menduto, 2012). Concerning safety aspects, there is not a close correlation between the two types of process, so that information obtainable from accidents occurred with the former, are not necessarily applicable to the ones occurred with the latter. Methanol processes are carried out discontinuously, into pressurized and closed tanks (Ferraiolo, 1979), so that under these conditions, an exothermal reaction, whether not relieved, can cause a rapid increase in pressure and give rise to a hazardous scenario. On the contrary, EG processes operate at atmospheric pressure in a tank connected to the atmosphere so that, theoretically, such drawbacks are to be excluded unless occlusions, or abnormal evaporation of the solvent caused by a sharp increase of the temperature may take place (Ferraiolo, 1979). Milnes (1971) studied the thermal stability of the hydrolyzates of TCB, finding a decomposition temperature equal to 230 °C and it was concluded that secondary exothermal reactions occurred at temperatures higher than this one, although it was not possible reproducing the explosion. A critical survey covering the hypothesized causes of the accident, developed with the passing years, is postponed to next paragraph; at the moment it is highlighted as ICMESA Company ignored a lot of signs of concern coming from a sector parent of too many -unexplained- accidents, adopting an irresponsible attitude in the name of economic profit at the expense of safety, recalling us the monitus of T. Kletz that “accidents are not due to lack of knowledge, but by failure to use the knowledge we have” (Kletz, 2001).

#### 1.2.2 Hazardous attitudes

Before proceeding with the presentation of the most debated theories about the possible causes of the tragedy, we firstly address several aspects concerning the hazardous attitudes pursued in the ICMESA politics, contrasting them with currently acknowledged good practice.

Changes and modifications on original Givaudan patent

- The proportion of the reactants 1TCB : 2NaOH 11.5 glycol was modified into 1TCB : 3NaOH 5.5 glycol.
- Xylene was not foreseen in the original patent.
- Modification of the logical step sequence: distillation of xylene and part of EG before acidification instead of after acidification

As amply recognized, even limited changes in process design, operations, maintenance, and equipment can exert a high influence on reactive processes, so that any intended process change involving safety risk should follow a careful management of change procedure (MOC), including an evaluation of additional training needs.

#### Equipment

- The inadequacy of the measuring equipment (i.e. measurement of acidity was carried out manually by immersion of a rod with an indicator chart).
- The bursting disk was installed not to take care of any exothermic reaction, but to protect against overpressure when using of nitrogen (or air) to transfer the content into another tank; any flare or scrubbing system was designed to recover the possible discharged fluid.
- Lack of automatization in the process (too much reliance on manual operations; absence of an online control).

Runaway reaction can be prevented, or mitigated by several technical approaches, e.g., inhibition, emergency venting abatement, quenching and dumping, etc. (Palazzi et al., 2015). The mitigation system design should accurately consider the specific needs of the process involved in terms of maximum credible flow rates and chemical composition, taking into account possible side reactions and secondary products.

#### Previous accidents information

- Information gained about previous accidents, i.e. the Coalite one, or evidence from near-misses was not ennobled to process and corporate knowledge, in a climate of superficiality.

A systematic investigation on the state of art of knowledge in process chemical reactivity and the in-depth the analysis of previous accidents and near misses with shared knowledge to all involved can help to prevent accidents.

### 2.3 Underlying theories on runaway reaction evolution

The following sections describe the different theories on the evolution of runaway reaction in the Seveso incident.

#### The heated surface layer theory

Theofanous (1983) provided a well-known physical explanation of the event schematically depicted in Figure 5. In the distillation period, the non-cooled portion of the reactor wall (ref. Surface 2) approached the steam temperature ( $\approx 330$  °C at 12 bar), while the portion below, submerged, was maintained at about 160 °C, so that temperature gradients existed (Theofanous, 1983). In the mixing period, the relaxation of these gradients began and continued after the stirring stop; natural convection currents disturbed the quiescent liquid. Surface 1 was heated from the adjacent hot portion of the reactor vessel wall, which was the Surface 2. Owing to this theory, the formation of a

