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**CRITICAL PROCESSES IDENTIFICATION OF CCS CHAINS
TO SUPPORT BEST PRACTICES ADVANCEMENT**

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Abstract

Carbon capture and storage is the process of capturing waste CO₂ from large point sources, such as large fossil fuel power plants, transporting it to a storage site, and depositing it where it will not enter the atmosphere, normally an underground geologic formation. The aim of this study is to individuate the most critical processes concerning CCS plants in order to support the optimization of the known best practices in this field, in particular of the capture ones. The starting point has been the research, in the chemical plants history, of all the industrial accidents happened until today. Obviously in the investigation has not been reported CCS accidents since it is a new technology, not yet so widespread, evidently for the general barely capacity to sustain the costs for this pollution reduction technique. Thus, a collection of all the substances involved in the capture phase has been used to guide the research. Results have demonstrated that the capture process with MEA was potentially the most hazardous one, since the damages that could occur with that, would be huge. After that an Aspen Plus simulation has been run on an existing pilot plant to identify the most critical part of the plant: it will be verified to be the stripping section. In this part of the plant has been concentrated the attention: initially a hazard and operability study has been written about that section and after that, a fault tree and event tree analysis has been performed, with the choice of a release as Top event. So, first has been done some qualitative considerations and afterwards also the quantitative ones have been evaluated. To conclude the risk assessment, a software simulation on Aloha platform has been run to study all the possible consequences that a release of that type of substance can cause: different conditions has been hypothesized to include all the possible scenarios.

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Introduction

Nowadays it is becoming more and more evident that the rapid increase of the world population, the unchecked industrialization of the second world countries and the continue increase of energy demand of the world in general, it is increasing the presence of greenhouse gases in our atmosphere. In particular, the electric energy production is for the main part carried out with the combustion of fossil fuels, e.g. carbon and methane: this obviously creates some by-products and, between them, there is the carbon dioxide, one of the greenhouse gases that continue to fuel the global warming. Apart from the unknown effective availability of fossil fuels, their employment in the future can probably continue only if the CO₂ produced does not reach the atmosphere and keeps staying in. For this reason, the Carbon Capture and Storage technology, namely the capture of the carbon dioxide and its subsequently injection in the underground, is a solution that can satisfy both the fossil fuel utilization and the global warming reduction. In this thesis, a study on the capture section of a CCS plant is carried out using the tools, in general, provided by the risk analysis. The objective of this work is the identification of critical processes in CCS chains to support the advancement of best practices. Specifically, it is considered only what concerning the capture part of the process. For this purpose, this thesis starts from the study of all the dangerous substances that might be present in a carbon capture plant to identify the most hazardous process and consequently to improve the best practices in order to obtain a safer process. After the individuation of that, with a historical analysis of the industrial accidents involving all the substances that can be used for carbon capture, the work proceeds with a simulation of the ordinary operation of that process. Thereafter, alterations of the conditions are induced on a hypothetically flue gas exiting from a combustion power plant, to observe what is the “precarious” section of the capture. In the fifth section of this work the focus is on that section and an accurate risk analysis is performed, through its more common tools, i.e. Hazop, FTA and ETA, in order to evaluate the occurrence frequency of a flammable and toxic release and subsequently to provide all the countermeasures need to contrast it. Moreover, a simulation of consequent scenarios which may occur is also performed.

Chapter 1

Carbon Capture and Storage

Global-warming and climate change concerns have triggered global efforts to reduce the concentration of atmospheric carbon dioxide (CO₂).

Different approaches are considered and adopted by various countries to reduce their CO₂ emissions, including:

- Improve energy efficiency and promote energy conservation;
- Increase usage of low carbon fuels, including natural gas, hydrogen or nuclear power;
- Deploy renewable energy, such as solar, wind, hydropower and bioenergy;
- Apply geoengineering approaches, e.g. afforestation and reforestation;
- CO₂ capture and storage.

The application areas, advantages and limitations of these different approaches are compared in the Table 1.1. Some of these approaches deal with source emissions reduction, such as adopting clean fuels, clean coal technologies, while others adopt demand-side management, i.e. energy conservation. Each approach has intrinsic advantages and limitations that will condition its applicability. It is unlikely that adopting a single approach or strategy can adequately meet the IPCC goal of CO₂ reduction, i.e. 50–85% by 2050 from 2000 levels, and therefore, a complimentary portfolio of CO₂ emission reduction strategies needs to be developed [1].

Table 1.1. Summary of CO₂ reduction strategies

Strategy	Application area/sector	Advantages	Limitations
Enhance energy efficiency and energy conservation	Applied mainly in commercial and industrial buildings.	Energy saving from 10% to 20% easily achievable.	May involve extensive capital investment for installation of energy saving device.
Increase usage of clean fuels	Substitution of coal by natural gas for power generation.	Natural gas emits 40–50% less CO ₂ than coal due to its lower carbon content and higher combustion efficiency; cleaner exhaust gas (lower particulates and sulfur dioxide emissions).	Higher fuel cost for conventional natural gas. Comparable cost for shale gas.
Adopt clean coal technologies	Integrated gasification combined cycle (IGCC), pressurized fluidized bed combustor (PFBC) etc. to replace conventional combustion.	Allow the use of coal with lower emissions of air pollutants.	Significant investment needed to roll out technologies widely.
Use of renewable energy	Hydro, solar (thermal), wind power, and biofuels highly developed.	Use of local natural resources; no or low greenhouse and toxic gas emissions.	Applicability may depend on local resources availability and cost. Power from solar, wind, marine etc. are intermittent and associated technologies are not mature; most current renewable energies are more costly than conventional energy.
Development of nuclear power	Nuclear fission adopted mainly in US, France, Japan, Russia and China. Nuclear fusion still in research and development phase.	No air pollutant and greenhouse gas emissions.	Usage is controversial; development of world's nuclear power is hindered due to the Fukushima Nuclear Accident in 2011, e.g. Germany will phase out all its nuclear power by 2022.
Afforestation and reforestation	Applicable to all countries.	Simple approach to create natural and sustainable CO ₂ sinks.	Restricts/prevents land use for other applications.
Carbon capture and storage	Applicable to large CO ₂ point emission sources.	It can reduce vast amount of CO ₂ with capture efficiency >80%.	CCS full chain technologies not proven at full commercial scale.

1.1 Carbon Capture and Storage (CCS)

Amongst that different approaches, CCS can reduce CO₂ emissions (typically 85–90%) from large point emission sources, such as power production utilities, and energy intensive emitters, e.g. cement kiln plants. In this approach, CO₂ is first captured from the flue/fuel gases, separated from the sorbent, transported and then either stored permanently or reutilized industrially. CCS includes a portfolio of technologies, involving different processes for CO₂ capture, separation, transport, storage and monitoring that will be discussed later [1]. CO₂ is formed during combustion and the type of combustion process directly affects the choice of an appropriate CO₂ removal process. CO₂ capture technologies are available in the market but are costly in general, and contribute to around 70–80% of the total cost of a full CCS system including capture, transport and storage [2]. Therefore, significant R&D efforts are focused on the reduction of operating costs and energy penalty. There are three main CO₂ capture systems associated with different combustion processes, namely, post-combustion, pre-combustion and oxyfuel combustion. These three technologies are discussed in the following paragraphs.

1.1.1 Post-combustion

This process removes CO₂ from the flue gas after combustion has taken place, as can be seen in the Figure 1.1. Post-combustion technologies are the preferred option for retrofitting existing power plants. The technology has been proven at small-scale with CO₂ recovered at rates up to 800 ton/day [3]. However, the major challenge for post-combustion CO₂ capture is its large parasitic load.

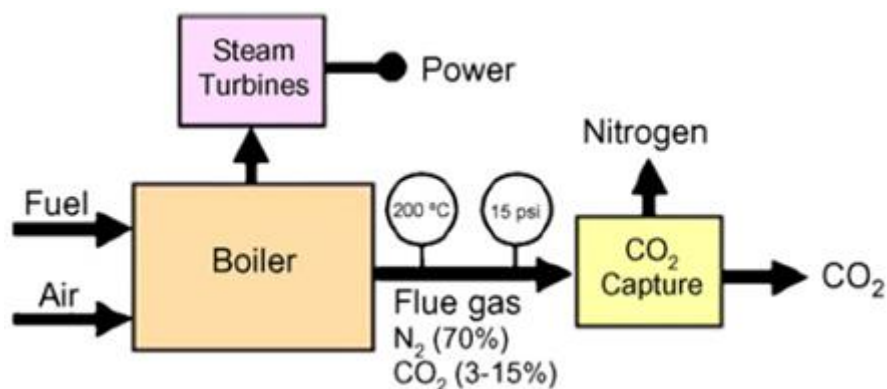


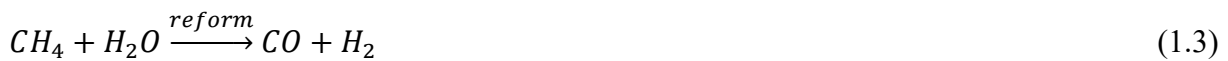
Figure 1.1. Post-combustion process scheme

Since the CO₂ level in combustion flue gas is normally quite low (i.e. 7–14% for coal-fired and as low as 4% for gas-fired), the energy penalty and associated costs for the capture unit to reach the concentration of CO₂ (above 95.5%) needed for transport and storage are elevated [4]. The U.S. National Energy Technology Laboratory estimated that CO₂ post-combustion capture would increase the cost of electricity production by 70% [5]. A recent study reported that the cost of electricity would increase by 32% and 65% for post-combustion in gas and coal-fired plants, respectively [6]. It has been identified that 16 large scale integrated CCS projects are

currently operating or under construction but two of them are of post-combustion technology [7].

1.1.2 Pre-combustion

In this process, the fuel (normally coal or natural gas) is pre-treated before combustion. For coal, the pretreatment involves a gasification process conducted in a gasifier under low oxygen level forming a syngas which consists mainly of CO and H₂, and is mainly free from other pollutant gases (Eq. 1.1). The syngas will then undergo water gas shift reaction with steam forming more H₂ while the CO gas will be converted to CO₂ (Eq. 1.2):



The high CO₂ concentration (>20%) in the H₂/CO₂ fuel gas mixture facilitates the CO₂ separation [4] (typical CO₂ separation methods will be discussed afterward). Subsequently, the H₂ is burned in air producing mainly N₂ and water vapor. Pre-combustion capture can be applied to Integrated Gasification Combined Cycle (IGCC) power plants using coal as fuel, but this will incur an efficiency loss of 7–8% [3,8]. EPRI and USDOE have developed a roadmap of IGCC technology developments that can potentially improve the IGCC efficiency matching or exceeding the current IGCC technology without capture [8]. Natural gas, as it mainly contains CH₄, can be reformed to syngas containing H₂ and CO (Eq. 1.3). The content of H₂ can be increased by the water gas shift reaction (Eq. 1.2) and the rest of the process is similar to that described above for coal [9]. A performance and cost analysis were conducted on advanced combined cycle gas turbine plants operated by natural gas with a pre-combustion CO₂ capture system and obtained a CO₂ capture efficiency of 80% with the cost of CO₂ avoided reaching \$29/ton CO₂ for an advanced design concept [10]. A schematic process flow diagram of a hypothetical pre-combustion process can be seen in the Figure 1.2.

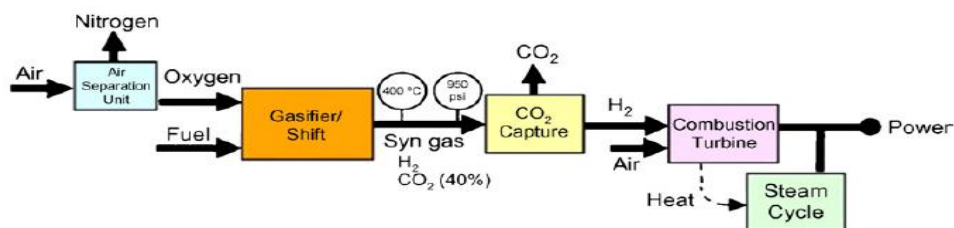


Figure 1.2. Pre-combustion process scheme

1.1.3 Oxyfuel combustion

In oxyfuel combustion, oxygen, instead of air, is used for combustion. This reduces the amount of nitrogen present in the exhaust gas that affects the subsequent separation process. Substantial reduction in thermal NO_x is another advantage of this process [11]. With the use of pure oxygen for the combustion, the major composition of the flue gases is CO_2 , water, particulates and SO_2 . Particulates and SO_2 can be removed by conventional electrostatic precipitator and flue gas desulphurization methods, respectively. The remaining gases, contain high concentration of CO_2 (80–98% depending on fuel used [12]), can be compressed, transported and stored. This process is technically feasible [11] but consumes large amounts of oxygen coming from an energy intensive air separation unit [13]. This results in high cost and the energy penalty may reach over 7% compared with a plant without CCS [14,15]. Also, high SO_2 concentration in the flue gas may intensify the system's corrosion problems. At present, there is no full scale oxyfuel-fired projects in the range of 1000–2000MWth under development but a few sub-scale commercial demonstration plants are under development worldwide such as the 25MWe and 250MWe oxy-coal units proposed by CS Energy and Vattenfall, respectively [15].

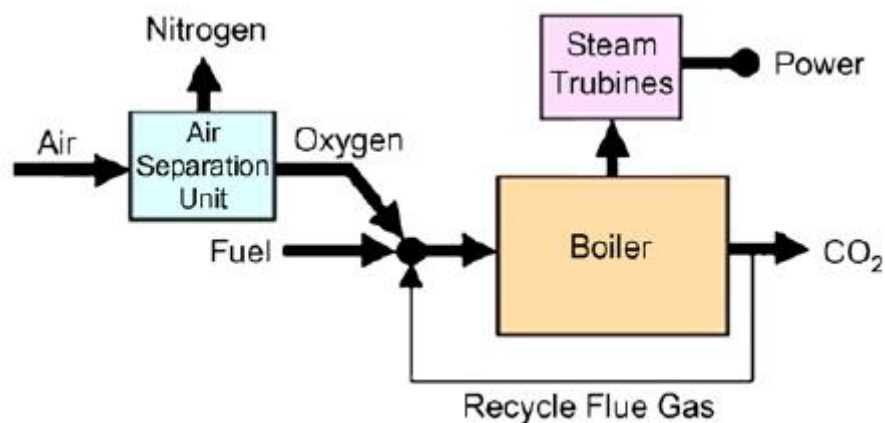


Figure 1.3. Oxyfuel combustion process scheme

1.2 Separation techniques for carbon dioxide

Capture of CO_2 contributes 75% to the overall CCS cost and CCS increases the electricity production cost by 50% [16]. Although these numbers may vary with different CCS schemes, reducing the capture cost is the most important issue for the CCS process to be acceptable to the energy industry. There are many options for CO_2 separation but the optimum CO_2 capture scheme could be determined by analyzing costs or the context of power generation. A wide range of technologies currently exist for separation of CO_2 from gas streams, although they have not been designed for power-plant scale operations [17]. They are based on different physical and chemical processes including absorption, adsorption, cryogenics and membranes [18]. The choice of a suitable technology depends on the characteristics of the flue gas stream,

which depend mainly on the power-plant technology. Various CO₂ separation techniques are discussed below.

1.2.1 Chemical absorption technology

A liquid sorbent is used to separate the CO₂ from the flue gas. The sorbent can be regenerated through a stripping or regenerative process by heating and/or depressurization. This process is the most mature method for CO₂ separation and is preferred for low to moderate CO₂ partial pressures [19]. Typical sorbents include monoethanolamine (MEA), diethanolamine (DEA) and potassium carbonate [20]. Among the various aqueous alkanolamines, such as MEA and DEA, Veawab et al. [21] found that MEA is the most efficient one for CO₂ absorption with efficiency over 90%. Subsequently, Aaron et al. [22] conducted a review on various CO₂ capture technologies and concluded that the most promising method for CO₂ capture for CCS is absorption using MEA. An absorption pilot plant with 1 tonCO₂/h was constructed and successfully tested together with the post-combustion capture technology for a coal-fired power plant using a solvent containing 30% MEA [23]. Some other sorbents, such as piperazine and anion-functionalized ionic liquid have also received attention in recent years [24]. Piperazine has been found to react much faster than MEA, but because it has a larger volatility than MEA, its application in CO₂ absorption is more expensive and is still under development [25]. One important challenge for the large deployment of this technology for CCS is its potential amine degradation, resulting in solvent loss, equipment corrosion and generation of volatile degradation compounds [26,27], while that atmospheric degradation has not been included. Moreover, amine emissions can degrade into nitrosamines and nitramines, which are potentially harmful to the human health and the environment. Chilled ammonia process uses aqueous ammonium salts (such as ammonium carbonate) to capture CO₂ that can make use of waste heat to regenerate the CO₂ at elevated temperature and pressures to reduce downstream compression [28]. This process will generate less problem as compared to those that amine is facing with degradation. A scheme of a chemical absorption technology for power plant flue gas is depicted in Figure 1.4.

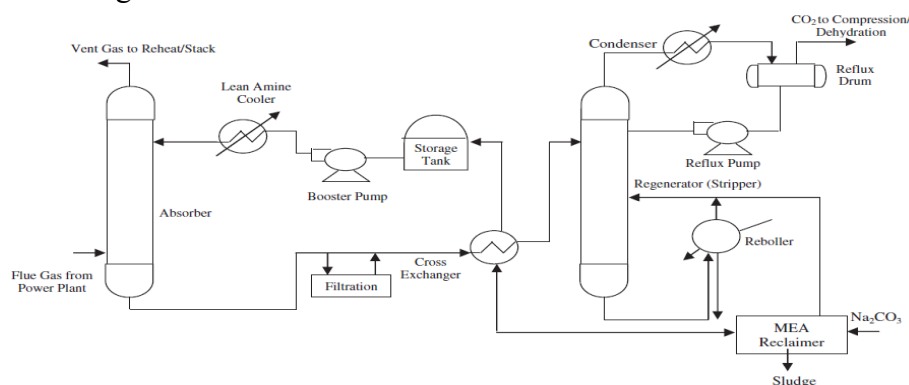


Figure 1.4. Process flow diagram of a typical chemical absorption system for CO₂ recovery from flue gas.

1.2.2 Physical absorption process

For physical absorption, CO₂ is physically absorbed in a solvent according to Henry's Law, which means that they are temperature and pressure dependent. Physical solvent processes use organic solvents to physically absorb acid gas components rather than reacting chemically. Removal of CO₂ by physical absorption processes are based on the solubility of CO₂ within the solvents and the solubility depends on the partial pressure and on the temperature of the feed gas. Higher CO₂ partial pressure and lower temperature favor the solubility of CO₂ in the solvents (Absorbent). The solvents are then regenerated by either heating or pressure reduction. Physical solvents scrubbing of CO₂ are commercially available. Selexol (dimethyl ether of polyethylene glycol), a liquid glycol based solvent, has been used for decades to process natural gas, both for bulk CO₂ removal and H₂S removal [29]. Glycol is effective for capturing both CO₂ and H₂S at higher concentration. The Rectisol process, based on low temperature methanol (cold methanol), is another physical solvent process that has been used for removing CO₂. Glycol carbonate is interesting because of its high selectivity for CO₂ but it has relatively low capacity [30]. Other physical solvents for CO₂ removal include propylene carbonate (FLUOR process) and N-methyl-2-pyrrolidone (Purisol). The physical absorption process is illustrated in the Figure 1.5.