thin liquid stratum with surface temperatures between 200 – 220 °C range was predicted. A two-step mechanism for the activation of the decomposition reaction was proposed: the preheating step consisted of a combination radiation-conduction-convection process which brought the surface temperature in the range 200 – 220 °C when the stirrer stopped; the induction step led to the additional heating required to reach the activation of an exothermic decomposition reaction 7.5 hours later (Theofanous, 1983). However, in a previous study, Ferraiolo (1979) already commented this mechanism hypothesis as a peculiar novelty, to be collocated at the “boundaries of surprising” founding his reasoning upon the characteristics of the reactor (10 m<sup>3</sup> capacity, stirrer equipped, heated with 12 ate vapour through outdoor coil covering part of the side surface and the bottom of the reactor vessel). Taking into account the condensing temperature of the vapour at 12 ate (190 °C), it is believed that, when the heating stopped, the temperature of the internal wall in contact with liquid was nearly 180-185 °C. Because of the high heat capacity of the reactor content (nearly 5,800 kg at the beginning, with a specific heat of 0.7 kcal/kg °C) with respect to the shell one (nearly 4,000 kg with a specific heat of 0.1 kcal/kg °C), it is easy to verify that the equilibrium temperature of the whole system, even neglecting the heat losses towards the environment, could not be far from 158 °C. Thus, the temperature of the internal wall of the reactor, once the stirrer stopped, could not be a heating source because it must be dropped below 180 °C. Even considering the fact that the vapour left the thermal power plant in superheated conditions and that probably it reached the reactor in this state, the issue does not change (Ferraiolo, 1979).

#### The thermal (in)stability of hydrolyzates theory

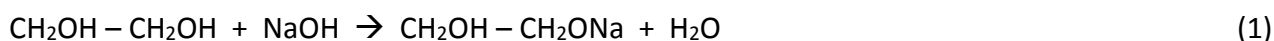
This paragraph gives us the opportunity of speaking about the inadequacy of the analytical instrumentation forty years ago (in terms of accuracy, resolution and sensitivity) and to gain awareness of the incomplete state of the art in that period. Milnes (1971) studied the thermal stability of the TCB hydrolyzates, after the accident at Coalite plant in 1968, similar to the Seveso one, finding a decomposition temperature of 230 °C. Starting from these findings, Cardillo and Girelli (2004) highlighted the fact that initial difficulties to explain Seveso mishap rose from this datum: how was it possible that the mass of reaction, left at 158 °C, decomposed itself, when the known instability limit was 72 degrees higher? The explanation stands in the fact that Milnes did not specify the utilized instrumentation, nor the conditions. The safety of the process was based upon the difference between the operative temperature and the hypothesized decomposition temperature. Indeed, it is now common knowledge that the beginning of an exothermal decomposition is observed (Lunghi, 2006) at the temperature at which the generated heat exceeds the detection threshold of the measuring instrument (Cardillo and Girelli, 2004). It follows that more sensitive instruments evidence a lower onset temperature for the same decomposition reaction, leading to different safety considerations. The authors conclude the article remarking that, with the sensitivity and accuracy of the current calorimeters, the first decomposition temperature of the Seveso mixture could result even lower than 180 °C. This finding was obtained in the Eighties (Salomon, 1982) through TGA/DSC tests, thus explaining a weakly exothermal reaction at 180 °C, previously unknown, while at 230 °C, according to Milnes theory, a more violent decomposition reaction takes place.

### The Givaudan patent changing theory.

Just a few months after the accident, a detailed investigation (Mazza and Scatturin, 1976) highlighted several critical items connected to the non-respect of the original Givaudan patent. Comparing the procedure adopted by ICMESA for the production of TCP, with the one foreseen in the Givaudan patent, several variants are noticed, mainly concerning the ratios between solvents and TCB (lower for ICMESA), and the anticipation of the distillation of solvents during the alkaline hydrolysis, instead of after the acidification. Mazza and Scatturin evidenced that according to Givaudan patent a low content of EG can be the main cause of low yield and quality of the TCP, so that the minimum acceptable value is set at 60% of the optimal one. The TCP production at ICMESA was carried on beneath this threshold, even considering the xylene content, non-contemplated in the original patent. Additionally, the solvent molar ratio can be still lowered during the alkaline hydrolysis in connection with the anticipated solvent distillation during the reaction. The comprehensive evaluation of the modifications brought to the Givaudan patent, ascribed to running cost saving choices, led to the following observations: 1) the lower amount of solvents reduced the thermal flywheel, making it possible wide fluctuations of the mass reaction temperature difficult to control even because of the poor instrumentation; 2) sodium trichlorophenate remained at high temperatures for a longer period of time than the one foreseen in the Givaudan patent owing to the modified process sequence with EG distillation before acidification and specifically during alkaline hydrolysis. It should be noted that in the subsequent years this theory was partially confuted by Canonica (1977), Ferraiolo (1979), Cardillo and Girelli (1981), Gustin (2002), who reported studies asserting the hazardous situation created by the contemporary presence of EG and NaOH at high temperatures. This reading of the situation brings the attention to a further potential determining factor: EG distillation completed on the 10<sup>th</sup> July 1976 just for the percentage of 15% instead of the conventional target value of 50%.