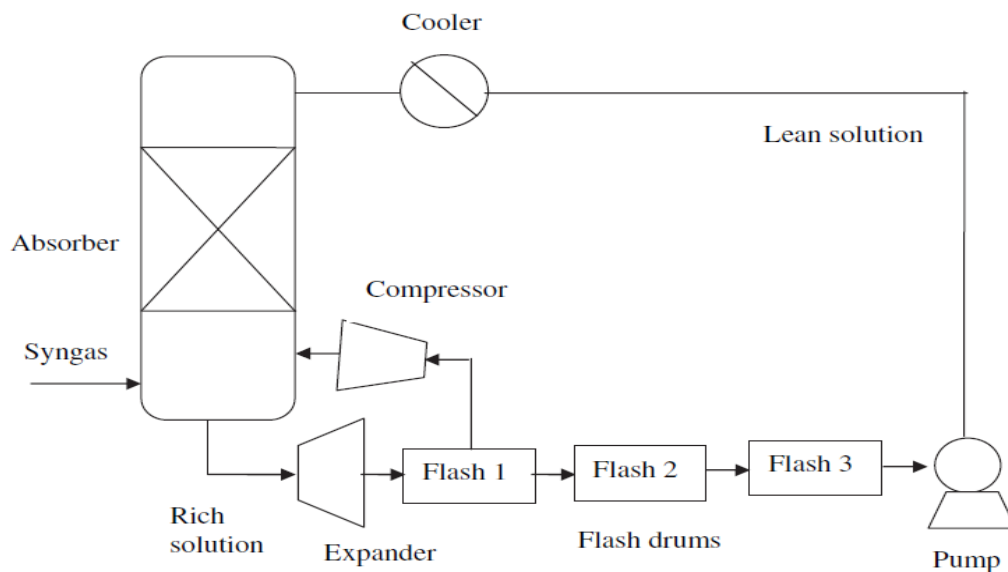


Figure 1.5. Physical absorption to capture CO₂ from syngas.

CO₂ dissolved in the solvent is recovered by reducing pressure in various flash drums. No heat is required to release CO₂ due to the low heat of absorption. After depressurization, pure CO₂ streams are released at different pressures. Some CO₂ capture applications benefit from a mixture of physical and chemical solvents.

1.2.3 Physical adsorption

In contrast to absorption processes which use a liquid absorbent, a solid sorbent is used to bind the CO₂ on its surfaces. Large specific surface area, high selectivity and high regeneration ability are the main criteria for sorbent selection. Typical sorbents include molecular sieves, activated carbon, zeolites, calcium oxides, hydrotalcites and lithium zirconate. The adsorbed CO₂ can be recovered by swinging the pressure (PSA) or temperature (TSA) of the system containing the CO₂-saturated sorbent. PSA is a commercial available technology for CO₂ recovery from power plants that can have efficiency higher than 85% [31,32]. In this process, CO₂ is preferentially adsorbed on the surface of a solid adsorbent at high pressure, which will swing to low pressure (usually atmospheric pressure) to desorb the adsorbent and release CO₂ for subsequent transport. In TSA, the adsorbed CO₂ will be released by increasing the system temperature using hot air or steam injection. The regeneration time is normally longer than PSA but CO₂ purity higher than 95% and recovery higher than 80% can be achieved [33]. Operating cost of a specific TSA process was estimated to be of the order of 80–150 US \$/ton CO₂ captured [34]. Finally, the use of residues from industrial and agricultural operations to develop sorbents for CO₂ capture has attracted significant attention to reduce the total costs of capture [35–38].

1.2.4 Cryogenic distillation

Cryogenic distillation is a gas separation process using distillation at very low temperature and high pressure, which is similar to other conventional distillation processes except that it is used to separate components of gaseous mixture (due to their different boiling points) instead of liquid. For CO₂ separation, flue gas containing CO₂ is cooled to desublimation temperature (-100 to -135 °C) and then solidified CO₂ is separated from other light gases and compressed to a high pressure of 100–200 atmospheric pressure. The amount of CO₂ recovered can reach 90–95% of the flue gas. Since the distillation is conducted at extremely low temperature and high pressure, it is an energy intensive process estimated to be 600–660 kWh per ton of CO₂ recovered in liquid form [39]. Several patented processes have been developed and research has mainly focused on cost optimization [40,41].

1.2.5 Chemical looping combustion

Chemical-looping combustion (CLC), proposed by Richter and Knoche in 1983 [42], divides combustion into intermediate oxidation and reduction reactions that are performed separately with a solid oxygen carrier circulating between the separated sections. Suitable oxygen carriers are small particles of metal oxide such as Fe₂O₃, NiO, CuO or Mn₂O₃. A basic CLC system is shown in Fig. 1.6 [43]. The CLC has two reactors, one each for air and fuel. The oxygen carrier circulates between the reactors. In the air reactor, the carrier is oxidized by oxygen according

to reaction (1.1). In the fuel reactor, the metal oxide is reduced by the fuel, which is oxidized to CO₂ and H₂O according to reaction (1.2).

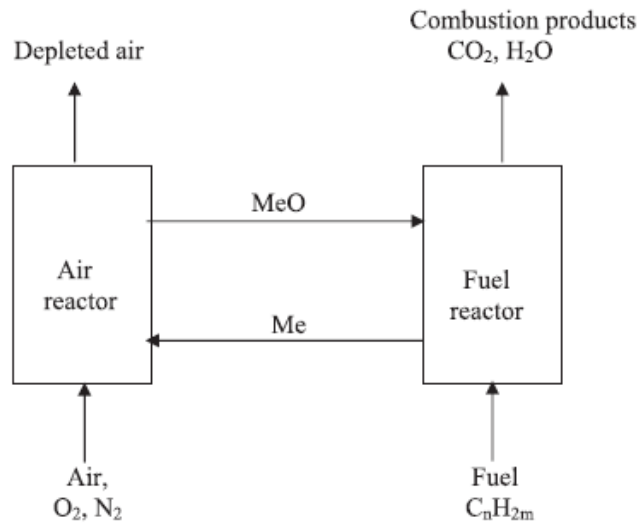
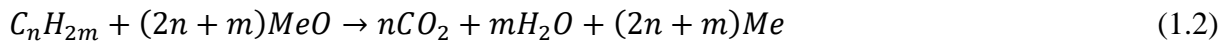


Fig. 1.6. Chemical-looping combustion.



The amount of energy released or required in the reactors depends on these two reactions, as well as the temperature of reactions. CLC has several advantages compared with conventional combustion. The exhaust gas stream from air reactor is harmless, consisting mainly of N₂. In a well-designed system, there should be no thermal formation of NO_x since the regeneration of oxygen carrier takes place without flame and at moderate temperatures. The exhaust gas from the fuel reactor consists of CO₂ and H₂O. Separation of CO₂ can be done by a condenser, a major advantage with CLC which avoids the huge energy penalty necessary in traditional amine-scrubbing process to capture CO₂, and thus leads to less operational cost. Research in metal oxide air separation is focused on cost and the physical and chemical stability of the oxygen carriers over many cycles. The particles usually consist of a reactive oxide and a supporting inert oxide. While various oxygen carrier particles are under consideration, copper, iron, manganese and nickel are the most promising reactive metals [44]. No large-scale demonstration has been performed but models predict that a power system utilizing metal oxide air separation has significant advantages. The lower irreversibility associated with the regeneration step relative to conventional combustion add to the already low energy requirement of the inherent separation of CO₂ from nitrogen. Brandvoll and Bolland [45] reported that the resulting overall energy penalty could be as low as 400 kJ/kg CO₂ for a natural gas combined-cycle plant, assuming idealized chemical stability of the oxygen carrier.

1.2.6 Hydrate-based separation

Hydrate-based CO₂ separation is a new technology by which the exhaust gas containing CO₂ is exposed to water under high pressure forming hydrates. The CO₂ in the exhaust gas is selectively engaged in the cages of hydrate and is separated from other gases. The mechanism is based on the differences of phase equilibrium of CO₂ with other gases, where CO₂ can form hydrates easier than other gases such as N₂ [46]. This technology has the advantage of small energy penalty (6–8%) [5] and the energy consumption of CO₂ capture via hydrate could be as low as 0.57kWh/kg-CO₂ [46]. Improving the hydrate formation rate and reducing hydrate pressure can improve the CO₂ capture efficiency [46]. Tetrahydrofuran (THF) is a water-miscible solvent, which can form solid clathrate hydrate structures with water at low temperatures. So, the presence of THF facilitates the formation of hydrate and is frequently used as a thermodynamic promoter for hydrate formation. Englezos et al. [47] found that the presence of small amount of THF substantially reduces the hydrate formation pressure from a flue gas mixture (CO₂/N₂) and offers the possibility to capture CO₂ at medium pressures. Recently, Zhang et al. [48] studied the effects and mechanism of the additive mixture on the hydrate phase equilibrium using the isochoric method and confirmed the effect of THF on hydrate formation. US DOE considers this technology to be the most promising long term CO₂ separation technology identified today and is currently in the R&D phase [5,49,50].

1.2.7 Membrane separation

Membranes can be used to allow only CO₂ to pass through, while excluding other components of the flue gas. The most important part of this process is the membrane which is made of a composite polymer of which a thin selective layer is bonded to a thicker, non-selective and low-cost layer that provides mechanical support to the membrane [51]. This method has also been used to separate other gases such as O₂ from N₂, and CO₂ from natural gas. Through the development of high efficient membranes, Audus [52] and Gielen [53] achieved a CO₂ separation efficiency from 82% to 88%. The development of ceramic and metallic membranes [22] and polymeric membranes [54] for membrane diffusion could produce membranes significantly more efficient for CO₂ separation than liquid absorption processes. Brunetti et al. [55] conducted a general review on current CO₂ separation technology using membranes and compared with other separation technologies such as adsorption and cryogenic. It pointed out that the performance of a membrane system is strongly affected by the flue gas conditions such as low CO₂ concentration and pressure, which are the main hurdles for applying this technology. Furthermore, Bernardo et al. [56] revealed that although there are significant developments in gas separation membrane systems, they are still far away to realize the potentialities of this technology.

1.3 CO₂ transport

Once CO₂ is separated from the rest of the flue gas components it needs to be transported to the storage site or to the facilities for its industrial utilization. Whatever the chosen final fate of CO₂, a reliable, safe and economically feasible system of transport is a key feature of any CCS project. Depending on the volumes involved a variety of means of transport may be utilized, ranging from road tankers to ships and pipelines. Pipelines are considered to be the most viable method for onshore transport of high volume of CO₂ through long distances as CCS would likely involve when widely deployed [57]. Pipelines are also the most efficient way for CO₂ transport when the source of CO₂ is a power plant which lifetime is longer than 23 years. For shorter period road and rail tankers are more competitive [58]. In order to optimize the mass/volume ratio CO₂ is carried as dense phase either in liquid or supercritical conditions. Supercritical is the preferred state for CO₂ transported by pipelines, which implies that the pipelines operative temperature and pressure should be maintained within the CO₂ supercritical envelop, i.e. above 32.1 °C and 72.9 atm. [59]. The typical range of pressure and temperature for a CO₂ pipeline is between 85 and 150 bar, and between 13 °C and 44 °C to ensure a stable single-phase flow through the pipeline [60]. The drop in pressure due to the reduction of the hydraulic head along the pipeline is compensated by adding recompression stations. Larger diameter pipelines allow lower flow rates with smaller pressure drop and therefore a reduced number of recompression stations; on the other hand, larger pipelines are more expensive therefore a balancing of costs needs to be considered [60]. Impurities in the CO₂ stream represent a serious issue because their presence can change the boundaries of the pressure and temperature envelope within which a single-phase flow is stable. Moreover, the presence of water concentration above 50 ppm may lead to the formation of carbonic acid inside the pipeline and cause corrosion problems. Hydrates may also form that may affect the operation of valves and compressors. The estimated values of corrosion on the carbon steel commonly used for pipeline's construction can be up to 10 mm/year [60,61]. Currently only a few pipelines are used to carry CO₂ and are almost all for EOR projects. The oldest is the Canyon Reef Carriers pipeline, a 225 km pipeline built in 1972 for EOR in Texas (USA). CO₂ pipelines are mostly made of carbon steel and composed of insulated 12 m sections with crack arresters every 350 m and block valves every 16–32 km. The onshore pipelines are buried in trenches of about 1 m deep. Offshore pipelines in shallow water also need to be deployed in trenches as protection from fishing and mooring activities. Deep water pipelines generally do not need to be buried unless their diameter is below 400 mm [60,62]. The rate of accidents involving CO₂ pipelines is relatively low with a value of 0.30/year for every 1000 km calculated during the period 1990–2001 considered for an overall pipelines extension of 2800 km [63]. The enlargement of the pipelines network leads to an increase in the number of accidents up to 0.76/year for every 1000 km in 2002–2008 calculated over an overall pipeline length of 5800 km [64]. These values are still well below the ones involving pipelines for gas/oil or other hazardous fluids. However, the

current CO₂ pipeline network is far smaller than that for gas/ oil transport, and therefore, the statistical significance of these values is somewhat uncertain. For commercial scale CCS projects an extensive network of CO₂ pipelines needs to be developed. An integrate network, where different sources will merge for their final transport to the storage areas, can reduce the total pipelines length by 25%, but it will require that all sources produce CO₂ stream with the same quality (e.g. pressure, T, water content) before being combined together [61]. When the flow managed through a network of pipelines increases there is an exponential decrease in the cost of transport; models highlight that the cost for transporting CO₂ along a 1000 km pipeline is around 8 USD/ton for a mass flow of 25 MtCO₂/year with a further reduction down to 5 USD/ton if the flow increases to 200 MtCO₂/year [65]. Further cost saving may be achieved from there use of existing gas pipelines but their suitability is to be verified. One of the biggest uncertainties is the effects on the pipelines' integrity of long term exposure to CO₂ fluxes in terms of corrosion and potential brittle fractures propagation due to the sharp cooling of the pipelines in case of leak of supercritical CO₂ [66]. The pipelines have to be periodically monitored to assess their integrity and an accurate fiscal metering system is to be in place to assure the quantification of the stored fluxes. The equipment used for gas/oil pipelines need to be modified to withstand the challenging environment experienced inside a CO₂ pipeline. Poor lubrication capacity of CO₂, high chemical reactivity and high pressure may all affect the performance of both monitoring and metering equipment [67]. Other issues could arise from the trans-national transport of CO₂ and offshore storage due to legal aspects.

1.4 CO₂ geological storage

CO₂ can be stored into geological formations such as deep saline aquifers which have no other practical use, and oil or gas reservoirs. Geological storage is at present considered to be the most viable option for the storage of the large CO₂ quantities needed to effectively reduce global warming and related climate change [68–71]. A typical geological storage site can hold several tens of million ton of CO₂ trapped by different physical and chemical mechanisms [72]. Suitable geological sites for CO₂ storage have to be carefully selected. General requirements for geological storage of CO₂ include appropriate porosity, thickness, and permeability of the reservoir rock, a caprock with good sealing capability, and a stable geological environment [73]. Requirements such as distance from the source of CO₂, effective storage capacity, pathways for potential leakage and in general economic constrains may limit the feasibility of being a storage site. Bachu [74] described the criteria and approaches for selecting suitable geological sites for storing CO₂, including the tectonic setting and geology of the basin, its geothermal regime, hydrology of formation waters, hydrocarbon potential and basin maturity. In addition, economic aspects related to infrastructure and socio-political conditions will also affect the site selection. Furthermore, although techniques for geological storage can be derived from existing

processes, mostly enhanced oil recovery (EOR) projects, there is no real experience yet at commercial scale, and the potential long term environmental effects of large amounts of CO₂ stored is also limited. Three different geological formations are commonly considered for CO₂ storage: depleted (or nearly depleted) oil and gas reservoirs, unmineable coal beds, and saline aquifers. Deep ocean storage is also a feasible option for CO₂ storage although environmental concerns (such as ocean acidification and eutrophication) will likely limit its application. It has been shown that CO₂ storage potential can reach 400–10,000 GT for deep saline aquifers compared with only 920 GT for depleted oil and gas fields and 415 GT in unmineable coal seams [75]. Different geological settings have different criteria of consideration for their reliability as CO₂ storage areas.

1.4.1 Enhanced Oil Recovery (EOR)

CO₂ can be injected into depleted (or nearly depleted) oil/gas reservoirs to increase their pressure and provide the driving force to extract residual oil and gases, while the injected CO₂ remains stored there permanently. Up to 40% of the residual oil left in an active reservoir can be extracted after primary production [76]. In fact, fluids injection methods have been widely used in the oil and gas extraction industry for decades to enhance the recovery of the residual oil and gases. Therefore, there is an economical incentive for injecting CO₂ (recovered from an associated capture process) into depleted oil and gas reservoirs in order to offset the high CCS cost commonly involved in the process. Technologies for injection of CO₂ for EOR are mature and there are studies on various aspects of EOR, such as migration simulation [77,78], geochemical modeling [79,80], and leakage/risk assessment [81]. Several EOR projects for CO₂ storage are ongoing. The large stone is the Weyburn project that started in 2000 in the Weyburn oil reservoir in Saskatchewan, Canada. Although the aim of the project is not to investigate the potential for CO₂ storage, the reservoir is estimated to be able to store more than 30 million ton of CO₂ captured from a gasification plant in North Dakota, USA and transported to the site through a 320 km pipeline. A number of larger EOR projects with much larger storage capacity are planned (such as Hatfield and California DF2) and will be commissioned in the next few years. This will build confidence in operators for the feasibility of larger CO₂ storage demonstration projects.

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Chapter 2

Risk analysis

Nowadays, environment and safety constitute two equivalent terms of a duo considered the base for a sustainable equilibrium or, more in general, for the anthropic activity. The problems linked with safety and environmental impact of the process industry are becoming more and more crucial to obtain a correct and sustainable advancement of the industrial society. In this context, risk analysis is becoming a fundamental tool to deal with that issues.

2.1 Introduction to Risk Analysis

The term “risk” (R) is a probabilistic quantity defined as the product between occurrence frequency of an undesired event (f) and the damage magnitude (M):

$$R = f * M \quad (2.1)$$

which is different from the common meaning given to “danger” that is an intrinsic property. As we can see from (2.1), a risk could be large when it refers to frequent events with modest consequences, but also when it refers to seldom events but with catastrophic consequences. This distinction is important in the risk reduction phase, in fact it is possible to limit the risk of accidental events through the realization of preventive measures, namely reducing the probability that an accident occurs, otherwise applying protective measures, that is mitigating the consequences. A simple diagram of the conceptual points of the risk analysis is reported in the Figure. 2.1:

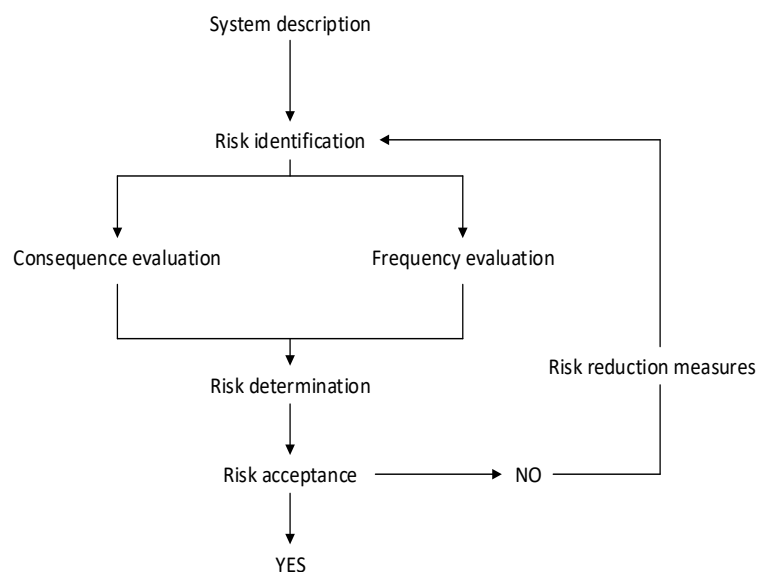


Figure 2.1. Risk analysis conceptual diagram

The frequency and magnitude study occurs in a distinct and independent manner; it is their combination which gives a certain risk. Although, while adopting all the possible interventions, it is not possible to achieve a zero-risk situation, but there always be a risk called residue which have to be managed and controlled. In order to perform a risk analysis in a plant, two different groups of methods could be used: qualitative one and quantitative one. Both of them are necessary, the first kind of methods are less accurate but cheaper: these usually are used to find out the most critical part of the plant. The second kind of methods that are more accurate but expensive are applied on the results came from the qualitative methods. The accidents historical analysis, Hazop, FTA and ETA are the techniques applied in this work to accomplish the risk analysis, that are going to be described in the following.

2.2 Accidents historical analysis

This is a qualitative method based on the collection of all the accidents that are “similar” at the supposed one, happened:

- In the same place;
- In similar plants;
- Regarding the same type of substances;
- In similar climate conditions.

Several databases are available (ex. MHIDAS, ARIA, EGIG, CONCAWE, WOAD). They are essential for this technique: they have to be detailed at the right point, have a significant number of gathered events and contain quasi-accidents too. This hazard identification method permits to apply the lessons learnt from accidents occurred in the past, a really good advantage in terms of risk prediction. On the other hand, weak points arise:

- Limited reliability and homogeneity of the sources;
- Limited information regarding root causes and first phases of the development of the scenarios;
- Difficulties in the elaboration of the information at statistical level.

In conclusion, this is a useful tool, but needs to be integrated with more systematic techniques.

2.3 HAZOP (HAZard and OPerability study)

This is a technique which allows the individuation of potential risks and operability issues caused by deviations from the project goals and linked, in particular, to malfunctions during the plant operation. Malfunctions mean not only mechanical failures or equipment breakdowns but also all the phenomena that influence the standard design parameters. The Hazop technique is based on a complete plant description and on the systematic analysis of each part or element; in the Figure 2.2 is summarized the logic procedure. This work is drove by an experts team having lots of experience and with solid bases of risk analysis.

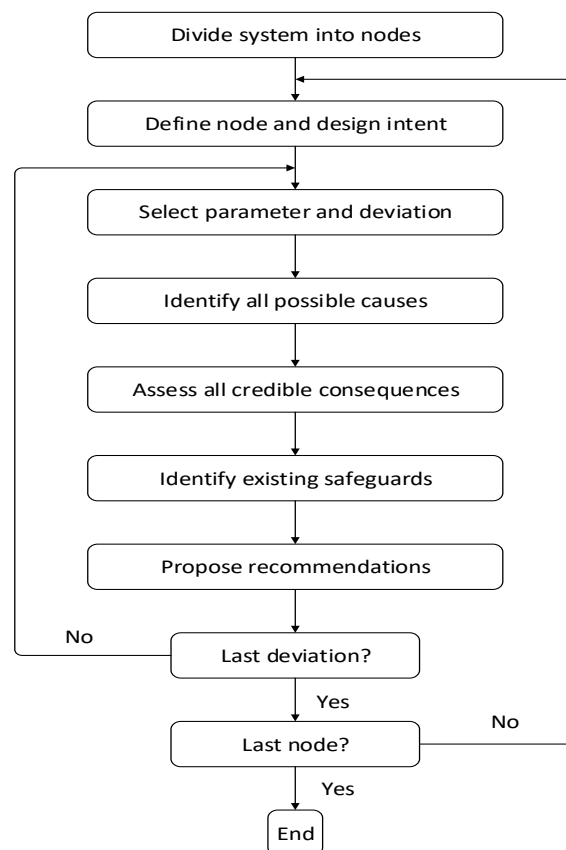


Figure 2.2. Methodology of HAZOP

A typical team for Hazop evaluation include:

- Chairman (safety engineer);
- Scribe (safety engineer);
- One representatives of each discipline involved in design (Process, Mechanical, Control and Instrumentation, etc.)
- Representatives of commitment;
- On call basis: other specialists (according to specific issues).

They identify the most critical points (nodes) with the aim of foresee accidents that would never be found out from the historical analysis.

There is also the need of a big amount of information regarding all plant aspects:

- Process Flow Diagram (PFD);
- Piping & Instrumentation Diagram (P&ID);
- Lay-out;
- Chemical hazard data;
- Blowdown and venting systems;
- Other specific documentation.

The study is founded on the use of guide words coupled with the most important process parameters and permits to identify the possible accidents with the consequent creation of the fault tree; the guide words summary is presented in Table 2.1.

Table 2.1. *Guide words of Hazop*

Guide words	Meaning	Comments
NO, NOT, NONE	The complete negation of the intention	No part of the design intention is achieved, but nothing else happens.
MORE, HIGHER, GREATER	Quantitative increase	Applies to quantities such as flowrate and temperature and to activities such as heating and reaction.
LESS, LOWER	Quantitative decrease	Applies to quantities such as flowrate and temperature and to activities such as heating and reaction.
AS WELL AS	Qualitative increase	All the design and operating intentions are achieved along with some additional activity, such as contamination of process streams.
PART OF	Qualitative decrease	Only some of the design intentions are achieved, some are not.
REVERSE	The logical opposite of	Most applicable to activities such as flow or chemical reaction. Also applicable to substances, for example, poison instead of antidote.
OTHER THAN	Complete substitution	No part of the original intention is achieved – the original intention is replaced by something else.
SOONER THAN	Too early or in the wrong order	Applies to process steps or actions.
LATER THAN	Too late or in the wrong order	Applies to process steps or actions.
WHERE ELSE	In additional locations	Applies to process locations, or locations in operating procedures.

The plant is divided into cells with entrance and exit and the process/plant behavior is analyzed with the variation of properties like temperature, pressure, flowrate, level, composition, etc. It permits to obtain a logic-probabilistic analysis for the identification of the most critical points of the plant and the determination of the expected frequencies. To conclude, it has to be said that this is a powerful tool, but time consuming due to the large amount of details of the analysis that have to be taken into account.

2.4 FTA (Fault Tree Analysis)

Once the possible failures and the relative consequences have been identified, in a qualitative way, it can go on with the quantification of their damage; this means give the frequency and magnitude evaluation. The FTA is a graphical representation of the different logic relations between the system components damages, human errors, failure mechanisms or whatever other cause which contributes to generate relevant accidents permitting additionally, thanks to data regarding the failure rate, to quantify the occurrence probability. It starts from a *Top event* (accidental event with unwanted consequences) and ends to the origin. It has to be considered each cause that has been found as a new consequence; the method is repeated until the elementary causes have been identified. The FTA construction permits a qualitative evaluation, concerning the elementary causes individuation which determine the unwanted event, and a quantitative evaluation, which consists in calculating the occurrence frequency of that *Top event*. The various base events are in relation each others through logic operators and with a defined symbology, presented in the Figure 2.3.











Symbol	Name	Description
<i>Primary Event Symbols</i>		
	Circle	Basic Event – a basic initiating fault requiring no further development
	Oval	Conditioning Event – specific conditions or restrictions that apply to any logic gate (used with INHIBIT gate)
	Diamond	Undeveloped Event – an event that is not developed further because it is of insufficient consequence or because information is unavailable
	House	External Event – an event which is normally expected to occur (not a fault event)
<i>Intermediate Event Symbols</i>		
	Rectangle	A fault event that occurs as a result of the logical combination of other events
<i>Gate Symbols</i>		
	OR Gate	The union operation of events, i.e. the output event occurs if (at least) one or more of the inputs occur
	AND Gate	The intersection operation of events, i.e. the output event occurs if and only if all the inputs occur
	INHIBIT Gate	The output event occurs if the (single) input event occurs in the presence of an enabling condition (i.e. Conditioning Event (oval) drawn to the right of the gate)
<i>Transfer Symbols</i>		
	Triangle-in	Indicates that the tree is developed further someplace else (e.g. another page)
	Triangle-out	Indicates that this portion of the tree is a sub-tree connected to the corresponding Triangle-In (appears at the top of the tree)

Figure 2.3. Symbology of the FTA

Every equipment part has a failure frequency, which represents how many failures occur in a defined period of time: for example, a failure frequency of $3.6e-7 \text{ years}^{-1}$ means that there will occur 3.6 failures in 10,000,000 years. These values are means taken from failure distribution curves. Now a brief and simple FTA example is made in Figure 2.4.

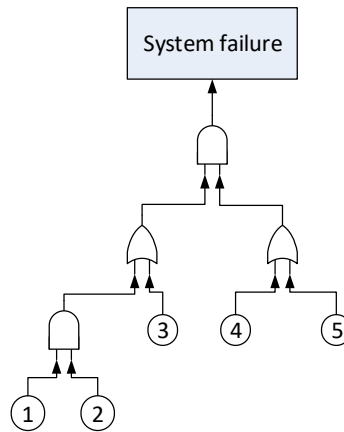


Figure 2.4. FTA example. All the failures are linked together only through “and” and “or” gates.

It can be seen that for the failures 1 and 2 there is an “and” gate, which means the event will verify only if both failures occur. For the failures 4 and 5 it is different, because they are linked together with an “or” gate, meaning that the event occurs only if at least one of the failures will verify.

$$\text{Event probability} = [(1 * 2) + 3] * (4 + 5) \quad (2.1)$$

Once the FTA is built it permits the quantification of failure frequency and Top event frequency with the Boolean algebra. The safety engineer task is to reduce that frequency, by the introduction, for instance, of alarms, indicators, valves, by-pass, etc. in the proper manner and location, until an acceptable value is reached.

2.5 ETA (Event Tree Analysis)

This is a graphical representation which individuates the frequencies and the different scenarios that can occur starting from a given Top event. Its construction and study are made after the FTA, and in a different way, in particular an inductive path is followed: starting from a determined Top event, all the possible scenarios related to it are identified with their occurrence frequencies. This analysis doesn’t demand to postulate a Top event, as in the Fault Tree, but needs to individuate preliminarily all the systems, phenomena and conditions that can influence a phenomenon evolution. Each of these systems, phenomena, etc. constitute a *Node* of the tree, which can have two exits, often indicated with “Yes” or “No”, respectively indicating if the

event occurs or not. At every exit, an occurrence probability is associated, which can be also calculated with the FTA application. In an overall analysis, these two techniques are complementary. An example of the event tree is in the Figure 2.5.

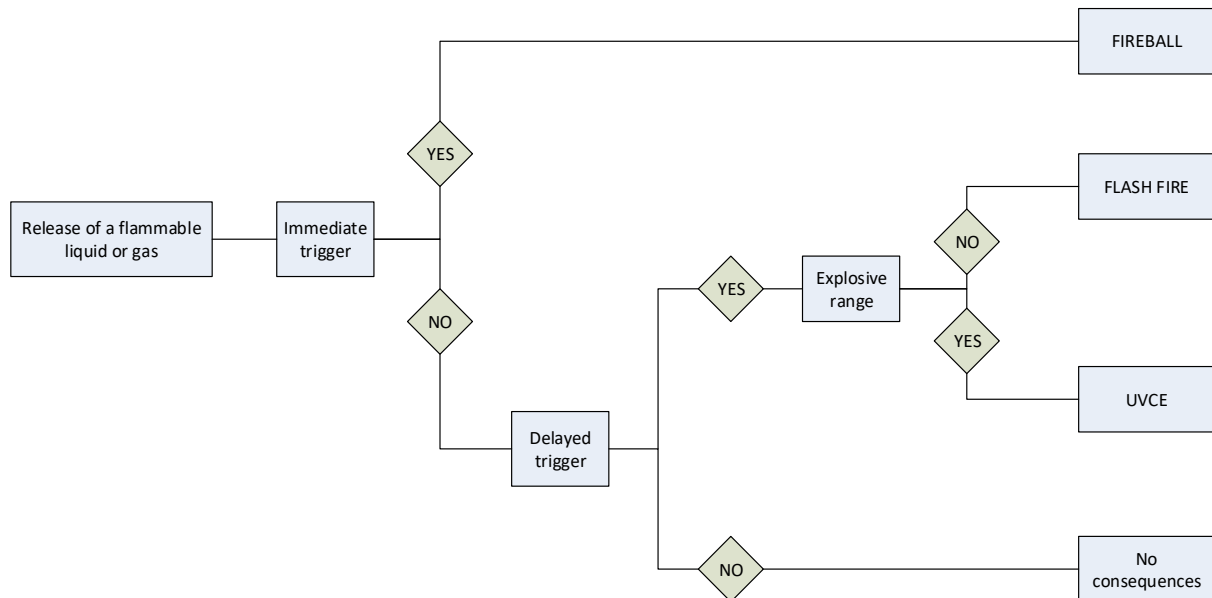


Figure 2.5. ETA example

The ETA can be used to study the failure combination of components which lead to different possible failure and operating conditions of the system; it is commonly used, however, for the definition and calculation of the scenario probability which can derive from the same starting point. The tree nodes are made up of phenomena like the immediate or delayed ignition, the occurrence of different weather conditions, the protection or mitigation systems intervention etc. When the FTA and ETA are included together, they form the so called *Bow-tie Diagram*.

Chapter 3

Accidents historical analysis

In order to improve the CCS best practices, it was performed an accidents historical analysis with the objective of find all the industrial accidents happened involving all the substances which can be used in the capture section of a CCS plant. There are a lot of flammable and toxic chemicals that can be encountered in this type of plant, and the amount required is great too, due to the large flue gas flowrate. At the end, the most disastrous events will be useful to detect the potential most dangerous substance.

3.1 Accidents historical analysis

Between all the phases of CCS processes, the focus of this work is on the capture section and its relative technologies (chemical absorption, physical absorption and adsorption, cryogenic distillation, chemical looping combustion and hydrate-based separation); transport and storage are not considered. The carbon capture, as seen in the Chapter 1, can be done with a wide range of techniques, exploiting all the various physical and chemical phenomena. The choice of a suitable technology relies on the characteristics of the flue gas stream, which depends mainly on the power-plant technology. The list of substances which can be used for the carbon capture was served to address the research; the accidents found are listed in the following paragraphs.

3.1.1 Accidents regarding CO₂

- Date: 2008;

Dead:0;

Hospitalized:19;

Description: approximately 15 tons of CO₂ was accidentally released from a fire extinguishing installation in Monchengladbach, Germany. Due to coincidental failure of door seals, the released CO₂ was not contained by the building and it spreads outside where there were very still air conditions. There were no fatalities from the incident but 107 people were intoxicated, 19 of whom were hospitalized [1].

3.1.2 Accidents regarding MEA (monoethanolamine)

- Date: 23/07/1984;
Dead:17;
Hospitalized:22;

Description: a vapor leak was noticed on a vessel, precisely from an amine absorber removing H₂S from acid stream, pressured. Refinery workers, including the outside operator and an assistant outside operator, unsuccessfully attempted to by-pass the vessel and to depressurize it. The leak in the vessel wall had spread around the entire 8 feet circumference of the vessel and it erupted like a missile. The top 45 feet of the vessel was lifted by the vapor cloud. The bottom 10 feet of the vessel stayed intact on the ground. The eruption of the vessel released a massive vapor cloud which ignited, causing a fire ball. This explosion engulfed much of the refinery in flames. Firefighters from the Union Oil Fire Brigade responded immediately with the company's two engines, followed closely by the Romeoville Fire Department. As a result of the explosion, many towers, tanks, and other refinery structures began to rupture or collapse and the site's fire hydrant system was damaged. So, firefighters were forced to draft water from a nearby sanitary canal. They were just beginning to attack the flames when a tank containing LPG erupted. The explosion created a huge fireball that rose thousands of feet into the air. Several members of the Union Oil Fire Brigade were caught in the blast. Once the burning structures were isolated, fire officials determined that allowing the fires to burn out on their own was the safest way to extinguish the blaze. The cause of this incident was the presence of cracks in the vessel walls [2].

3.1.3 Accidents regarding NH₃ and (NH₄)₂CO₃

- Date: 21/02/1991;
Dead:0;
Hospitalized:0;

Description: the accident occurred in one of the two glass lined storage tanks, 35 m³ capacity each, holding the recirculated acid solution (about 29% of sulfuric acid) used to absorb the residual ammonia from the gaseous effluents of the phtalocyanines process unit. This solution was enriched with ammonium carbonate coming from the ammonia treatment unit. The pH of the solution was manually controlled once per shift and adjusted if necessary by adding sulfuric acid solution so that the pH was maintained within the slightly acidic range (5 to 6). The solution's pH was periodically checked (every 8 hours) by an operator. When the accident occurred, the operator realized too late that the ammonium sulfate and ammonium carbonate solution was becoming basic and suddenly added a 60% sulfuric acid solution to it. This resulted in an abnormal

production of carbon dioxide that over pressurized the tank which exploded because of inadequate pressure relieving capacity (the hydraulic trap with which the tank was equipped was not sufficient to withstand the peak pressure generated). The collapse of the tank caused the release of the solution (about 20 m³), which was partially recovered in the containment basin of the 2 glass lined tanks and partially in the yard. The rest of the solution was collected, through the sewer network, in the emergency basin of ACNA [3].