### The sodium glycolate and oxalates theory

An alternative explanation of the fact is provided by Gustin (2002), and deepened by Cardillo (2016) according to whom EG heated with the presence of NaOH produces sodium glycolate or sodium oxalate that, afterwards, decomposes developing hydrogen. This theory was discarded in the past (Ferraiolo, 1979) because of the hypothesis that the abovementioned reaction is endothermic both in the case of solid NaOH and, even more, in case of NaOH solutions. Gustin (2002) and Cardillo (2016) reviewed this hypothesis suggesting an exothermic reaction in case of solid NaOH. This amounts to saying that, according to Gustin's theory, at the given conditions, in the presence of anhydrous NaOH, sodium glycolates and water, EG was not anymore just a solvent, but a reactant according to:



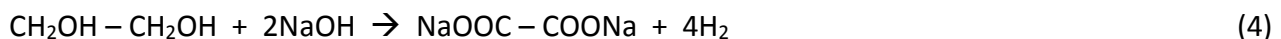
being the reaction (1) and (2) favoured by the under vacuum distillation of the azeotrope xylene/water. Furthermore, under alkaline conditions, diethylene glycol (DEG) was formed too

(Cardillo, 2016): starting from  $\Delta H_{fEG}^{\circ} = -454.93$  kJ/mol ;  $\Delta H_{fDEG}^{\circ} = -637.03$  kJ/mol;  $\Delta H_{fH_2O}^{\circ} = -285.83$  kJ/mol (Perry and Green, 2007),  $\Delta H_r$  at operative conditions reveals a weakly exothermic value.



Additionally, Gustin (2002) underlines the fact that other reactions were known since long times: In 1904, by heating an equimolecular mixture of ethylene glycol and caustic soda at 230 °C, Nef obtained hydrogen, di/tri-ethylene glycol, methanol, ethanol, sodium formate, acetate, oxalate, and carbonate.

In 1928, Fry and Schulze through a more elaborate mechanism, confirmed the formation of sodium oxalate and carbonate and hydrogen, by following reactions:



Starting from Eq. (5) and referring to thermodynamics data  $\Delta H_{fEG}^{\circ} = -454.93$  kJ/mol ;  $\Delta H_{fNaOH}^{\circ} (s) = -425.80$  kJ/mol ;  $\Delta H_{fNaOH}^{\circ} (aq.) = -469.86$  kJ/mol ;  $\Delta H_{fSodiumOxalate}^{\circ} = -1315$  kJ/mol (Perry and Green, 2007) it can be concluded that at the given operative conditions the reaction is endothermic in case of aqueous solution of NaOH, while it is exothermic in case of solid NaOH (Cardillo, 2016).

Trifirò (2004) evidenced further peculiarities of the process chemistry, evidencing that Cardillo and Girelli (1981) indicated the reaction between DEG and NaOH event at 140 °C and Gustin (2002) proposed the reaction between EG and NaOH at only 160 °C. As a concluding remark, Trifirò (2004) suggested that, according to this interpretation, it is not necessary to invoke the overheating of the surface layer by the reactor to find an explanation for the onset of the runaway reaction at the operative reactor temperature. Whichever factual explanation one could accept among the different competing theories, all involve human factor, at different organizational level. In order to obtain a reliable and more truthful picture of the situation that verified on the 10<sup>th</sup> July 1976 in the ICMESA Seveso plant, in the following section we approach and discuss accident analysis by means of three different structured methods.

### 3. SEVESO ACCIDENT ANALYSIS

Several questions seem to deserve a response, or even just an attempt to further investigation:

- Could the accident have been prevented?
- Was it a “black swan”?
- Could the deficiencies in the organizational field be considered as main issues in the accident?
- Were the deficiencies in technical matters the only ones to be considered?
- Was there a lack of knowledge concerning the process?
- What was the role of the economic interest in ICMESA decisions?
- Could have been the information given to the population more efficiently?



The available material can be classified as: scientific papers and reviews; articles from non-scientific magazines ; technical material from ICMESA and official reports; websites; published interviews. The above considered material is used into a combined approach by means of three methods of analysis: the High-Reliability Organizations (HRO) theory with the AcciMap approach (standardized method); the Energy Barrier Model; the Systems Theoretic Accident Model & Processes (STAMP) through a dynamic approach. The abovementioned methods were selected for the survey among the available ones, because of their immediate capability, even graphical, in highlighting failures occurred at different levels (process control, legislative, safety management system, human factor, etc.) both in prevention and in protection. Moreover, we perform the selection on the basis of their particular attitude to effectively describe accidents which, because of their characteristics, could be superficially considered as “black swans”. From an ideal viewpoint, the optimal approach lies in the systemic nature of the selected methods applied to the whole socio-technical hierarchy of the considered process/plant.