- Date: 29/07/2012;

Dead:0;

Hospitalized:6;

Description: the detailed course of the accident was as follows: about 7:00 a.m., after regular check of the installation, a worker reported to his supervisor emission of the process solution (containing ammonium carbonate). The emission occurred in the upper part of the exchanger. The person responsible for maintenance works was called in deal with the damage. In the meantime, the affected exchanger was being prepared for the examination and repair. The exchanger was washed with water. This task involved opening and closing the proper valves on a pump and injection of water. After the exchanger had been washed, the process solution was added to the installation but with omitting the damaged exchanger. This allowed the maintenance staff to remove the isolation of the exchanger in order to examine it. After the examination of the exchanger was performed, it was decided that leakage would be temporary stopped with a caulker band. In order to do this, the internal rescue unit was called. They noticed punctual leaks in a few places. Before they started sealing operation it was decided to wash the exchanger again (doing this twice, in the same way as for the first time). While the caulker band was installed inside the exchanger there was water at a low pressure. After installation of the band it was decided to check the tightness using water. It appeared that it was not tight enough because water was leaking. The worker closed one valve to stop the water flow. At the same time, he also opened another valve allowing the process solution to get into the system. The other worker, not being aware that process solution was being injected, thought the tightness tests were going on so he cut (with the valve) the flow of the process solution. This caused the process solution to go the broken exchanger. Suddenly, the upper part of the exchanger ruptured causing the emission of the process solution. Due to its evaporation, toxic cloud was formed. One worker fell down because of the gust that appeared. The other five workers were intoxicated. All of them were injured and taken to the hospital. The analysis of the course of the accident showed that together with the emission of ammonium carbonate also ammonia was released, most probably from the absorption column due to the fact that one valve was partially opened [4].

- Date: 08/05/1991;
Dead:0;
Hospitalized:0;
Description: as a small leak was observed in a valve packing joint, it was tightened causing the valve insertion point to rupture. The attempt to isolate the valve was unsuccessful as two other valves could not be closed. A large amount of ammonia could escape through the broken valve. The fire brigade intervened using protective clothing. The accident occurred during normal operation of an ammonia plant in a food additives industry. The component involved was a valve on an ammonia pipeline operating at 2 bar and at a temperature of -10°C [5].
- Date: 01/06/1992;
Dead:0;
Hospitalized:0;
Description: the ammonia pipes leaked due to a faulty screw connection. Material defects caused damage in the screw connection. Liquid ammonia in the pipes was at constant pressure of 1.2 MPa [6].
- Date: 19/04/1996;
Dead:2;
Hospitalized:0;
Description: two workers of a subcontractor (external company) were performing the repair (maintenance) of an engine throttle valve for the level control of a spherical tank. During the repair the spindle was pushed out of the fitting. Liquid ammonia was released with 14 bars through the section of the opening [7].
- Date: 16/06/1997;
Dead:0;
Hospitalized:6;
Description: while carrying out repair works, one staff member of a construction company damaged an underground ammonia pipeline with a concrete cutting apparatus. This caused a release of liquid ammonia through the breach [8].
- Date: 04/01/2005;
Dead:1;
Hospitalized:0;
Description: during the morning, it was foreseen to raise the ammonia level in the ammonia storage tank to a perceivable level by pumping cold ammonia through a drain pipe. As preparation of this operation the injection of cold ammonia on the tank head was interrupted and a refrigerant compressor was started. In the context of this operation at 11:05 a.m. the tank drainage valve, used as intake, was completely opened while the valve on the other end of the drain pipe was opened to $\frac{1}{4}$. During this operation, a worker

was staying on a platform at 3 m height, whereas another worker was standing below the platform. Both workers were permanently in contact over radio with the control room. Both workers heard an unusual noise after opening the valve of the drainage pipe. The worker on the platform closed the drain valve of the tank a few seconds after and left the platform over an access ladder. The control room operator noticed approximately at the same time a rapid pressure increase in the tank. In that moment 11:10 a.m. a loud bang occurred with the sudden release of ammonia gas which dispersed around against the wind [9].

- Date: 24/09/1996;

Dead:0;

Hospitalized:11;

Description: the release occurred due to a valve opened in error. The release occurred in an installation for the dilution of anhydrous ammonia into a 10% ammonia solution employed in order to limit (reduce) the corrosion during the distillation of crude oil. This release occurred on one (or two) 1/4 turn valves isolating the dissolving column from a tank of 7 cubic meters of capacity (containing 3.8 tons of liquefied ammonia under 8 bars of pressure at the time of the accident) [10].

- Date: 06/07/1989;

Dead:2;

Hospitalized:5;

Description: at 3:30 p.m. the crankcase of an Uraca horizontal action 3 throw pump, used to boost liquid ammonia pressure from 300 psi to 3400 psi, was punctured by fragments of the failed pump-ram crankshaft. The two operators investigating the previously reported noises from the pump were engulfed in ammonia and immediately overcome by fumes. Once the pump crankcase was broken, nothing could be done to prevent the release of the contents of the surge drum (10 tons were released in the first three minutes). The supply of ammonia from the ring main could only be stopped by switching off the supply pump locally. The crankshaft of the Uraca pump failed catastrophically smashing itself through the crankcase. Failure of the crankshaft was due to the propagation of a fatigue crack through the web separating the first and second crank pins. Metallurgical investigations found no initiating defect leading to crack propagation. It is thought that the failure was due to some overload of the web/crank pin radius at some unknown time. No inspections were foreseen for this component. The pump design was not adequate [11].

- Date: 07/07/1989;

Dead:0;

Hospitalized:0;

Description: a storage tank for aqueous ammonia solutions was up for maintenance (replacement of the bottom part). The tank got a new bottom on Wednesday (05/07/89) and was replaced Wednesday evening. After mechanical completion of the replacement work, the Thursday evening a trial had been undertaken to fill the tank up, but overpressure was registered in the tank and also the flange connecting the feeding line to the tank leaked. Consequently, the filling operation was stopped. The problems were reported to the maintenance department, the flange connection was repaired and the pressure relief line checked. The trial to fill the tank was not reported to the shift supervisor. A shift change took place and the supervisor recorded in the production log-book that the tank was empty. The next day (Friday 07/07/89) a safe work permit was issued by the supervisor of the next shift to the mechanics to disconnect the piping associated with this tank for further repair. The repair work proceeded and during the grinding of a disconnected pipe, a mechanic noticed a whistling sound and hid, together with the 3 others mechanics, behind a concrete tank farm wall. Soon afterwards, the tank exploded. The top of the tank was blown over an adjacent manufacturing building, landing at the grass-strip between the adjacent building and the office-buildings and struck into another office building (approximately 60 meters away) which was empty. The ammonia vapors/air explosive mixture formed in the storage tank after the trial was probably ignited by the grinding of the disconnected pipe. The pressure relief lines also failed to operate as expected but from the Original Report is not fully clear if it was caused by a wrong component design or not [12].

3.1.4 Accidents regarding Selexol (dimethyl ether of polyethylene glycol)

- Date: 01/09/1993;

Dead:0;

Hospitalized:4;

Description: the accident occurred in a plant producing synthesized active ingredients for the pharmaceutical industry. An explosion and a fire occurred in one of the workshops of the plant. At 6:30 a.m. the operation started, 30 min before shift end. At 6:45 a.m. the temperature threshold was reached, the operators started to cool the reactor (it contains aluminum trichloride anhydrous, sodium tetrahydroborate, imide, dimethyl ether triethylene glycol) in order to maintain the temperature around 65°C but the reaction ran away causing temperature and the pressure rise in the vessel. The operator nearest to the reactor smelled an unpleasant odor: through the sight glass he saw a glow preceding the explosion. Employees at 15 m distance perceived a blow. A flame

projected through the workshop, other flames shot out from a joint and other damaged connections of the reactor. Employees outside the building perceived a blow just before the explosion. A flame several meters high was visible for some seconds at the exit of a chimney connected with the reactor rupture disk (calibrated at 0.5 bar) that burst, allowing the decompression of the reactor [13].

3.1.5 Accidents regarding Rectisol (methanol)

- Date: 25/09/1981;
Dead:0;
Hospitalized:6;
Description: during normal operation, there was an unexpected and unwanted formation of methyl nitrate in a vessel for collecting chlorine residuals, which was collecting also methanol. Probably this has been caused by the introduction of hydrogen chloride contaminated with methanol in the electrolysis system. The explosion in the vessel caused a break in the pipe connecting it to the chlorine condensation plant, and hence a partial evaporation on the contents followed. The plant was shut-down and the population outside the establishment was alerted [14].
- Date: 08/09/1982;
Dead:0;
Hospitalized:0;
Description: an unintentional spillage of methanol into an electric cable way caused a short-circuit which ignited the flammable liquid resulting in a large fire. The operators were able to leave the site of the fire. The population external to the establishment was alerted and preparations for an extended evacuation were initiated [15].
- Date:15/03/1993;
Dead:1;
Hospitalized:1;
Description: on a alcoholysis band (rubber transport-band) took place an explosion through the open inspection valve air arrived in the band-case, which together with the existing vapors (methanol and methyl acetate, about 25 kg) created an explosive mixture. The releasing ignition spark arose obviously in the cutter, that is directly connected to the band and that during the inspection was on duty. Due to the explosion, the shift leader died and the department head was injured. Immediately after the explosion got into fire the rubber-transport-band, part of the facing building front and the asphalted tar paper. The firemen brought the fire under control. The quenching water was collected in a vessel of the biological clarification plant, but about 7 kg of methanol arrived in the nearby river. Due to the explosion, the polymerization from polyvinyl acetate should be interrupted. Emergency disconnection caused a rupture of the rupture-

disk and of the vessel which in turn provoked the escape of a mixture (1000 kg) of methanol and polyvinyl acetate circa 250 kg, leaked mixture flowing over the roof of the installation. The fire brigade ordered as a precaution the evacuation of the installation and of the neighboring buildings. Dioxin analysis showed the usual values in burnt components [16].

- Date: 07/11/1998;

Dead:0;

Hospitalized:0;

Description: due to a leak in a container, the release of substances caused a fire in an experimental fatty acid methyl esters production plant (causes are unknown). After the leak had been discovered, at 11:50 a.m. the shut-down of whole plant (the container's stirring system and the pumps) was initiated, and the valves were closed. At 12:02 p.m. the shut-down was complete. At 12:34 p.m., a fire involving the leaking container was noticed. The fire brigade was informed, the emergency plan was activated, extinguishing operations started with the help of transportable firefighting gear. At 12:47 p.m., the disintegration of the tank and a release of flammable material into the plant hall could be observed from the control room. The smoke production became more intense and a major fire developed. The fire brigade's main concern was cooling the methanol tank and a roof. The extinguishing operations were concluded at 4:00 p.m., but had to be started again at 5:00 p.m., and went on, with several pauses, until the late evening [17].

- Date: 12/02/1985;

Dead:0;

Hospitalized:4;

Description: while two operators were charging fiber drums of a penicillin material into a reactor containing a mixture of acetone and methanol, an explosion occurred at the reactor man-hole. The two operators were blown back by the force of the explosion. They were covered with a wet burnt powder. Two other operators, who were opening the drums 2 meters away, were also blown back and covered with wet powder. Subsequently, all four operators were drenched under emergency showers. They suffered superficial burns to the hands and face and spent one night in a local hospital. They suffered no side-effects. Investigations showed that the incident was initiated by the ignition of solvent vapors, which resulted in a dust explosion of the dry powder. The solvent mixture in the reactor did not ignite. Tests carried out on the polyethylene liners inside the fiber drums showed they were earthed to the reactor at the time of the explosion but they were of the non-conducting type. The most probable cause of the ignition was an electrostatic discharge from the polyethylene bags during the reactor charging. The underlying causes were inadequate process analysis and design plant,

together with a lack of safety culture, that allowed to operate with the risk of a dust explosion [18].

- Date: 15/05/1987;

Dead:4;

Hospitalized:1;

Description: taking also into account witnesses who heard a first big explosion and a few seconds later two other more suffocated explosions, it was deduced that most likely the empty tank No 43 exploded first causing the explosions of tanks No 44 and 45. The explosions of tanks No 44 and 45 were followed by the fire of the contained methanol. Tank No 42 was also partially damaged because of the explosion of the adjacent No 43: it was still emitting hexane vapors during the inspection. Probably the explosion was caused by the ignition of a mixture of residual methanol vapors with air formed during the degassing operations of tank No 43 (it was degassed with air in order to recover nonane). According to Carmagnani's officials the tank's cleaning was considered a routine operation: depending on the substances to remove, water or air were used for cleaning purposes. In case of purging with water, washing water gathered by a draining system was conveyed to a waste-water treatment plant. In case that two incompatible substances had to be loaded subsequently into the same tank, purging with air was used (air was pumped in the vessel through a man-hole and was discharged from other openings). This situation occurred for tank No 43 because methanol residues were considered incompatible with nonane that had to be stored. All purging operations were normally carried out without neither nitrogen protection nor by monitoring the surrounding environment for the presence of flammable gases. No fixed explosimeter or smoke detectors were installed but the operators could make use of portable explosimeters and personal protection devices (breathing apparatuses, filters, masks). The first aid room was equipped with stretches and medical supplies and fire extinguishers were placed as laid down under the Fire Brigade's Regulations [19].

3.1.6 Accidents regarding cryogenic distillation

- Date: 07/06/1996;

Dead:0;

Hospitalized:0;

Description: during the start-up phase of the cryogenic unit a separator exploded, releasing ethane, ethylene, methane and hydrogen. The bursting of a tank was caused by a 1600 mm long incipient crack which had been formed at the inside of the tank along a weld line (a ferritic basis metal had been welded with an austenitic weld metal). The hydrogen induced incipient crack that was caused by the alternating load during start-up and shut-down phases in the course of the operating time. This hydrogen

induced cracking has been originated by the geometric form variation and the resulting plastic deformation in the area of the damaged longitudinal weld. This incipient cracking was favored by the high tensile strength of the austenitic weld metal with its particularly accentuated martensitic composite area along the transition between weld metal and basis metal and was also favored by its physical characteristics which differ strongly from the basis metal. There was possibly a lack of maintenance [20].

- Date: 21/09/2003;

Dead:0;

Hospitalized:1;

Description: on September 21th, at about 7:30 a.m., the Isotec on-call system operator received an automatic pager alert indicating an alarm condition in a cryogenic nitric oxide (NO) distillation unit. Arriving at the facility at about 7:50 a.m., he observed reddish-brown gas venting from the distillation unit vacuum pump exhaust - which indicated a breach in the column piping within the vacuum jacket. Nitric oxide - a toxic gas - was venting to the atmosphere and reacting with air to form nitrogen dioxide (NO₂), also a toxic gas. The responding employee immediately notified his supervisor, who called the 911 dispatcher. Isotec management and Sigma-Aldrich, the parent company of Isotec, were then notified. The reddish-brown gas cloud was observed drifting southwest from the site and slowly dissipating. By 8:15 a.m., employees secured the leak by closing the vacuum pump suction valve. Shortly thereafter, the vapor cloud was no longer visible. The operations manager and the other five Isotec employees believed they could safely remove the nitric oxide from the N3 distillation column and vacuum jacket, and proceeded with the necessary preparations. Their position was based on successful application of the same strategy to a column malfunction on September 18, 1998. Distillation column N4 (same design as N3) had developed a NO leak into the vacuum jacket and vented nitric oxide from the vacuum exhaust. While closely monitoring pressure and temperature, operators successfully emptied the nitric oxide from the column and vacuum jacket. Once the September 21 leak was secured, personnel began installing temporary tubing to empty the nitric oxide in the malfunctioning column. Concurrently, they closely monitored the pressure inside the column, which was behaving as in 1998 when column N4 leaked nitric oxide. The pressure stabilized at no more than 130 pounds per square inch (psi) - well below the vacuum jacket calculated burst pressure of 1645 psi. Isotec personnel noted that the condenser was "vigorously venting nitrogen vapor", which indicated increased heat load in the column. At 10:15 a.m. - with no warning - a violent explosion destroyed the distillation column, the blast containment structure, and nearby buildings. Windows were blown out of the main office building, about 140 feet from the explosion; and glass shards lacerated the hand of an Isotec employee. No other injuries were reported. Small

chunks of concrete and metal shards were propelled as far as 1000 feet and fell on adjacent property. Three houses north of the facility were struck by debris, causing minor damage to two roofs and a picture window. A large steel panel from the blast containment structure struck and dislodged a 52000 - pound gaseous carbon monoxide (CO) storage vessel, pushing it about 10 feet off its foundation. A second steel panel severely damaged adjacent equipment. A ruptured fill line vented CO gas, which then ignited and burned for about 1 hour, until the vessel was empty. As a precaution, the fire department requested that the police evacuate a 1-mile radius to protect the community from metal shards or other debris in the event that the CO vessel exploded. The evacuation order was lifted after 24 hours [21].

- Date: 30/07/2000;

Dead:0;

Hospitalized:0;

Description: an explosion occurred at a specialty gas manufacturing facility in Dayton, Nevada. The plant manufactured small quantities of nitrogen trifluoride (NF₃), a specialty chemical used for etching silicon wafers and for cleaning silicon production equipment in the microprocessor fabrication industry. While the building housing the process was damaged, no personnel were injured. Exponent conducted an engineering investigation of the incident to determine the cause of the explosion, to understand the chemical reactions leading to the incident, and to quantify the explosive energy of the blast. The incident occurred in the last stage of the manufacturing process, inside a distillation column/reboiler assembly that separates residual nitrogen (N₂) and fluorine (F₂) gas from condensed NF₃. A process disruption occurred approximately 90 minutes before the explosion, when the plant received a liquid nitrogen delivery that was significantly colder than the nitrogen already present in the onsite tank. Liquid nitrogen was used as the heat exchange fluid inside the distillation column condenser and the influx of the colder delivery caused sufficient temperature decrease within the column condenser to liquefy fluorine. Analysis revealed that the condensed fluorine reacted with the stainless steel packing material to initiate a localized exothermic event inside the column/reboiler. The hot spot spread and initiated combustion between the stainless steel packing material and the liquid NF₃. The energy released by these exothermic reactions evaporated NF₃ and caused a rapid increase in the temperature and pressure of the column/reboiler contents. The gaseous outflow choked at the column/reboiler outlets and the resulting pressure buildup, estimated at approximately 8000 psi, ultimately failed the reboiler. The total energy yield was low (approximately 1.5 lb-TNT) and no one was injured. However, this incident serves to highlight the care necessary in manufacturing highly reactive fluorinated gases [22].

3.1.7 Accidents regarding NiO

- Date: 21/02/2000;
Dead:0;
Hospitalized:6;

Description: the accident occurred in a foundry. Six persons were injured by the explosion of the furnace. The treatment operation which was being carried out at the time of the accident was the fusion of a batch composed of metals and minerals, in order to obtain alloy ingots. The batch was composed of 836 kg of sand (mainly nickel oxide, silicon dioxide and aluminum), 6690 kg of Fe - Mo - Co - Ni alloy in ingots of 350 kg, 540 kg of ordinary steel and 240 kg of lime. The nickeled sand in the bottom of the furnace did not melt completely; the intense mixing of the metal by the injection of gaseous oxygen helped the nickeled sand rise to the surface. The nickel oxide was deoxidized by passing through the metal; the oxygen thus released combined with the carbon present in the bath and produced large quantities of CO and CO₂ very rapidly. This hypothesis is substantiated by the recording of the gas analyzers; a calculation shows that this reaction produces 73 m³ of CO in a few seconds. The not melted nickel sand in the bottom of the furnace contained a certain quantity of water and gas, held under pressure by a layer of pasty metal. The blast would have been due to the release of these during the fusion operation was an aggravating factor in the number of people injured gases; a calculation shows that this phenomenon generates 8 m³ of steam. The analysis of the causes concludes that the loading method (nickeled sand in the bottom of the furnace) was the origin of the accident [23].

3.1.8 Accidents regarding THF (tetrahydrofuran)

- Date: 03/12/2004;
Dead:1;
Hospitalized:0;

Description: at the end of every week the coating pan of the coating tower was to be cleaned. Normally this is done using scraping knives. However, it is easier to clean the pan if the pan is soaked in solvent for some time. For this purpose, methyl ethyl ketone (MEK) can be tapped into safety cans. A second solvent, tetrahydrofuran (THF), was available on site and is more effective in soaking the pan than MEK. The operators knew this and got the THF from the first floor of the coating tower using a bucket (no safety cans were available here since this was not the normal operation). In the accident, the victim also filled a bucket with THF on the first floor, but this time the liquid ignited (most likely from an electrostatic discharge). Knowing that the coating tower was a classified area, the victim has tried to carry the burning bucket outside. For that he had

to go down the stairs. In the staircase, he fell and dropped the bucket. This had two effects: burning liquid was splashed onto his clothes and there was a larger burning surface, resulting in a large fire, surrounding the victim. He was able to get out of the staircase and ran (with his clothes burning) towards a colleague in a nearby room. This colleague was able to put out the fire on his clothes. However, the burns were so severe that the victim died one day later [24].

- Date: 24/10/1995;

Dead:0;

Hospitalized:1;

Description: an explosion and a fire of an organic chemical occurred at a chemical factory. By pressurizing a drum can with air, tetrahydrofuran (THF) was transferred to a tank. The drum can exploded and a fire occurred. The method was imperfect and unsuitable, although static electricity preventive measures were taken. Therefore, a combustible gas-air mixture in the drum can is considered to have been ignited by static electricity sparks generated by a liquid flow, followed by an explosion [25].

3.1.9 Accidents regarding an ASU (Air Separation Unit)

- Date: 1978;

Dead:0;

Hospitalized:0;

Description: the incident in Lae occurred in a very small plant (about 1 ton per day of oxygen). It was of modern design in that the liquid oxygen from the top column sump was pumped to cylinder-filling pressure then returned to the main exchanger to impart its cold to the feed air. The center of the explosion was the main exchanger, made of copper, not aluminum. This is the point at which the liquid oxygen evaporates, leaving behind the dissolved acetylene or other hydrocarbons, and the possibility of their accumulation. The ASU was closed to an acetylene works, which might have been a rich source of contamination [26].

- Date: 25/12/1997;

Dead:0;

Hospitalized:0;

Description: a serious explosion in an air separation unit in Bintulu (Malaysia) occurred. Since the cause of the explosion was not obvious, a large number of possible scenarios was generated, followed by a systematic process of elimination. Ultimately, conclusive evidence was obtained that combustible airborne particulates had passed the main purification section of the air separation unit. These combustible contaminants had accumulated on the aluminum main vaporizers of the distillation column. Once hydrocarbon combustion was triggered, it led to aluminum combustion which generated

heat and vaporized the cryogenic liquids. This led to rapid pressure build up and explosive rupture of the distillation column. The exact ignition mechanism remains unclear, but a low activation energy chemical mechanism, involving radical reactions to provide the initiating trigger, has been proposed. However, by designing a purification system capable of efficiently removing aerosol material and other fouling contaminants, and by a proper design of the oxygen reboiler it is possible to design a plant that can be operated safely in an aerosol polluted environment [27].

- Date: 31/12/2001;

Dead:1;

Hospitalized:0;

Description: on that day, the oxygen flow had been redirected for a certain period of time to the cooling tower over a by-pass line. In the same day, the oxygen flow was again switched from the by-pass line to the product pipe with the aim of directing the oxygen into the storage tank. Before starting oxygen storage operations, the product pipe had to be cleaned, due to the fact that the product pipe had not been used for a certain period of time and that contamination could not be excluded. The cleaning operation was performed by flushing the pipe with the product (oxygen). Due to the fact that the valve did not close correctly, oxygen was released over the pipe into the gravel bed near the tank and into the atmosphere instead of flowing into the oxygen storage tank. Switching from the by-pass line to the product pipe was made over a remote control from the control room of the other air separation unit. The monitoring system showed the opening of the flush valve and the closing of the valve after 2.5 min. In reality the flush valve was not closed. Oxygen spread over the site and it has to be assumed that it reached also the administration building at a distance of approximately 50 meters. At 4:55 p.m. a fire broke out inside the building and an employee was killed. The fire destroyed most rooms on the ground floor and on the first floor of the building. The fire detectors responded in rapid sequence, it has therefore to be assumed that the fire spread very rapidly. The fire brigade brought the fire rapidly under control and extinguished it. A collaborator was inside the building when the fire broke out because one of the plant operators had requested him to check directly on-site the alarm signal released by an analyzing device. The analyzer indicated an oxygen content in the nitrogen cooling circuit near to the threshold value of 0.3 ppm. A defect in the analyzer was suspected. The collaborator instructed to check the analysis came into the installation at 4:00 p.m. and controlled the corresponding analysis. He contacted the control room communicating that no errors could be found and his intention to leave the installation. Shortly after, the fire detectors responded. The oxygen content measurement in the nitrogen cooling circuit of the air separator is an essential control

parameter for the cooling process. The values measured do not give any clue with regards to the oxygen content of the ambient air in the surroundings [28].

3.2 Historical analysis results

It has been found that the most disastrous accident was the one regarding MEA happened in Romeoville, Illinois (USA); for this reason, it is described with more details in the following. Ethanolamine is an organic chemical compound which is flammable and toxic: in the Appendix is a present a detailed safety data sheet. This was a really destructive accident happened on 23 July 1984, which caused 17 deaths, 22 hospitalized persons and 530 million dollars for repairs and compensation. Everything starts with a vapor leak noticed on a vessel at 5.45 p.m.: it was a pressured amine absorber removing H₂S from an acid stream (55 feet tall, 1 in thick carbon steel, 34 tons of storage). Refinery workers, including the outside operator and an assistant outside operator, unsuccessfully attempted to by-pass the vessel and to depressurize it. At 5.52 p.m., the leak in the vessel wall had spread around the entire 8 feet circumference of the vessel and it erupted like a missile. The top 45 feet of the vessel was lifted by the vapor cloud. The bottom 10 feet of the vessel stayed intact on the ground. The eruption of the vessel released a massive vapor cloud which ignited, causing a fire ball. This explosion engulfed much of the refinery in flames. Firefighters from the Union Oil Fire Brigade responded immediately with the company's two engines, followed closely by the Romeoville Fire Department. As a result of the explosion, many towers, tanks, and other refinery structures began to rupture or collapse and the site's fire hydrant system was damaged. So, firefighters were forced to draft water from a nearby sanitary canal. They were just beginning to attack the flames when a tank containing LPG erupted. The explosion created a huge fireball that rose thousands of feet into the air. Several members of the Union Oil Fire Brigade were caught in the blast. Firefighters were needed to both put out the flames and also prevent more refinery structures from catching fire. Once the burning structures were isolated, fire officials determined that allowing the fires to burn out on their own was the safest way to extinguish the blaze. The fires burned throughout the night at temperatures of 2200 °C, luckily without further explosions or loss of life, even though some workers jumped into the Illinois & Michigan Canal to escape the extreme heat.

3.2.1 Amine vessel failure analysis

As required by law, the inside of the vessel was inspected every two years. The inspectors were Union Oil employees in management positions. The vessel was last inspected three months before the explosion and the vessel inspectors found no problems with the vessel. Testimony from one of Union Oil's own engineers indicated that his metallurgical testing performed after the explosion indicated that there were cracks in the vessel walls at least four years before the accident. The plaintiff's evidence established that Union Oil's vessel inspectors made only a

visual inspection which was inadequate to detect cracking within the vessel walls. The evidence indicated that Ultrasonic and wet magnetic particle testing techniques were well known and used in the oil industry to detect vessel wall cracking, but Union Oil did not use them on this vessel. In the Figure 3.1 it can be seen the amine vessel after the amine vessel after the explosion.

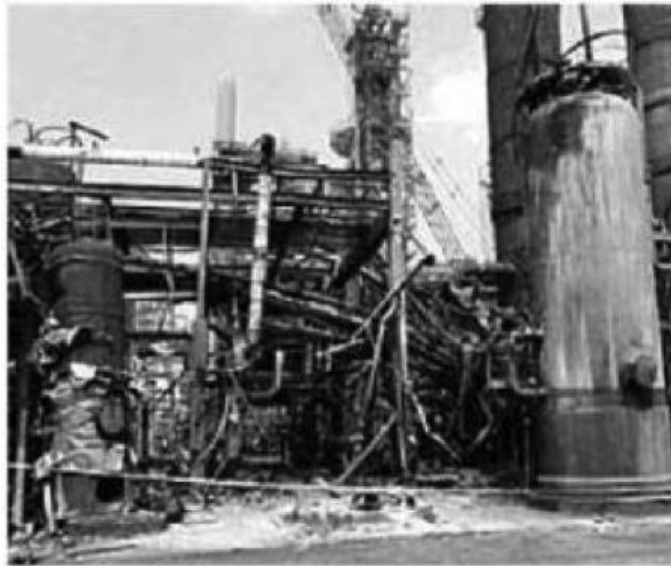


Figure 3.1. Amine absorber column after the explosion, Romeoville, Illinois (USA), 1984

Three other primary contributors to the settlement, Santa Fe Braun, Inc., UOP, Inc., and the Ralph M. Parsons Company, had responsibilities relating to the erection, process design and functioning of this vessel. One of Santa Fe Braun's corporate predecessors, C.F. Braun and Company, was the general contracting firm that erected the vessel. Its engineers helped to determine the process requirements and capabilities of this vessel, specifically including what amount of chemical activity would go on within the vessel. UOP was also involved in those decisions, made with respect to process engineering. The Ralph M. Parsons Company has been hired by Union Oil to revamp part of the refinery, including the subject vessel. In its revamp, Parsons altered some of the process requirements of that vessel, and as well, made independent determinations of the suitability of the vessel and its characteristics for use in the amine treating system. The Union Oil Company alleged that the process design work done by these three companies was inadequate in that it failed to provide for sufficient safeguarding against corrosion which contributed to the cracking and the failure of the vessel. Union Oil determined that the operation of the subject vessel had caused significant metallurgical problems to the bottom portion of the vessel and that one of the vessel sections would need to be replaced. Welders from the Morrison Construction Company attempted to replace a major section of the vessel but due to poor quality control and inadequate welding work, were taken off the job by Union Oil and replaced by welders from the Nooter Corporation. Nooter's welders finished the

job using specifications which the Union Oil Company claimed were inadequate. The welding specifications used by Morrison and Nooter contributed to the "high hardness" of the metal adjacent to the weld, which made it more brittle and subject to failure. Metallurgical testing work done after the explosion, both by engineers retained by Union Oil and engineers retained by the Illinois State Fire Marshall, showed that the cracking in this vessel which lead to the explosion and fire started in the metal adjacent to the welds done by Morrison and Nooter [2].

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Chapter 4

Capture process simulation

Starting from the point that the capture process using MEA is probably the most dangerous one, the next step is to perform a simulation in Aspen Plus of this process, in particular an existing pilot plant is taken as reference. The aim will be to perturb the flue gas operating conditions and see if and how the process will respond to them. The simulation will be brought to its physical and chemical limits: in this way, the most critical section will be identified.

4.1 Carbon capture process with MEA

The previous research and analysis have been useful to understand that capture processes involving MEA can really increase the riskiness of a plant and that a particularly high level of attention is absolutely needed. MEA is an organic chemical compound well known for its use in gas scrubbing, particularly in this case for flue gas scrubbing; it is unfortunately also a toxic and flammable substance. To find out the most hazardous part of a carbon capture plant working with MEA, it has been run a simulation with Aspen Plus. Feed conditions and unit operation block specifications in the rate-based model was provided from a pilot plant study at the University of Kaiserslautern (2012) [1].

4.1.1 Model components

In the Table 4.1 are represented the chemical species present in the process.

Table 4.1. *Components used in the model*

ID	Type	Name	Formula
MEA	Conventional	Monoethanolamine	C ₂ H ₇ NO
H ₂ O	Conventional	Water	H ₂ O
CO ₂	Conventional	Carbon dioxide	CO ₂
H ₃ O ⁺	Conventional	H ₃ O ⁺	H ₃ O ⁺
OH ⁻	Conventional	OH ⁻	OH ⁻
HCO ₃ ⁻	Conventional	HCO ₃ ⁻	HCO ₃ ⁻
CO ₃ -2	Conventional	CO ₃ ⁻²	CO ₃ ⁻²
MEAH ⁺	Conventional	MEA ⁺	C ₂ H ₈ NO ⁺
MEACOO ⁻	Conventional	MEACOO ⁻	C ₃ H ₆ NO ₃ ⁻
N ₂	Conventional	Nitrogen	N ₂
O ₂	Conventional	Oxygen	O ₂
CO	Conventional	Carbon monoxide	CO
H ₂	Conventional	Hydrogen	H ₂

H ₂ S	Conventional	Hydrogen-sulfide	H ₂ S
HS ⁻	Conventional	HS ⁻	HS ⁻
S ⁻²	Conventional	S ⁻	S ⁻²
CH ₄	Conventional	Methane	CH ₄
C ₂ H ₆	Conventional	Ethane	C ₂ H ₆
C ₃ H ₈	Conventional	Propane	C ₃ H ₈

4.1.2 Physical properties

The unsymmetrical electrolyte NRTL property method (ENRTL-RK) and PC-SAFT equation of state are used to compute liquid and vapor properties, respectively, in this rate-based MEA model. CO₂, H₂S, N₂, O₂, CH₄, C₂H₆, and C₃H₈ are selected as Henry-components (solutes) to which Henry's law is applied. Henry's constants are specified for these components with water and MEA. In the reaction calculations, the activity coefficient basis for the Henry's components is chosen to be Aqueous. Therefore, in calculating the unsymmetrical activity coefficients (GAMUS) of the solutes, the infinite dilution activity coefficients will be calculated based on infinite-dilution condition in pure water, instead of in mixed solvents.

The Henry's constant parameters of CO₂, H₂S, CH₄, C₂H₆, and C₃H₈ are obtained from the literatures or regressed with the VLE data (see Table 4.2). The other Henry's constants are retrieved from the Aspen Databank.

Table 4.2. Henry's constants

Solute	Solvent	Source
CO ₂	H ₂ O	Yan and Chen (2010) [4]
H ₂ S	H ₂ O	Regression with H ₂ S-H ₂ O VLE data [5-12]
CH ₄	H ₂ O	Regression with CH ₄ -H ₂ O VLE data [13]
C ₂ H ₆	H ₂ O	Regression with C ₂ H ₆ -H ₂ O VLE data [14]
C ₃ H ₈	H ₂ O	Regression with C ₃ H ₈ -H ₂ O VLE data [15]
CO ₂	MEA	Zhang and Chen (2011) [16]
H ₂ S	MEA	Set to that of H ₂ S in H ₂ O
CH ₄	MEA	Regression with CH ₄ -H ₂ O-MDEA VLE data [17,18]
C ₂ H ₆	MEA	Regression with C ₂ H ₆ -H ₂ O-MDEA VLE data [18]
C ₃ H ₈	MEA	Regression with C ₃ H ₈ -H ₂ O-MDEA VLE data [19]

The PC-SAFT parameters of MEA are regressed from the vapor pressure data [20-23], the heat of vaporization data [24-25], the liquid heat capacity data [26-27] and the liquid density data [28-30]. Those of H₂O are obtained from Gross and Sadowski [31], and those of the other components are retrieved from the Aspen Databank. The characteristic volume parameters of H₂O for the Brelvi-O'Connell Model, VLBROC, are obtained from Brelvi and O'Connell [32], those of CO₂ are obtained from Yan and Chen [4], those of CH₄ and C₂H₆ are regressed with the CH₄-H₂O [13] and C₂H₆-H₂O [14] binary VLE data, and those of MEA, H₂S, C₃H₈, N₂, O₂

and CO are defaulted to their critical volume in the Aspen Databank. Unless specified otherwise, all molecule-molecule binary parameters and electrolyte-electrolyte binary parameters are defaulted to zero. All molecule-electrolyte binary parameters are defaulted to (8, -4), average values of the parameters as reported for the electrolyte NRTL model [33]. The nonrandomness factor is fixed at 0.2. The NRTL interaction parameters between MEA and H₂O are determined from the regression with binary VLE data [23,33-37], excess enthalpy data [33,38-40] and heat capacity data [27, 1,42]. The interaction energy parameters between H₂O and (MEAH⁺, HCO₃⁻), GMENCC, and those parameters between H₂O and (MEAH⁺, MEACOO⁻), GMENCC and GMENCD, are regressed using the VLE data [43-46], absorption heat data [47], heat capacity data [42,45] and speciation concentration data [48]. The interaction energy parameters between H₂O and (MEAH⁺, HS⁻), GMENCC and GMENCD, are regressed with the H₂S solubility data in aqueous MEA solution [49-50]. The dielectric constants of nonaqueous solvents are calculated by the following expression:

$$\varepsilon = A + B \left(\frac{1}{T} - \frac{1}{C} \right) \quad (4.1)$$

The parameters A, B and C for MEA are 35.76, 14836.0 and 273.15, which are derived from Dean et al. [51]. The liquid molar volume model and transport property models have been validated and model parameters regressed from literature experimental data. Specifications of the transport property models include:

- For liquid molar volume, the Clarke model, called VAQCLK in Aspen Plus, is used with option code 1 to use the quadratic mixing rule for solvents. The interaction parameter VLQKIJ for the quadratic mixing rule between MEA and H₂O is regressed against experimental MEA-H₂O density data from Kapadi et al. [52]. The Clarke model parameter VLCLK/1 is also regressed for the main electrolyte (MEAH⁺, HCO₃⁻), (MEAH⁺, MEACOO⁻) and (MEAH⁺, CO₃⁻²) against experimental MEA-H₂O-CO₂ density data from Weiland [53]; that for (MEAH⁺, HS⁻) is set to that of (MEAH⁺, HCO₃⁻);
- For liquid viscosity, the Jones-Dole electrolyte correction model, called MUL2JONS in Aspen Plus, is used with the mass fraction based Aspen liquid mixture viscosity model for the solvent. There are three models for electrolyte correction and the MEA model always uses the Jones-Dole correction model. The three option codes for MUL2JONS are set to 1 (mixture viscosity weighted by mass fraction), 1 (always use Jones and Dole equation when the parameters are available), and 2 (Aspen liquid mixture viscosity model), respectively. The interaction parameters between MEA and H₂O in the Aspen liquid mixture viscosity model, MUKIJ and MULIJ, are regressed against experimental MEA-H₂O viscosity data from Kapadi et al. [52] and Wadi et al. [54]. The Jones-Dole model parameters, IONMUB, for MEAH⁺, and MEACOO⁻ are regressed against MEA-

H₂O-CO₂ viscosity data from Weiland [53]; that of HCO₃⁻ is regressed against KHCO₃-H₂O viscosity data from Palaty [55]; that of CO₃²⁻ is regressed against K₂CO₃-H₂O viscosity data from Pac et al. [56]; and that of HS⁻ is regressed against MDEA-H₂OH₂S viscosity data from Rinker et al. [57];

- For liquid surface tension, the Onsager-Samaras model, called SIG2ONSG in Aspen Plus, is used with its option codes being -9 (exponent in mixing rule) and 1 (electrolyte system), respectively. Predictions for the MEA-H₂O-CO₂ system can be in the range of the experimental data from Weiland [53], which themselves have questionable qualities due to MEA degradation during experiments;
- For thermal conductivity, the Riedel electrolyte correction model, called KL2RDL in Aspen Plus, is used;
- For binary diffusivity, the Nernst-Hartley model, called DL1NST in Aspen Plus, is used with option code of 1 (mixture viscosity weighted by mass fraction).