### 3.1 AcciMap analysis

The locution “High-Reliability Organization” was born in the early 1980s by a group of Berkley’s researchers. They tried to answer to the question “why so few serious accidents occur” rather than “why accidents occur” (Rosness et al., 2010). On the basis of empirical investigations, HRO theorists made various lists of specific characteristics that describe several kind of organizations (i.e. aviation, nuclear, power stations, etc.), which, despite operating highly hazardous and complex technologies, appeared to function without any mishap. Concerning the organizational factor Weick and Sutcliffe (2007), as well as Braut et al. (2004), define HRO as a “mindful” organization according to five items: preoccupation with failures rather than success; reluctance to simplify interpretations; sensitivity to operations; commitment to resilience; fluid-decision-making system.

Concerning resilience (Weick and Sutcliffe, 2007), it means that an organization is conscious of its own ignorance and has to provide an elastic system way of thinking to bounce back solicitations that could tend to bring the system out of its normal condition functioning. According to a resilient approach, safety is considered as “control of work processes”, and accidents are identified as results of the loss of control, so that within Seveso context resilience absence is to be considered as the non-ability to recover a process from unforeseen and unexpected disturbance that potentially leads to mishap (De Rademaeker et al., 2014). The AcciMap approach involves the construction of a causal diagram depicting the events and the conditions that interacted to result in an accident. The accident is located near the bottom and the causes are branching upward, with the more immediate causes in the lower section and the more remote causes towards on the top (Branford et al., 2009). An AcciMap diagram enables analysts to compile large amounts of information, within a single diagram; then, the diagram permits to understand how and why an accident happened; last but not least, the approach assists in safety recommendation development.

Figure 6 illustrates the Seveso accident through Acci-Map modality, taking account that TCP production is, albeit in hindsight, an activity which could cause a Major Accident Hazard. Table 2 summarizes the consequent safety recommendations. The accident itself is located in the lowest section of the diagram, and it is possible to reach it towards a logical chain of events with causal links facing downwards. No indication of a “time line moving” is given, but the temporal order must be ascertained from the causal connection. Just the causes of “practical significance”, or the ones

necessary for making sense of how (rectangles with curved edges) and why (rectangles) the accident occurred are included in the map. Analyzing the Acci-Map diagram, external factors are of primary relevance if we think that Seveso accident has been a watershed. The inadequate legislation concerning these kind of activities, was the natural precursor of an undeveloped safety culture, from which ICMESA did not escape: similar accidents happened in other industries producing TCP were ignored (from this point of view, it has been a case of “unknown known” and not a perfect black swan “unknown unknown”). Hence, the conflicting object perspective saw the victory of efficiency against safety, with people and environment losers of their life and health condition. In the name of economic efficiency, the inadequate knowledge of the process led to relevant changes respect to the original Givaudan patent. The ratio among reactants was changed, by diminishing the amount of EG, which was expensive, and by adding xylene, which was not foreseen in a first time; Givaudan foresaw the distillation of the solvents at the end of the process, after acidification, while ICMESA started already during the alkaline hydrolysis, weakening the temperature control. The lack of automatization reflected in an inadequate control system and instrumentation, so that no online device was controlling temperature and pressure trends. Stopping the process after the alkaline hydrolysis, when sodium trichlorophenolate was already obtained and xylene/EG were at most distillate, meant stopping both heating and stirring. It can be supposed that due to inhomogeneity in concentration and temperature, preferential areas for the beginning of an exothermic reaction (probably:  $2 \text{ sodium trichlorophenolate} \rightarrow 1 \text{ (2,4,7,8 - TCDD)}$ ) occurred (Marshall, 1980); hence, gradually, the whole mass of reaction was involved in the abovementioned reaction. No sensor was controlling the increase in T and p: at 3.5 atm, the disc ruptured, causing a huge dispersion of TCDD in the atmosphere; any tank was foreseen to keep possible releases. To worsen the situation following items should be highlighted: the inadequate information given to the population, despite ICMESA knew the identity of the dispersed substance few days after the mishap. Two weeks passed after the evacuation of the A-zone; irreversible and serious damages to people who lived in the surroundings occurred, as well as to environment too (Bert et al., 1976). Even though following Seveso accident, current legislation regulates the use of land in many Countries, there are still some unexplored possibilities of managing safety for man and the environment extending the LUP approach also to different contexts (Vairo et al., 2016). Additionally, the importance of a correct urban and land planning in the areas around major risk installations still represents a critical issue requiring a multidisciplinary approach while local authorities are often not sufficiently prepared for this kind of multilevel analysis (Demichela et al., 2014).