In addition to the updates with the above transport properties, the aqueous phase Gibbs free energy and heat of formation at infinite dilution and 25°C (DGAQFM and DHAQFM) and heat capacity at infinite dilution (CPAQ0) for MEAH⁺ and MEACOO⁻ are regressed with the VLE data [43-46], absorption heat data [47], heat capacity data [42, 45] and speciation concentration data [48]. The CPAQ0 of HCO₃⁻, CO₃²⁻ and HS⁻ are the average values of heat capacity between 298 K and 473 K taken from Criss and Cobble [58], and that of S²⁻ is calculated from the Criss-Cobble correlation [58] with the entropy value from Wagman et al. [59].

4.1.3 Reactions

MEA is a primary ethanolamine, as shown in Figure 4.1. It can associate with H⁺ to form an ion MEAH⁺, and can also react with CO₂ to form a carbamate ion MEACOO⁻.

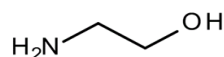


Figure 4.1. MEA molecular structure

The electrolyte solution chemistry has been modeled with a CHEMISTRY model with CHEMISTRY ID = MEA (as seen in Figure 4.2).

1	Equilibrium	$\text{MEA}^+ + \text{H}_2\text{O} \leftrightarrow \text{MEA} + \text{H}_3\text{O}^+$
2	Equilibrium	$\text{MEACOO}^- + \text{H}_2\text{O} \leftrightarrow \text{MEA} + \text{HCO}_3^-$
3	Equilibrium	$2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^-$
4	Equilibrium	$\text{CO}_2 + 2\text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}_3\text{O}^+$
5	Equilibrium	$\text{HCO}_3^- + \text{H}_2\text{O} \leftrightarrow \text{CO}_3^{2-} + \text{H}_3\text{O}^+$
6	Equilibrium	$\text{H}_2\text{S} + \text{H}_2\text{O} \leftrightarrow \text{HS}^- + \text{H}_3\text{O}^+$
7	Equilibrium	$\text{HS}^- + \text{H}_2\text{O} \leftrightarrow \text{S}^{2-} + \text{H}_3\text{O}^+$

Figure 4.2. Chemistry ID: MEA

This CHEMISTRY ID is used as the global electrolyte calculation option in the simulation by specifying it on the **Global** sheet of the **Properties | Specifications** form. Chemical equilibrium is assumed with all the ionic reactions in the CHEMISTRY **MEA**. In addition, two REACTION models called **Absorber** (used in the absorber, 303-353 K) and **Stripper** (used in the stripper, 353-393 K) have been created. In **Absorber/Stripper**, all reactions are assumed to be in chemical equilibrium except those of CO₂ with OH⁻ and CO₂ with MEA (as seen in Figure 4.3).

1	Equilibrium	$\text{MEA}^{\text{H}^+} + \text{H}_2\text{O} \leftrightarrow \text{MEA} + \text{H}_3\text{O}^+$
2	Equilibrium	$2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^-$
3	Equilibrium	$\text{HCO}_3^- + \text{H}_2\text{O} \leftrightarrow \text{CO}_3^{2-} + \text{H}_3\text{O}^+$
4	Equilibrium	$\text{H}_2\text{O} + \text{H}_2\text{S} \leftrightarrow \text{HS}^- + \text{H}_3\text{O}^+$
5	Equilibrium	$\text{H}_2\text{O} + \text{HS}^- \leftrightarrow \text{S}^{2-} + \text{H}_3\text{O}^+$
6	Kinetic	$\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$
7	Kinetic	$\text{HCO}_3^- \rightarrow \text{CO}_2 + \text{OH}^-$
8	Kinetic	$\text{MEA} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{MEACOO}^- + \text{H}_3\text{O}^+$
9	Kinetic	$\text{MEACOO}^- + \text{H}_3\text{O}^+ \rightarrow \text{MEA} + \text{H}_2\text{O} + \text{CO}_2$

Figure 4.3. Reaction ID: Absorber/Stripper

The equilibrium constants for reactions 1-7 in **MEA** are calculated from the standard Gibbs free energy change. DGAQFM, DHAQFM, and CPAQ0 of MEAH⁺ and MEACOO⁻, which are used to calculate the standard MEAH⁺ and MEACOO⁻ Gibbs free energy, are determined in this work. The DGAQFM (or DGFORM), DHAQFM (or DHFORM), and CPAQ0 (or CPIG) parameters of the other components can be obtained from the databank of Aspen Plus. Power law expressions are used for the rate-controlled reactions (reactions 4-7 in **Absorber/Stripper**). The general power law expression is:

$$r = k(T/T_0)^n \exp\left[\left(\frac{-E}{R}\right)\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \prod_{i=1}^N (x_i \gamma_i)^{a_i} \quad (4.2)$$

Where:

- r = rate of reaction;
- k = pre-exponential factor;
- T = absolute temperature;
- T₀ = reference temperature;
- n = temperature exponent;
- E = activation energy;
- R = universal gas constant;
- N = number of components in the reaction;
- x_i = mole fraction of component i;
- γ_i = activity coefficient of component i;
- a_i = the stoichiometric coefficient of component i in the reaction equation.

If T_0 is not specified, the reduced power law expression is used:

$$r = kT^n \exp\left(\frac{-E}{RT}\right) \prod_{i=1}^N (x_i \gamma_i)^{a_i} \quad (4.3)$$

In this work, the reduced expression is used. In equation (4.3), the concentration basis is mole gamma, the factor n is zero, k and E are given in Table 4.3

Table 4.3. Parameters k and E in equation (3.3)

Reaction No.	k	E [cal/mol]
6	1.33e+17	13249
7	6.63e+16	25656
8	3.02e+14	9855.8
9 (Absorber)	5.52e+23	16518
9 (Stripper)	6.50e+27	22782

Note that **Absorber** and **Stripper** share all kinetic parameters except those of reaction 9. The kinetic parameters for reaction 6 (forward reaction) are taken from the work of Pinsent et al. [60], and the kinetic parameters for reaction 7 (reverse reaction) are calculated by using equation (3.4) with the kinetic parameters of reaction 6 and the equilibrium constants of the reversible reactions 6 and 7:

$$k_r^a = \frac{k_f^a}{K_{eq}^a} \quad (4.4)$$

Where:

- k_f^a = rate constant of the forward reaction, mole gamma basis;
- k_r^a = rate constant of the reverse reaction, mole gamma basis;
- K_{eq}^a = equilibrium constant, mole gamma basis.

The kinetic parameters of reaction 8 in Table 3.3 are derived from the work of Hikita et al. [3] and the kinetic parameters of reaction 9 are calculated by using the kinetic parameters of reaction 8 and the equilibrium constants of the reversible reactions 8 and 9. Two sets of linear approximations (respect to $1/T$) for the equilibrium constants (calculated from the Gibbs free energy change) are used for **Absorber** and **Stripper**, respectively. One is the linear approximation of the equilibrium constant for the temperature from 303 to 353 K (for the absorber) and the other is the linear approximation for the temperature from 353 to 393 K (for the stripper). Two sets of kinetic parameters of reaction 9 for **Absorber** and **Stripper** are obtained using equation (3.4), as listed in Table 3.3.

4.1.4 Simulation approach

The flowsheet, which can be seen in the Figure 4.4, closely simulates of the pilot plant cited in Notz, Mangalapally, and Hasse [1] which incorporates an absorption and stripping column, heat exchange between the two columns, and water and amine recycles. The operating conditions of this plant were chosen to be as close to those used in case 1 as possible. Where data necessary for the simulation were not reported reasonable estimates for these missing data were made. An amine makeup stream and a water makeup stream were not present in the pilot plant, but were added to the simulation to maintain mass balance and to aid convergence.

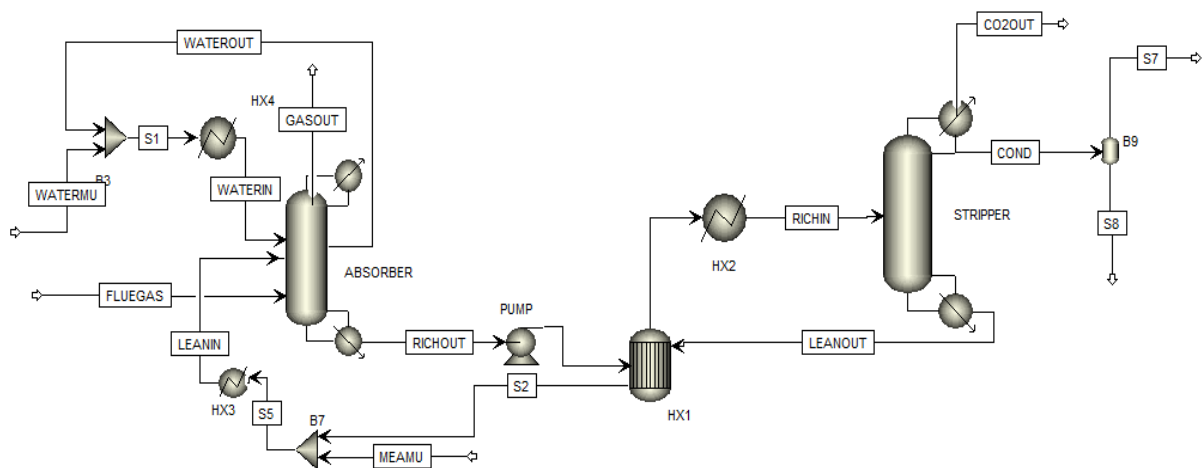


Figure 4.4. Rate-based MEA simulation flowsheet in Aspen Plus

Major unit operations in this model have been represented by Aspen Plus blocks as outlined in Table 4.4.

Table 4.4. Aspen Plus unit operations blocks in the rate-based MEA model

Unit operation	Aspen Plus block	Comments / Specifications
Absorber	RadFrac	<ol style="list-style-type: none"> 1. Calculation type: Rate-Based 2. 20 stages 3. Top pressure: 0.97708 bar 4. Reaction: Reaction ID is ABSORBER for all stages 5. Packing type: FLEXIPAC® 250Y 6. Diameter: 0.125m 7. Total height: 4.62m 8. Wash section height: 0.42m 9. Absorber section height: 4.2m 10. WATEROUT flowrate: 28.53 kg/h 11. Mass transfer coefficient method: Bravo (1985) [61] 12. Interfacial area method: Bravo (1985) [61] 13. Flooding method: Wallis [62] 14. Heat transfer coefficient method: Chilton and Colburn

Stripper	RadFrac	<p>15. Film resistance options: Discrxn for liquid film; Film for vapor film</p> <p>16. Flow model: VPlug</p> <p>17. Estimates: provide temperature at stages 1, 12 and 20. These estimates are intended to aid convergence</p> <p>1. Calculation type: Rate-Based</p> <p>2. 20 stages</p> <p>3. Top pressure: 1.999 bar</p> <p>4. Reaction: Chemistry ID is MEA for condenser and reboiler, and then Reaction ID is STRIPPER for all other stages</p> <p>5. Packing type: FLEXIPAC® 250Y</p> <p>6. Diameter: 0.125m</p> <p>7. Total height: 2.92m</p> <p>8. Wash section height: 0.42m</p> <p>9. Stripper section height: 2.5m</p> <p>10. Distillate rate: 6.93 kg/h</p> <p>11. Reboiler duty: 7.05 kW</p> <p>12. Condenser temperature: 18°C</p> <p>13. Mass transfer coefficient method: Bravo (1985) [61]</p> <p>14. Interfacial area method: Bravo (1985) [61]</p> <p>15. Flooding method: Wallis [62]</p> <p>16. Heat transfer coefficient method: Chilton and Colburn</p> <p>17. Film resistance options: Discrxn for liquid film; Film for vapor film</p> <p>18. Flow model: VPlug</p> <p>19. Estimates: provide temperature at stages 20. This estimate is intended to aid convergence</p>
HX1	HeatX	<p>1. Calculation type: Shortcut</p> <p>2. Hot inlet – Cold outlet temperature difference: 5.27°C</p> <p>3. Cold side outlet pressure: 2.9bar</p> <p>4. Valid phases: vapor-liquid both sides</p>
HX2	Heater	<p>1. Outlet temperature: 112.85°C (set to match experimental data for inlet temperature for stripper caused by heat losses after heat recovery exchanger)</p> <p>2. Outlet pressure: 2.9bar</p> <p>3. Valid phases: vapor-liquid</p>
HX3	Heater	<p>1. Outlet temperature: 40°C</p> <p>2. Outlet pressure: 2bar</p> <p>3. Valid phases: vapor-liquid</p>
Pump	Pump	<p>1. Discharge pressure: 2.9bar</p>

Major inlet and outlet streams and properties are summarized in Table 4.5. The stream LEANIN, LEANOUT and WATERIN are tear streams in the simulation. Initial guesses for LEANIN and WATERIN were taken from the experimental data and shown in Table 4.5.

Table 4.5. Major experimental stream properties

Stream ID	FLUEGAS	LEANIN	RICHOUT	CO2OUT	COND	WATERIN	WATEROUT
Temperature [°C]	48.01	40.01	51.66	18.27	16.02	43.87	47.70
Pressure [mbar]	1004.49	2000	1065.06	2000	~1000	~1000	~1000
Total flow [kg/h]	72	200.1	206.5	4.67	2.04	30.87	28.53
Mass fractions							
MEA	0	0.275	0.265	0	0	0.0083	0.009
H ₂ O	0.071	0.673	0.661	0.004	1.0	0.9917	0.991
CO ₂	0.085	0.052	0.074	0.996	0	0	0
N ₂	0.743	0	0	0	0	0	0
O ₂	0.101	0	0	0	0	0	0
Molar CO ₂ loading	--	0.262	0.387	--	--	--	--

The water makeup stream flowrate was determined using a standard balance block. The inlet stream was FLUEGAS and the water makeup stream, WATERMU, was introduced for the water balance. The outlet streams were GASOUT, CO2OUT and S7. The MEA makeup stream flowrate was determined using another standard balance block. The MEA makeup stream, MEAMU, was introduced for the MEA balance. The outlet streams were GASOUT, CO2OUT and S7.

4.1.4.1 Simulation results

A comparison of key simulation results with the measurements is given in the Table 4.6. It can also be demonstrated that these rate-based model correlations can reproduce quite accurately the experimentally measured temperature profiles in both the absorber and the stripper, the CO₂ weight fraction profiles in both columns, as well as the CO₂ and water partial pressure profiles in both columns.

Table 4.6. Key simulation results

Variable	Measurement	Rate-based model
CO ₂ loading of LEANIN [molCO ₂ /molMEA]	0.262	0.262
CO ₂ loading of RICHOOUT [molCO ₂ /molMEA]	0.387	0.384
CO ₂ removal [%]	76.1	79.1
Specific energy requirement of the reboiler excluding heat losses [MJ/kgCO ₂]	5.01	5.25
Makeup water [kg/h]	1.95	2.01
Makeup MEA [kg/h]	n/a	0.007
Stripper reboiler heat duty excluding heat losses [kW]	6.47	7.05
Heat recovery exchanger duty [kW]	13.52	12.39

temperature for this type of plants, it can happen only, for example, in the case of an external fire and consequent irradiation of the stripper. If it will be tried to overcome that FLUEGAS temperature, warning messages will be found in the stripper block, as can be seen in Figure 4.6.

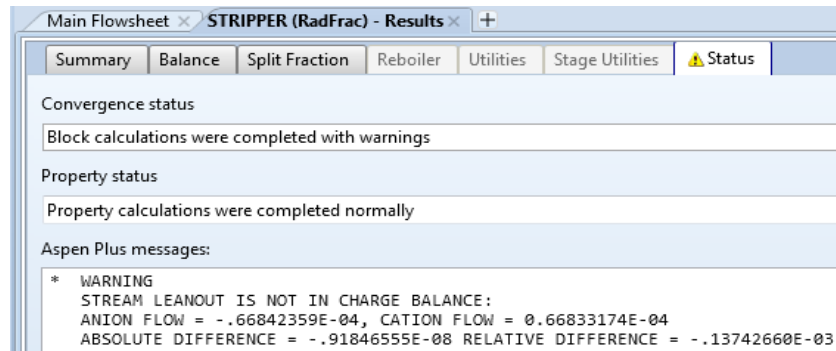


Figure 4.6. Screenshot of the stripper block warning resulted in Aspen Plus after the attempt to overcome 268°C on FLUEGAS stream

At this point material balances, precisely the charge balance, will not be respected anymore in the stripper section; moreover, this part of the process is the one operating at the highest temperature (usually between 100 and 140°C) and pressure (~2 bar). From these considerations, it can be stated that the stripper operation is the most hazardous one in the entire process, thus there is the need to perform a complete risk analysis.

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Chapter 5

Stripping section risk assessment

In this chapter, a risk assessment will be done to evaluate the occurrence frequency of a release in the stripper section of a CCS plant. In order to achieve this task, the more common, useful and effective tools of the risk analysis will be employed: in particular, Hazop, fault tree and event tree analysis, respectively. To complete the study a release simulation on a hazard modeling program will be carried out.

5.1 Hazop

After the achievement and the examination of the results obtained by the simulation in Aspen Plus that have shown the “sore point” of the process, the risk analysis can start right there. The first step consists in the construction of the Hazop. This is a technique which allows the individuation of potential risks and operability issues by deviations from the project goals and linked, in particular, to malfunctions during the plant operation. This method has been applied at a simple P&ID of the section studied, that is represented in Figure 5.1.

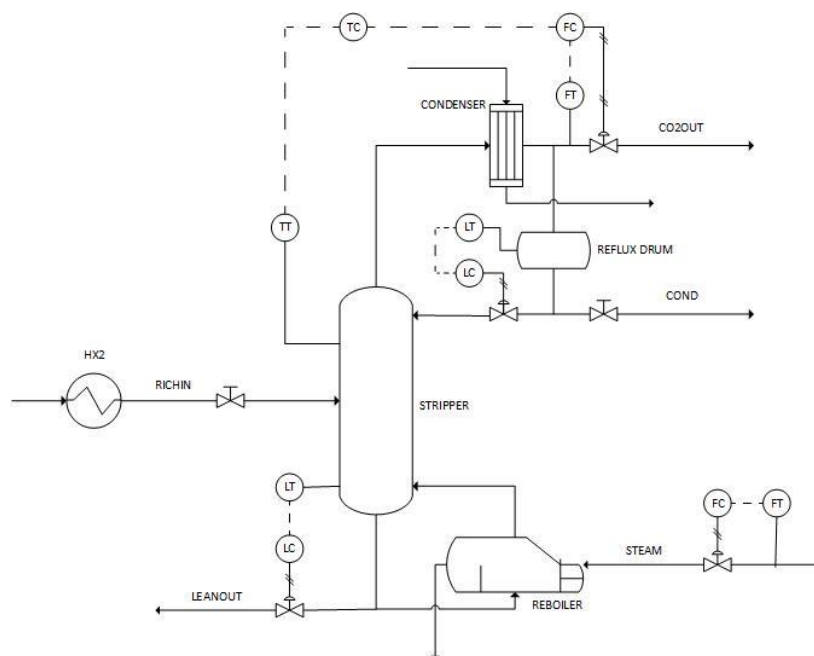


Figure 5.1. P&ID of the stripping section of the capture process with MEA

The results of this procedure have been written in Table 5.1, 5.2, 5.3, 5.4, 5.5 and 5.6, as can be seen in the following, each one regarding a specific stream entering or existing the stripping column.

Table 5.1. Hazop of the RICHIN stream

Guide word	Deviation	Possible causes	Consequences	Proposed measures	
NO	Flow	Catastrophic rupture of HX2.	Economic loss for serious plant damage. Release of toxic and/or flammable substances. Possible explosions.	Frequent inspections and maintenance. Advancement of an emergency plan.	1
		Rupture of the pipe.	Release of toxic and/or flammable substances. Possible explosions.	Analogous measures of the point 1. Installation of both high pressure and low flowrate alarms.	2
		Manual valve blocked in fully-closed position.	Increase of pressure in the pipe before the valve. Cooling of the stripper.	Installation of a by-pass. Installation of both low pressure and low flow alarms after the valve.	3
MORE	Flow	Manual valve blocked in partially or fully-open position.	Stripper could achieve flooding conditions. Possible release of toxic and/or flammable substances.	Installation of a control valve in series and of a large flow alarm.	4
		Electrical or mechanical malfunctioning of the pump.	Analogous consequences of the point 4.	Frequent inspections and maintenance. Installation of an emergency generator that would start automatically. Installation of high flowrate alarm after the valve.	5
		Richout flowrate larger than expected.	Analogous consequences of the point 4.	Analogous measures of the point 4. Monitoring of Richout flowrate.	6
	Pressure	Manual valve blocked in partially or fully-closed position.	Pressure rises before the valve. Possible disconnection of the flange with release of toxic and/or flammable substances.	Installation of control system and control valve in parallel. Installation of both low flow and high pressure alarms.	7
	Temperature	Malfunctioning of HX2 or of its control system. Too high steam pressure or steam flow.	Possible evaporation of CO ₂ . Possible formation of carbamate.	Installation of high temperature and high pressure alarms on Richin stream.	8

		Richout stream hotter than expected.	Analogous consequences of point 8.	Installation of high temperature and high pressure alarms on both streams.	9
		Irradiation from external fire.	Possible evaporation of CO ₂ . Possible formation of carbamate. Possible failure of the pipe.	Analogous measures of the point 7. Installation of water curtain.	10
LESS	Flow	Manual valve blocked in partially-closed position.	Analogous consequences of point 3.	Analogous consequences of the point 7.	11
		Electrical or mechanical malfunctioning of the pump.	Possible cooling of the stripper with consequent performance decreased.	Frequent inspections and maintenance. Installation of an emergency generator that would start automatically. Installation of both low flowrate and low pressure alarms after the valve.	12
		Rupture or loss from the pipe or flange loss.	Release of toxic and/or flammable substances. Possible cooling of the stripper.	Frequent inspections and maintenance. Installation of low pressure alarm.	13
	Pressure	Electrical or mechanical malfunctioning of the pump.	Possible evaporation of CO ₂ .	Analogous measures of the point 12.	14
		Rupture or loss from the pipe or flange loss.	Analogous consequences of the point 13. Possible evaporation of CO ₂ .	Analogous measures of the point 13.	15
	Temperature	Malfunctioning of HX2 or of its control system. Insufficient steam pressure or steam flow.	Decreased stripper performance, if the reboiler control system does not work properly.	Installation of both low temperature and low pressure alarms on Richin stream.	16
PART OF	Composition	Feed composition changes.	Possible economic loss.	Accurate monitoring and control of the feed.	17
		Absorber performance drops.	Analogous consequences of the point 16.	Accurate monitoring of the composition after the absorber to evaluate an eventual intervention.	18

Table 5.2. Hazop of the LEANOUT stream

Guide word	Deviation	Possible causes	Consequences	Proposed measures	
NO	Flow	Catastrophic rupture of the stripper.	Economic loss for serious plant damage. Release of toxic and/or flammable substances. Possible explosions.	Frequent inspections and maintenance. Advancement of an emergency plan.	1
		Control valve blocked in fully-closed position.	Stripper goes in flooding conditions. Release of toxic and/or flammable substances. Possible explosions.	Installation of a by-pass. Installation of low pressure and low flowrate alarms after the control valve.	2
		Wrong calibration of the level sensor, failure of the control circuit or failure of the actuator.	Analogous consequences of the point 2.	Installation of valve and control system in parallel.	3
		Rupture of the pipe.	Release of toxic and/or flammable substances. Possible explosions.	Analogous measures of the point 1. Installation of low pressure and low flowrate alarms.	4
MORE	Flow	Control valve blocked in partially open position.	Stripper operation can be compromised.	Addition of a manual valve in series. Installation of a high flowrate alarm.	5
		Wrong calibration of the level sensor, failure of the control circuit or failure of the actuator.	Analogous consequences of the point 5.	Installation of a valve and control system in parallel.	6
		Excessive Richin flowrate.	Maintaining the same composition, temperature and pressure drop in the stripper when the reboiler does not increase its duty.	Careful monitoring of the process conditions. Installation of pressure and temperature indicators.	7
	Pressure	Control valve partially or fully-closed.	Possible flange disconnection and release of toxic and/or flammable substances.	Installation of control system and control valve in parallel. Installation of low flowrate and high pressure alarms.	8
		Wrong calibration of the level sensor, failure of the control circuit	Analogous consequences of the point 8.	Analogous measures of the point 8.	9

		or failure of the actuator.			
	Temperature	Increase of Richin temperature.	Increase of temperature in the pipe, with possible collapse and consequent release. Possible formation of carbamate.	Installation of safety valve and rupture disc. Careful monitoring of the process conditions. Addition of temperature indicators.	10
		Irradiation from external fire.	Possible formation of carbamate. Possible collapse of the pipe with consequent release.	Installation of water curtain.	11
		Malfunctioning of the reboiler.	Analogous consequences of the point 10.	Analogous measures of the point 10.	12
LESS	Flow	Insufficient Richin flowrate.	Maintaining the same composition, temperature and pressure decrease in the stripper.	Careful monitoring of the process conditions. Addition of pressure and temperature alarms and indicators. Monitoring of Richin flowrate.	13
		Rupture or loss from the pipe, loss from the flange.	Release of toxic and/or flammable substances. Economic loss for decreased absorption capacity for the recycled stream.	Frequent inspections and maintenance. Installation of low flowrate alarm.	14
		Control valve blocked in partially-closed position.	Economic loss for decreased absorption capacity for the recycled stream.	Installation of control system and control valve in parallel. Installation of low flow and high pressure alarms.	15
		Wrong calibration of the level sensor, failure of the control circuit or failure of the actuator.	Analogous consequences of the point 15.	Analogous measures of the point 15.	16
	Pressure	Wrong calibration of the level sensor, failure of the control circuit or failure of the actuator.	Possible increase of temperature and pressure in the stripper, if the reboiler control system does not work properly.	Addition of a control valve in series. Installation of a low pressure alarm.	17
		Rupture or loss from the pipe, loss from the flange.	Release of toxic and/or flammable substances.	Frequent inspections and maintenance. Installation of low pressure alarm.	18

	Temperature	Richin at lower temperature than expected.	Decreased stripper performance.	Addition of temperature indicators and alarms. Monitoring of the feed conditions.	19
		Reboiler steam at lower pressure, lower flowrate or lower temperature.	Analogous consequences of the point 19.	Addition of temperature, pressure and flowrate indicators and alarms for the steam.	20
PART OF	Composition	Decreased stripper performance, more CO ₂ and less MEA in this stream.	Economic loss for less CO ₂ separated and worse composition quality for Leanout that is going to the absorber.	Accurate monitoring of the Leanout stream composition to evaluate an eventual intervention.	21
		Richin composition changed.	Possible formation of flammable mixtures and possible economical loss.	Accurate monitoring and control of the Richin stream.	22

Table 5.3. *Hazop of the CO₂OUT stream*

Guide word	Deviation	Possible causes	Consequences	Proposed measures	
NO	Flow	Catastrophic rupture of the stripper.	Economic loss for serious plant damage. Release of toxic and/or flammable substances. Possible explosions.	Frequent inspections and maintenance. Advancement of an emergency plan.	1
		Control valve blocked in fully-closed position.	Pressure rises in the stripper, with possible collapse of the equipment and release.	Installation of safety valve and rupture disc. Accurate monitoring of pressure drops and installation of gauge and pressure alarm.	2
		Wrong calibration of the flow or temperature sensor, failure of the control circuit or failure of the actuator.	Analogous consequences of the point 2.	Installation of valve and control system in parallel.	3
		Rupture of the pipe.	Release of CO ₂ .	Frequent inspections and maintenance. Arrest of the feeding. Installation of low pressure and low flowrate alarms.	4
MORE	Flow	Wrong calibration of the flow or	Increased pressure and flow in the pipe, with possible	Installation of a safety valve and a rupture disc.	5

		temperature sensor, failure of the control circuit or failure of the actuator.	collapse and consequent release.	Careful monitoring of the process conditions. Addition of pressure indicators.	
		Control valve blocked in partially open position.	Stripper pressure decreases.	Addition of a control valve in series. Installation of a high flowrate alarm.	6
		Excessive pressure of the CO ₂ coming from the condenser and consequent inability of flowrate control from the valve.	Analogous consequences of the point 5.	Analogous measures of the point 5.	7
		Malfunctioning of the stripper (reboiler is heating more than necessary).	Analogous consequences of the point 5. Possible formation of carbamate. Possible MEA evaporation.	Analogous measures of the point 5.	8
		Excessive Richin flowrate and/or temperature.	Analogous consequences of the point 5. Possible formation of carbamate. Possible MEA evaporation.	Analogous measures of the point 5.	9
	Pressure	Control valve partially or fully-closed.	Possible condensation of CO ₂ . Possible disconnection of the flange with release of CO ₂ .	Installation of the control system and control valve in parallel. Installation of low flowrate and high pressure alarms.	10
		Excessive Richin flowrate and/or temperature.	Increase of stripper and pipes pressure, with possible collapse of the equipment and consequent release. Possible formation of carbamate.	Installation of safety valve and rupture disc. Careful monitoring of process conditions. Addition of pressure and temperature indicators.	11
		Wrong calibration of the flow or temperature sensor, failure of the control circuit or failure of the actuator.	Analogous consequences of the point 10.	Analogous measures of the point 10.	12
		Irradiation from external fire.	Possible collapse of the pipes with release of CO ₂ . Possible formation of carbamate.	Installation of water curtains and temperature and pressure alarms.	13

		Malfunctioning of the stripper (reboiler is heating more than necessary).	Analogous consequences of the point 8. Possible formation of carbamate.	Analogous measures of the point 8.	14
	Temperature	Excessive Richin temperature.	Increased temperature and pressure in the pipe with possible collapse and consequent release. Possible formation of carbamate.	Analogous measures of the point 5.	15
		Malfunctioning of the stripper (reboiler is heating more than necessary and/or condenser is cooling less than necessary).	Analogous consequences of the point 15. Possible formation of carbamate.	Analogous measures of the point 5.	16
		Irradiation from external fire.	Analogous consequences of the point 13. Possible formation of carbamate.	Analogous measures of the point 13.	17
			Control valve blocked in partially closed position.	Economic loss due to less CO ₂ separated. Stripper pressure increases.	Installation of control system and control valve in parallel. Installation of low flowrate and high pressure alarms.
LESS	Flow	Wrong calibration of the flow or temperature sensor, failure of the control circuit or failure of the actuator.	Analogous consequences of the point 18.	Analogous measures of the point 18.	19
		Rupture or loss of the pipe, flange loss.	Analogous consequences of the point 18. Possible release of CO ₂ .	Frequent maintenance and inspections. Installation of a low pressure alarm.	20
		Insufficient pressure of CO ₂ coming from the condenser.	Analogous consequences of the point 18. It is possible that some CO ₂ comes back.	Addition of a check valve after the control valve. Addition of a low pressure alarm.	21
		Insufficient Richin flowrate.	Maintaining the same composition, temperature and pressure decrease in the stripper. Economic loss due to less CO ₂ separated.	Careful monitoring of the process conditions. Addition of low flowrate and pressure indicators and alarms. Monitoring of Richin flowrate.	22

		Temperature lower than expected.	Volume contraction for the CO ₂ out stream. Economic loss due to low pressure that afterwards will need to be increased.	Addition of pressure and temperature indicators and alarms. Frequent inspections and maintenance of the cooling equipment.	23
	Pressure	Wrong calibration of the flow or temperature sensor, failure of the control circuit or failure of the actuator.	Economic loss due to low pressure that afterwards will need to be increased.	Addition of a control valve in series. Installation of a low pressure alarm.	24
		Rupture or loss of the pipe, flange loss.	Economic loss for the release of CO ₂ .	Frequent inspections and maintenance. Installation of low pressure alarm.	25
		Insufficient stripper pressure.	Analogous consequences of the point 24.	Addition of low pressure alarm.	26
		Temperature lower than expected.	Volume contraction of CO ₂ out stream. Analogous consequences of the point 24.	Addition of pressure and temperature indicators and alarms. Frequent inspections and maintenance of the condenser.	27
		Excessive cooling of the condenser.	Analogous consequences of the point 27.	. Analogous measures of the point 23. Automatic control of the cooling water flowrate.	28
	Temperature	Temperature drop in the stripper (insufficient heat from the reboiler and/or cold Richin stream).	Analogous consequences of the point 27.	Addition of pressure and temperature indicators and alarms. Monitoring of the stripper feeding.	29
PART OF		Composition	Decreased performance of the stripper (more water and MEA and less CO ₂ in CO ₂ out stream).	Economic loss for reduced CO ₂ content.	Accurate monitoring of the CO ₂ out stream composition to evaluate an eventual intervention.
	Richin composition changed.		Possible formation of flammable mixtures and possible economical loss.	Accurate monitoring and control of the Richin stream.	31

Table 5.4. Hazop of the COND stream

Guide word	Deviation	Possible causes	Consequences	Proposed measures		
NO	Flow	Catastrophic rupture of the stripper.	Economic loss for serious plant damage. Release of toxic and/or flammable substances. Possible explosions.	Frequent inspections and maintenance. Advancement of an emergency plan.	1	
		Rupture of the pipe.	Release of water.	Frequent inspections and maintenance. Installation of low pressure and low flowrate alarms.	2	
MORE	Flow	Manual valve blocked in fully-open position.	Reflux flowrate decreases until it reaches zero, thus tripper performance worsens.	Installation of a control valve in series and of a large flow alarm.	3	
	Pressure	Manual valve partially or fully-closed.	Possible flange disconnection with release of water.	Installation of control system and control valve in parallel. Installation of low flowrate and high pressure alarms.	4	
		Irradiation from external fire.	Possible collapse of pipes with release of water. Possible formation of carbamate.	Installation of water curtains. Installation of high pressure and temperature alarms.	5	
	Temperature	Excessive Richin temperature.	No consequences if excess is limited. Possible evaporation of MEA, thus Cond changes its composition. Possible formation of carbamate.	Addition of high temperature alarm. Monitoring of Cond composition.	6	
		Malfunctioning of the stripper (reboiler is heating more than necessary and/or condenser is cooling less than necessary).	Analogous consequences of the point 6.	Installation of high temperature and high pressure alarms on Cond stream.	7	
		Irradiation from external fire.	Possible collapse of pipes. Possible MEA evaporation and formation of carbamate.	Analogous measures of the point 5.	8	
	LESS	Flow	Manual valve blocked in partially-closed position.	Increased reflux flowrate, thus increased heat duty.	Installation of control system and control valve in parallel. Installation of low flowrate and high pressure alarms.	9

		Rupture or loss of the pipe, flange loss.	Loss of water from the pipe.	Frequent inspections and maintenance. Installation of low flowrate and low pressure alarms.	10
		Insufficient Richin flowrate.	Maintaining the same composition, temperature and pressure decrease in the stripper. Reflux flowrate, as well as Cond flowrate, decreases, thus stripper performance worsens.	Careful monitoring of the process conditions. Addition of pressure and flowrate indicators and alarms. Monitoring of Richin flowrate.	11
		Stripper temperature lower than expected (ex. Reboiler is heating less than wanted).	Reflux flowrate decreases thus stripper performance worsen.	Addition of pressure and temperature indicators and alarms. Monitoring of steam conditions.	12
	Pressure	Rupture or loss of the pipe, flange loss.	Analogous consequences of the point 10.	Analogous measures of the point 10.	13
	Temperature	Condenser is cooling more than necessary.	No consequences if cooling is not excessive.	Installation of low temperature alarms on Cond stream. Installation of temperature indicators in condenser utility stream.	14
PART OF	Composition	Temperature higher than expected.	Possible increased presence of MEA. Possible formation of carbamate.	Accurate control and monitoring of the stream composition.	15