### 3.2 Energy-barrier model

This kind of model looks at barriers between a harmful energy source and a vulnerable object (Haddon, 1970; Rosness et al., 2010) and can be defined a “complex linear model” or “Swiss cheese” model, according to Reason’s definition (Reason, 2000). In this context, an accident develops when hazards succeed to penetrate the barriers through aligned holes, which are defects and deficiencies in the considered activity. The barriers should create understanding, suggest operating safely, provide alarms, provide the means to escape and restore the system. These barriers, either physical or non-physical are currently classified as proactive or reactive ones. In this optics, improve safety means to implement and to reinforce barriers. Before approaching the developed energy-barrier model, a simplified conceptual “bow-tie” diagram is proposed in Figure 7, in order to introduce the

discussion on proactive and reactive barriers. “Runaway reaction” with the loss of containment via bursting disk is the centre of the bow tie (Critical Events), toxic release is the Dangerous Phenomenon and the Major Events are toxic load causing damage to people/environment. Figure 8 shows the barrier function of the proactive barrier: “prevent loss of containment of a reactor due to the bursting of the rupture disc” which may be broken down into barrier sub-functions “prevent the bursting of the rupture disc” and “prevent the loss of containment of the reactor”. Each barrier sub-function has barrier systems which are linked to several barrier elements. The barrier sub-function “prevent the bursting of the rupture disc” is realized by the barrier system “adequate control of T and p of the process, even to ensure the quality and stability of the product”. The barrier elements of this barrier system are: “Thermocouples + alarm” and “Pressure switches + alarm”. The barrier sub-function “prevent the loss of containment of the reactor” is realized by the barrier system “reactor security” and the responding barrier elements are: “vessel for containment” and “knocking down unit”. The lack in the control system and in a containment after the bursting disc rupture led to fail the proactive barrier system. Figure 9 shows the barrier function of the reactive barrier representing major factors impacting the mitigation side of the bow-tie: “prevent injuries and fatalities after the loss of containment”. Two barrier sub-functions exist: the “evacuation from contaminated areas” and the a priori principle “do not localize a MAH activity nearby an inhabited area and vice-versa”. The two barrier systems are respectively: “organizational factors” and “decision policies”. Barrier elements are, for the former, the “internal emergency plan” and the “external emergency plan” and, for the latter, the dispositions of the “municipal plan land”. In the Seveso mishap, it is possible to observe the timeline in Table 3 and to affirm that a lot of superficiality and ignorance accompanied each moment of the drama; a lot of time passed before the area was evacuated. People lived with no awareness and any protection for days and days, compromising, inevitably, their health in an irreversible way. This kind of model, explains the accident through failures of barrier functions. After the runaway reaction, the proactive barriers failed to prevent the loss of containment due to the bursting disc and the consequent toxic release and injuries. Looking at these barriers, actual organizations should get ideas on how to improve their technical/organizational/human factors, in order to close the holes in the cheese. In the last years, the need to regulate specific aspects of hardware and software controls especially used on critical process systems gave birth to a specific legislation through International Standard IEC61511 based on IEC61508 (a generic standard for design, construction, and operation of electrical/electronic/programmable electronic systems). In particular, the evaluation of the functional requirements of a SIS (Safety Instrumented system), refers to clause number 8 of EN/IEC61511 and to clause 5 of IEC61511 (Fanelli, 2004). According to this legislation, the correct operation of a SIS requires a series of equipment to function properly: sensors, in order to detect abnormal operating conditions; logic solver, to receive the sensor input signals and make appropriate decisions; final elements, in order to take action according to logic solver dispositions. Furthermore, the support systems should be designed to provide the required integrity and reliability.

### 3.3 STAMP theory

It is an accident analysis model based on Systems Theory and is a sort of holistic approach to safety; it provides a broad insights into accidents via the integration of the analysis from both direct and

indirect factors involved. Systems are viewed as hierarchical structures with multiple control levels; STAMP considers the dynamic nature of systems, in contrast with many traditional accident analysis techniques such as Event Tree Analysis, Fault Tree Analysis, which deal with systems and environment as a static design and unchanging structure (Leveson et al., 2003). Two different techniques come from the more general STAMP theory: the “System Theoretic Process Analysis” (STPA), to improve the existing hazard analysis, and the “Causal Analysis based on STAMP”, to improve the existing accident analysis. This study particularly emphasizes the latter compared to the former. By this method, the detailed process analysis is not considered in depth, as these aspects mainly covered by the other methods are already amply explored in the scientific literature. The holistic approach means: to elaborate a framework able to identify the systems involved in the accident, to document the safety control structure, to determine the near-misses and proximate events leading to the accident, to analyze the accident at a physical system level, to analyze the contributors to the accident, to determine the existence of any changes to the system hierarchical safety control structure, to develop recommendations (Kim et al., 2016). A customized framework based on SD with causal loop diagram and a numerical evaluation through stocks & flows diagram is an innovative appeal to describe the net of events, which led to the mishap, taking account of feedback loops, time delays and the effect of the variables that interact and affect one another in complex shapes and structures.

### 3.4 A dynamic approach

The third kind of investigative tool, which is based on a dynamic approach, aims at deepening the management errors that led to the tragedy. As lately admitted by the last technical director of the ICMESA plant (Sambeth, 2004), apart from technical causes, Seveso accident was set into motion by serious management errors a long time before it happened. He suggested that two lessons were to be learnt: the former concerned the technical aspects, while the latter, the more important, was about the company politics. The dynamic simulation of the accident simulation is intended to be a sort of guided tour through the accident happened 40 years ago. The worked out model is schematized in Figure 10 and three determining steps can be identified: the alkaline hydrolysis in the batch reactor; the TCDD formation along with the runaway reaction; the bursting disc rupture. The simulation is based upon the credit factor (CF) concept: each section is represented by a stock (a rectangle), which is something similar to a noun, for it accumulates. In this case, each section is characterized by certain number of dynamic credit factors: wrong policy decisions cause the decrease of these CFs in each section, exposing the system to hazardous situations which create the accident. The right/wrong decision-making policies are delegated to conveyors (such as adverbs, for they modify): towards special logical functions they activate/deactivate the CF removal from each stock. Through several specific built-in functions, it is possible to develop a code for each variable, which took account of the time of the simulation (specific events have to come at specific hours during the simulation). 28 variables were used for model development: references about the variable name, the associated code and a brief description of the functions are summarized in Table 4. The description of the mechanism of simulation is herein given:

- Section 1: alkaline hydrolysis in the batch reactor. Reactants (NaOH, TCB) and solvents (EG, xylene) are entered and their molar ratios are checked, according to the fact that, in

hindsight, it is known that original protocol was ignored. Because of this fact, the Credit Factor Flow IN gives the unit just 4 credits in spite of 5. CFs are removed from the alkaline hydrolysis reactor unit because of the wrong/hazardous decisions about distillation of solvents and the stop of the stirring.

- Section 2: TCDD formation and runaway. Central issue of this part is the lack of a temperature and pressure control so that this design decision allowed the uncontrolled development of the phenomenon.
- Section 3: bursting disc rupture. CFs are removed because of the lack of a further containment as well as a knocking down unit. Then, any emergency plan was foreseen and the population was left in ignorance concerning the presence of dioxin in the release. Any recovery took place, in the name of economic interest, again.

As Sambeth admitted almost 30 years later, the technical aspects are one thing, company policies are quite another. A dynamic simulation based on CF places on records how an accident as Seveso was fostered by serious and incredible errors, arrogance and politics a long time before it happened. Figures 11, 12, 13, 14, 15 highlight particular moments of the simulation already described in the bullet listed reported above. Results in terms of system degradation evaluated through loss of credit factors during the simulation time, are summarized in Figure 16.

#### 4. RESULTS AND DISCUSSION

Each model discussed in the previous chapter describes the disaster of Seveso focusing on different aspects and allows performing different safety considerations.

- The HRO theory with the Acci-Map approach asserts that failure to anticipate the unexpected events and the inability to contain them are the main causes of the disaster; it also takes account of the fact that underdeveloped safety culture and missing learning orientation brought to consider "unexpected" something that was, instead, foreseeable. The system had neither the capability to prevent, nor to recovery, bouncing back solicitations received. For these reasons, the system didn't show the accomplishment of resilience and the process incident occurred with high consequences on nearby residents and environment.
- The Energy Barrier model shows that the incident was caused by an inadequacy of proactive and reactive barriers, with the absence of a further containment, as well as the absence of a blow-down or flaring system. Relevant elements include changes to process conditions coupled to the lack of "online" control system of operative conditions. Furthermore, emergency plan was not activated immediately and information to the public in the area was incomplete and late, not enabling the correct decisions to be made.
- The Dynamic Approach is useful because it foresees the construction of a simulation that shows how variables interact one another, taking account of feedback loops and time delays. The "credit factor" approach used in the simulation winks to LOPA (Layer of Protection Analysis), which is a fast method allowing to evaluate the goodness of a system to face a

single pair “cause-consequence” and to resist the impact. Mindful leadership, managerial aspects and decision policies are here mainly investigated.

Table 5 summarizes the results obtained by the three different methods and shows the different perspectives highlighting the different causes of the disaster. The main difference between accident investigation and accident prevention is whether it is in hindsight or in foresight (Hyungju et al., 2016). Each perspective describes the causes of the accident in a particular way, but some perspectives are complementary to one another. The Energy Barrier model provides a clear view of the accident sequence of events (Hyungju et al., 2016), so accident scenarios are prevented from occurring efficiently and effectively; however, it is restricted to specific accident scenarios. There is the inability, for the Energy Barrier model, to consider all kinds of accident scenarios. Thus, different models could be implemented to reach better results: the Energy Barrier model provides a concrete view of how the loss of containment from the reactor, due to the bursting of the rupture disc failed, as well as injuries and fatalities occurred owing to wrong decision policies and organizational factors; HRO theory with Acci-Map and the Dynamic Approach help identifying the Performance Influencing Factors (PIFs), which are the conditions that are significant for the ability of barrier functions and elements to perform as intended. A combination of these perspectives may help understanding the whole sequence of causes of the accident itself. These relations are illustrated in Figure 17. Globally, the development of a combined systemic and organizational accident model can allow identifying the system deficiencies and the need for changes. Additionally, the Italian legislation, at that time, did not allow to install any kind of item downstream rupture disc or PSV devices. In any case, it should have been clear that, in a reactor containing a two-phase fluid, the maximum allowable pressure must be designed considering the one corresponding to the vapour pressure of the liquid at the maximum allowable temperature. This statement is currently explicitly stated in the PED Directive 2014/68/CE (transposed in Italy by the Lgs. Decree 26/2016, integrating the 97/23/CE transposed by the Lgs. Decree 25/02/2000). The lessons from the Seveso accident and other subsequent events connected to reactive processes show that in many cases the accident is caused by lack of knowledge of the process, the bad design of the heat exchange system of the reactor (European Commission, 2016). In a recent survey (European Commission, 2016) covering 90 accidents related to runaway reactions from different international databases, it is surprising observing several analogies with Seveso, e.g. management of change (MOC) was not in place in at least seven events and mitigation measures for controlling reaction rate, such as venting were not considered in five accidents. As evidenced by the different models, the inadequate control system and instrumentation has resulted in the loss of temperature control up to the runaway reaction. According to a proactive approach, the introduction of control system and the implementation of appropriate prediction criteria, as the Early Warning Detection System (EWDS) are fundamental (Bosch et al, 2004a; Bosch et al, 2004b; Zaldivar et al, 2005; Westerterp and Molga, 2006; Ampelli et al. 2006). In the frame of the AWARD European Project, an early warning detection system (EWDS) was developed and successfully tested both in small-scale and pilot plant chemical reactors, as well as in an industrial chemical reactor under batch and semi batch conditions (Ampelli and Maschio, 2012). The methods for EWDS can be divided into three main categories depending upon the quantities being used: conventional limit check systems (Marco et al, 1997; Tufano, 1988), temperature derivatives (Hub and Jones, 1986; Strozzi et al., 1999), and model-based estimation

techniques (Semenov,1959; Thomas and Bowes,1961; Varma et al, 1999). In particular, the criteria that does not require models (such as the Hub and Jones and the Strozzi and Zaldívar criteria) are the most suitable for the application in real industrial systems with, for example, the use of the online sensors making them capable to prevent the runaway reactions. The use of appropriate control systems and the EWDS criteria could have prevented the Seveso incident. Comparison of criteria for the prediction of runaway reactions coupled with calorimetric screening analysis has been discussed recently (Casson and Maschio, 2012; Casson et al. 2012). An interesting question that could rise is whether Seveso mishap could be considered a “black swan” incident? Generally speaking, low probability/high consequence process incidents should be considered as “black swans”, according to the theory by which black swans are non-existent in spite of the white ones. Looking at different “black swans” definitions, provided by several authors, an answer to the abovementioned question is inquired into. Taleb (2007) describes a “black swan” incident as an improbable event having three peculiarities: it is not expected; it has an extreme impact; it is explainable and predictable after the fact. A hint in the description of events that may occur could be given by the Donald Rumsfeld’s four quadrants of “known” and “unknown”. In the reliability context, “known” means a possible scenario recognized and defined, while an “unknown” stands for a potential scenario as an overlooked possibility. The set of combinations between the two “knowns” and “unknowns”, forms the quadrants (Pasman and Rogers, 2016); in specific: “known knowns” are the events we know about and for which we can plan for a solution; the “known unknowns” are events we can foresee even if they have not occurred yet. “Unknown knowns” are intended to be events that have yet occurred but that are not remembered anymore, while the “unknown unknowns” are events not yet predicted or which have been considered not realistic. The last item refers to the “black swan” events. Aven (2013) defines a “black swan” event as follows, in two ways: an extreme event that is a surprise relative to the present knowledge of persons to be specified; from a risk perspective, an extreme event that is a surprise relative to the knowledge by the events of the Risk Analysis. These last definitions introduce the “knowledge”, which has to be distinct from the “information”: information becomes knowledge when it is interpreted by individuals and given a context and anchored in the beliefs and commitments of individuals (Piiro, 2012). Based upon these definitions and the original definition, an insight into Seveso accident concerning its “black swan” attitude is possible. Seveso mishap had an extreme impact; it was explainable in its deep after the fact, but it should be expected for several reasons, including technical and organizational factors. At last, the first condition of “black swan” event by Taleb is not satisfied so that Seveso accident cannot be considered as a perfect “black swan”. Referring to the Rumsfeld’s quadrants, it is not possible to consider the incident as an “unknown unknown” for several reasons: other similar accidents occurred in the preparation of TCP (Cardillo and Girelli, 2004), while modifications and changes from the original Givaudan patent and the consequent events fell within the scope of “known knowns”. At last, from a risk perspective, Seveso disaster had been a watershed and could be regarded as a “black swan” just considering the follow-out giving rise to a specific directives used as the basis for legislative frameworks also outside of the European Union (e.g. the Australian framework for major hazard facilities relies on Seveso II and the New Zealand framework is based on the Australian legislation). In this regard, it seems still evident the need of approaching both land use and emergency planning, conceiving risk assessment as part of

an integrated process composed by many important and interrelated phases, not only post-disaster emergency, but also structural interventions for the long-term prevention (Pilone al., 2016).

## 5. CONCLUSIONS

In this paper we investigated the Seveso accident by using three different accident theories and found fifteen main causes that contributed to the disaster: five from the Energy barrier model, seven from the HRO theory and three from the Dynamic approach. The results show that the accident is neither attributable to a single human error, nor to a single technical error, but rather to a combination of factors having the same basis of inaccuracy and superficiality (Sturloni, 2006) due to a lack of safety culture caused by the absence of specific legislation. In the Acci-Map approach, a “conflicting objective perspective” has been taken into account, evidencing how the organization was exposed to conflicting organizational pressures, which makes sociotechnical systems migrate toward the boundary of acceptable risk (Rasmussen, 1997). The analysis shows how each perspective described the accident in its own way, but how the better results would be reached through a combination of them. In other words, Seveso accident highlights the need of improving the understanding and the prevention of major accidents by a careful combined analysis which took account not just of the results of the single model, rather of a commingling of models. A lot of uncertainties and different opinions embrace the event that Seveso was, but this investigation prefers to focus on “why” something happened rather than on “how”, in the belief that the road travelled to reach the goal is more important than the goal itself. This paper from one side shows how Seveso accident could be considered a “black swan” just considering its “legislative fall-out” shaping development of process safety in Europe and the rest of the world. From the other side, addressing a risk perspective, it is the inevitable result of a sum of factors including lack of knowledge, lack of process understanding, ineffective supervising and managerial controls, failures in loss prevention and environmental protection, partially driven by lack of legislation and willed blindness in the name of economic interest.

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Figure 1: 2,4,5-Sodium trichlorophenate formation through alkaline hydrolysis of 1,2,4,5-TCB.

Figure 2: 2,4,5-TCP formation through acidification of sodium trichlorophenate.

Figure 3: 2,3,7,8-TCDD formation.

Figure 4: Alkaline hydrolysis reactor (adapted from Gustin, 2002).

Figure 5: Theofanous heated surface layer scheme (adapted from Theofanous, 1983).

Figure 6: The AcciMap diagram developed for Seveso accident.

Figure 7: Simplified conceptual bow-tie of Seveso incident.

Figure 8: The Energy Barrier Proactive diagram.

Figure 9: The Energy Barrier Reactive diagram.

Figure 10: The complete stock & flow diagram corresponding to the dynamic simulation.

Figure 11: Credit Factors mechanism of analysis (Flow in).

Figure 12: Credit Factors mechanism of analysis (Flow out).

Figure 13: Damage counter.

Figure 14: Pressure profile.

Figure 15: Temperature profile.

Figure 16: System degradation through loss of credit factors during the simulation time. CF in the range:  $4 \rightarrow 2$  green zone, acceptable risk ;  $2 \rightarrow 0$  orange zone, upset conditions ;  $0 \rightarrow -2$  red zone, critical conditions ;  $-2 \rightarrow -3$  black zone, catastrophic event.

Figure 17: Inter-relations and knowledge learning by a combined approach to Seveso accident investigation (see Table 5 for notations).