Table 5.5. Hazop of the Reboiler steam stream

Guide word	Deviation	Possible causes	Consequences	Proposed measures	
NO	Flow	Control valve blocked in closed position.	Stripper stops working.	Arrest of the feeding. Installation of a by-pass. Installation of low pressure and low flowrate alarms after the control valve.	1
		Rupture of the pipe.	Release of hot steam.	Frequent inspections and maintenance. Installation of low pressure and low flowrate alarms.	2
		Wrong calibration of the flow sensor, failure of the	Analogous consequences of the point 1.	Installation of valve and control system in parallel.	3

		control circuit or failure of the actuator.			
		Absence of steam generation upstream.	Analogous consequences of the point 1.	Addition of low flowrate and low pressure alarms upstream the control valve, and eventually plant shutdown.	4
MORE	Flow	Control valve blocked in partially or fully-open position.	Stripper temperature and pressure increase with possible formation of carbamate. Possible evaporation of MEA.	Addition of a manual valve in series. Installation of a high flowrate alarm.	5
		Wrong calibration of the flow sensor, failure of the control circuit or failure of the actuator.	Analogous consequences of the point 5.	Analogous measures of the point 5.	6
		Excessive steam pressure and consequent inability to control flowrate through the valve.	Analogous consequences of the point 5.	Analogous measures of the point 5. Addition of high pressure and flowrate alarms.	7
	Pressure	Control valve blocked in partially closed position.	Possible corruption of the control valve. Possible increase of stripper temperature and pressure. Possible disconnection of the flanges. Possible steam condensation.	Analogous measures of the point 5. Installation of high pressure alarm.	8
		Wrong calibration of the flow sensor, failure of the control circuit or failure of the actuator.	Analogous consequences of the point 8.	Installation of control system and control valve in parallel. Installation of high pressure alarm.	9
	Temperature	Increase of temperature upstream.	Analogous consequences of the point 5.	Addition of high steam pressure alarm.	10
		Irradiation from external fire.	Possible increase of stripper temperature. Possible formation of carbamate. Possible evaporation of MEA. Possible failure of the pipes.	Addition of high steam temperature alarm. Installation of water curtains.	11

LESS	Flow	Control valve blocked in partially closed position.	Stripper temperature decreases, thus performance decreases.	Analogous measures of the point 9. Installation of low flowrate alarm.	12	
		Wrong calibration of the flow sensor, failure of the control circuit or failure of the actuator.	Analogous consequences of the point 12.	Analogous measures of the point 12.	13	
		Insufficient incoming steam pressure.	Analogous consequences of the point 12.	Addition of low flowrate and low pressure alarms.	14	
		Rupture or loss of the pipe.	Analogous consequences of the point 12. Possible release of a hot steam jet.	Frequent inspections and maintenance. Installation of a flowrate alarm and plant shutdown in case of serious lack of steam. Installation of low pressure alarm.	15	
	Pressure	Insufficient incoming steam pressure.	Analogous consequences of the point 12.	Addition of a low pressure alarm.	16	
		Wrong calibration of the flow sensor, failure of the control circuit or failure of the actuator.	Analogous consequences of the point 12.	Installation of a low pressure and plant shutdown in case of serious lack of steam.	17	
		Rupture or loss of the pipe.	Analogous consequences of the point 15.	Frequent inspections and maintenance. Installation of low pressure alarm and eventual plant shutdown in case of serious lack of steam.	18	
	Temperature	Insufficient incoming steam temperature.	Possible stripper temperature diminution. Possible steam condensation.	Addition of a temperature alarm and eventual plant shutdown.	19	
	PART OF	Composition	Improper pre-treatment of water upstream.	Possible equipment corrosion.	Frequent inspections and maintenance.	20

Table 5.6. Hazop of the Reflux stream

Guide word	Deviation	Possible causes	Consequences	Proposed measures	
NO	Flow	Control valve blocked in closed position.	Stripper stops working.	Arrest of the feeding. Installation of a by-pass. Installation of low pressure and low flowrate alarms after the control valve.	1
		Rupture of the pipe.	Release of water.	Frequent inspections and maintenance. Installation of low pressure and low flowrate alarms.	2
		Wrong calibration of the level sensor, failure of the control circuit or failure of the actuator.	Analogous consequences of the point 1.	Analogous measures of the point 1.	3
		Catastrophic rupture of the stripper.	Economic loss for serious plant damage. Release of toxic and/or flammable substances. Possible explosions.	Frequent inspections and maintenance. Advancement of an emergency plan.	4
MORE	Flow	Control valve blocked in partially open position.	Stripper performance increased, but more heat duty needed.	Addition of a control valve in series. Installation of high flowrate alarm.	5
		Wrong calibration of the level sensor, failure of the control circuit or failure of the actuator.	Analogous consequences of the point 5.	Analogous measures of the point 5.	6
		Excessive Richin flowrate.	Maintaining the same composition, temperature and pressure drop in the stripper when the reboiler does not increase its duty.	Careful monitoring of the process conditions. Installation of pressure and temperature indicators.	7
	Pressure	Control valve partially or fully-closed.	Possible flange disconnection and release of water.	Installation of control system and control valve in parallel. Installation of low flowrate and high pressure alarms.	8
		Wrong calibration of the level sensor, failure of the control circuit	Analogous consequences of the point 8.	Analogous measures of the point 8.	9

		or failure of the actuator.			
	Temperature	Excessive Richin temperature.	Possible water evaporation with consequent pressure increase. Possible formation of carbamate.	Installation of high temperature alarm in the Richin stream. Addition of high pressure alarm.	10
		Irradiation from external fire.	Analogous consequences of the point 10. Possible collapse of the equipment.	Installation of water curtain. Addition of high pressure and temperature indicators and alarms.	11
		Malfunctioning of the condenser.	Possible water evaporation with consequent pressure increase.	Installation of control system and control valve in the condenser.	12
LESS	Flow	Insufficient Richin flowrate.	Maintaining the same composition, temperature and pressure decrease in the stripper. Decreased separation efficiency.	Careful monitoring of the process conditions. Addition of pressure and temperature alarms and indicators. Monitoring of Richin flowrate.	13
		Rupture or loss from the pipe, loss from the flange.	Release of water. Decreased stripper performance.	Frequent inspections and maintenance. Installation of low flowrate alarm.	14
		Control valve blocked in partially-closed position.	Decreased stripper performance.	Installation of control system and control valve in parallel. Installation of low flow and high pressure alarms.	15
		Wrong calibration of the level sensor, failure of the control circuit or failure of the actuator.	Analogous consequences of the point 15.	Analogous measures of the point 15.	16
	Pressure	Wrong calibration of the level sensor, failure of the control circuit or failure of the actuator.	No consequences if diminution is not large.	Addition of a control valve in series. Installation of a low pressure alarm.	17
		Rupture or loss from the pipe, loss from the flange.	Release of water. Decreased stripper performance.	Frequent inspections and maintenance. Installation of low pressure alarm.	18
	Temperature	Condenser is cooling more than expected.	Possible water solidification. Decreased stripper temperature and consequent performance diminution.	Addition of temperature indicators and alarms. Monitoring of reflux temperature.	19

		Lower stripper temperature.	Possible water solidification.	Addition of temperature, pressure and flowrate indicators and alarms.	20
PART OF	Composition	Higher stripper temperature.	Possible evaporation of MEA and consequent increased presence in the reflux.	Accurate monitoring of reflux composition.	21

5.2 Fault Tree and Event Tree Analysis

Although the Hazop was performed in a very accurate way, it is still a qualitative method. Now it is time to apply a technique which can give a quantitative evaluation of the occurrence frequency: this is the FTA. It starts from a Top event, which in this case is a release from the stripping column, that obviously can come from a lot of different causes linked to stream conditions, equipment malfunctioning, control systems failures, etc. The resulted FTA, which, for space reasons, will be shown divided into Figure 5.2 and Figure 5.3 in the following pages, is based on the simple P&ID presented in the previous paragraph, precisely in the Figure 5.1.

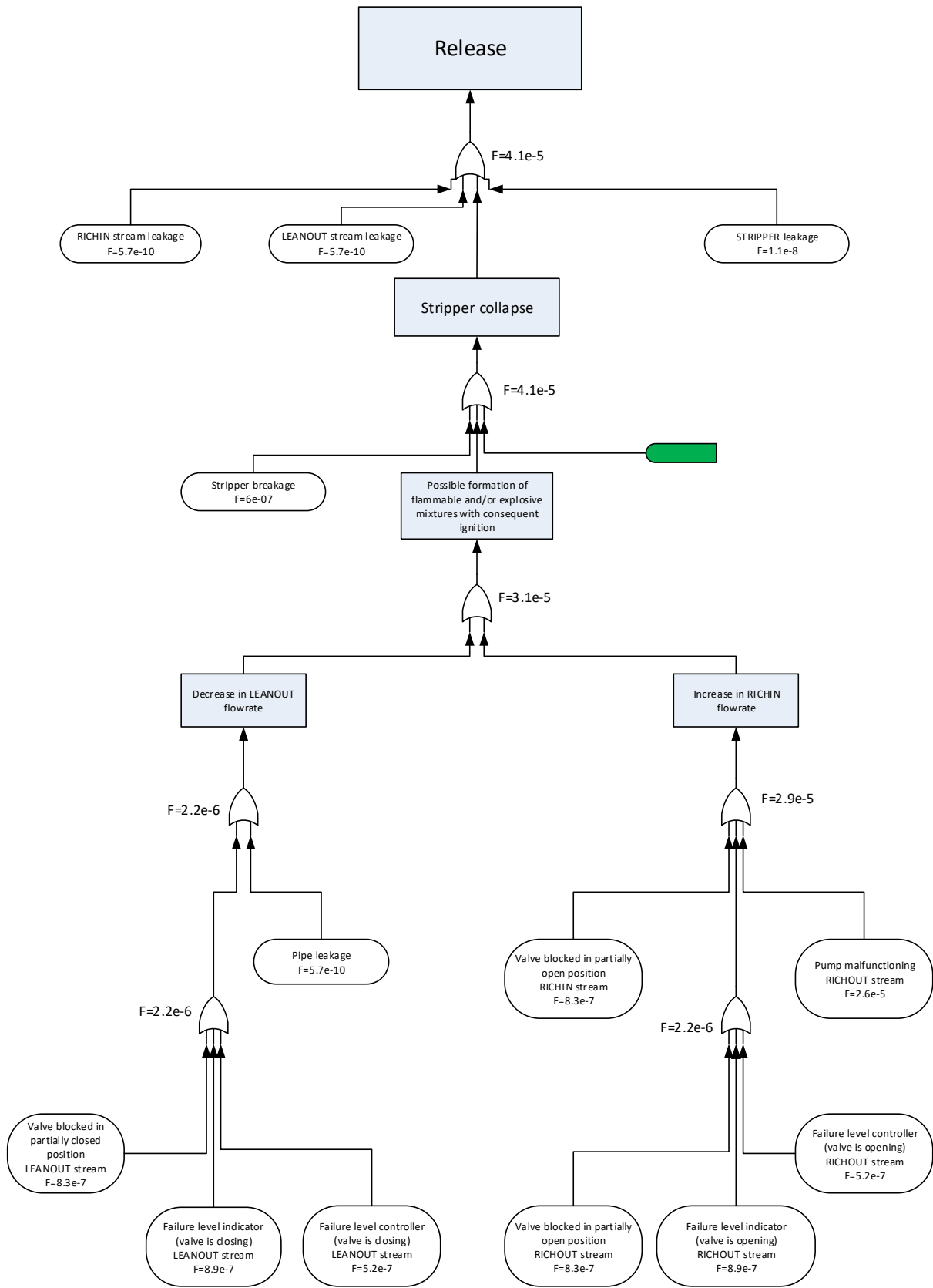


Figure 5.2. Part A of FTA of a MEA release from a stripping column

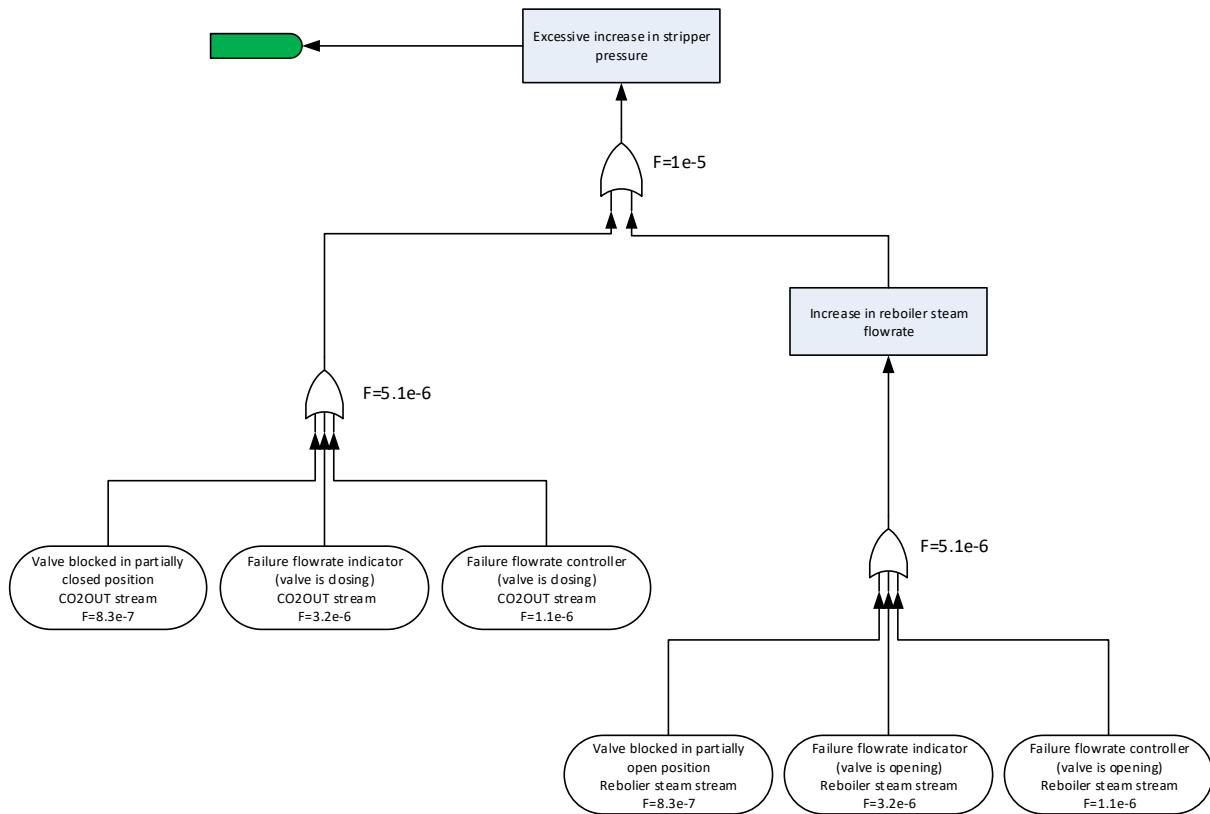


Figure 5.3. Part B of FTA of a MEA release from a stripping column

As can be seen in the figures, the resulted occurrence frequency of a release, for the piece of equipment represented in the P&ID, is really high, precisely about $4.1 \cdot 10^{-5}$ events/hour: this means 0.36 events/year, that is evidently not acceptable. Thus, the FTA needs some corrections to reach a more reasonable frequency. For this purpose, the Hazop analysis is absolutely helpful: by watching at it, the proposed measures to contrast the system alterations, e.g., installation of valves and alarms, can be inserted in the FTA and, consequently, the number of events per year will decrease of some orders of magnitude. The FTA with the modifications are represented in the Figure 5.4, 5.5, 5.6 and 5.7: for space reasons, they are in the following pages.

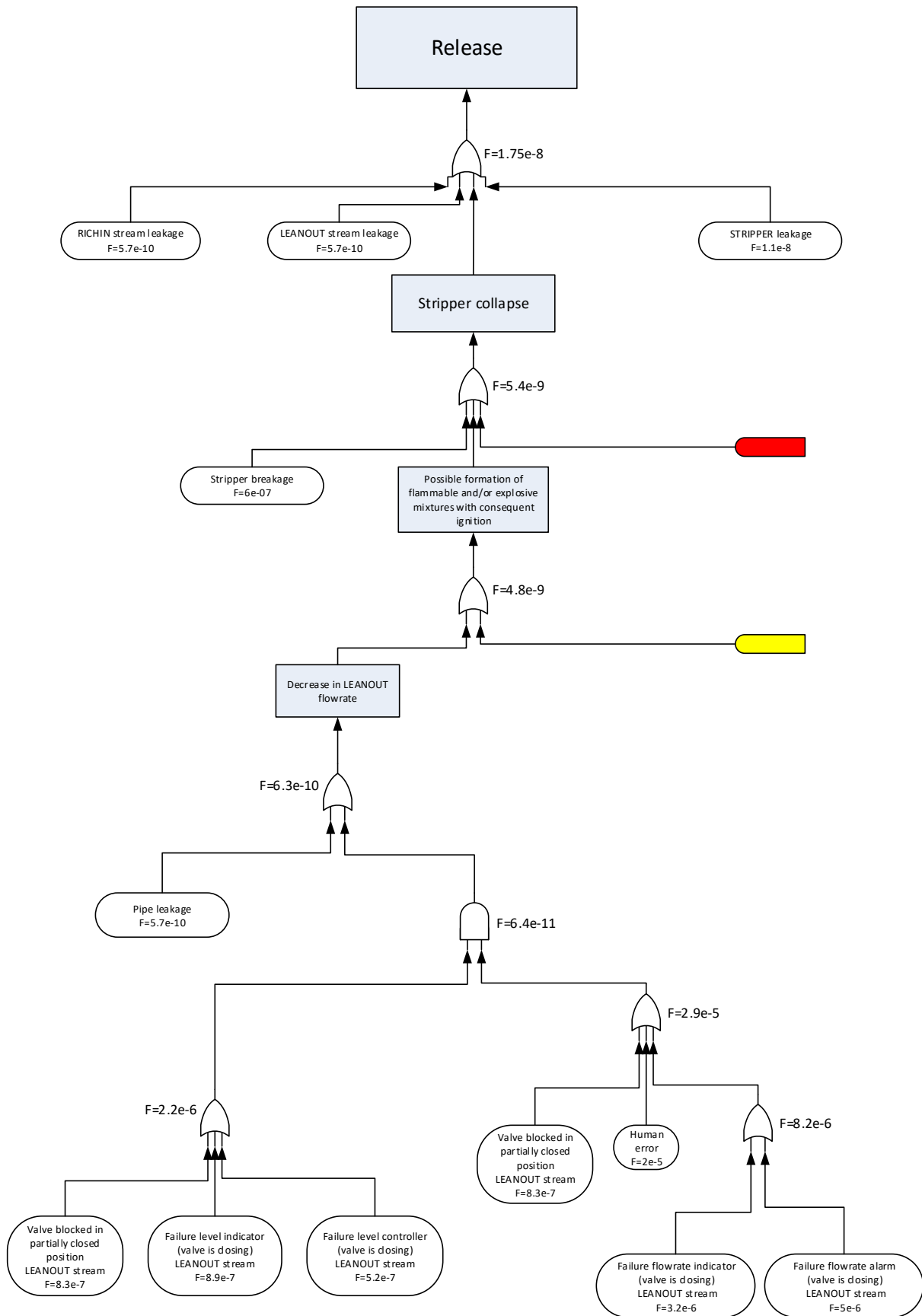


Figure 5.4. Part 1 of modified FTA of a MEA release from a stripping column

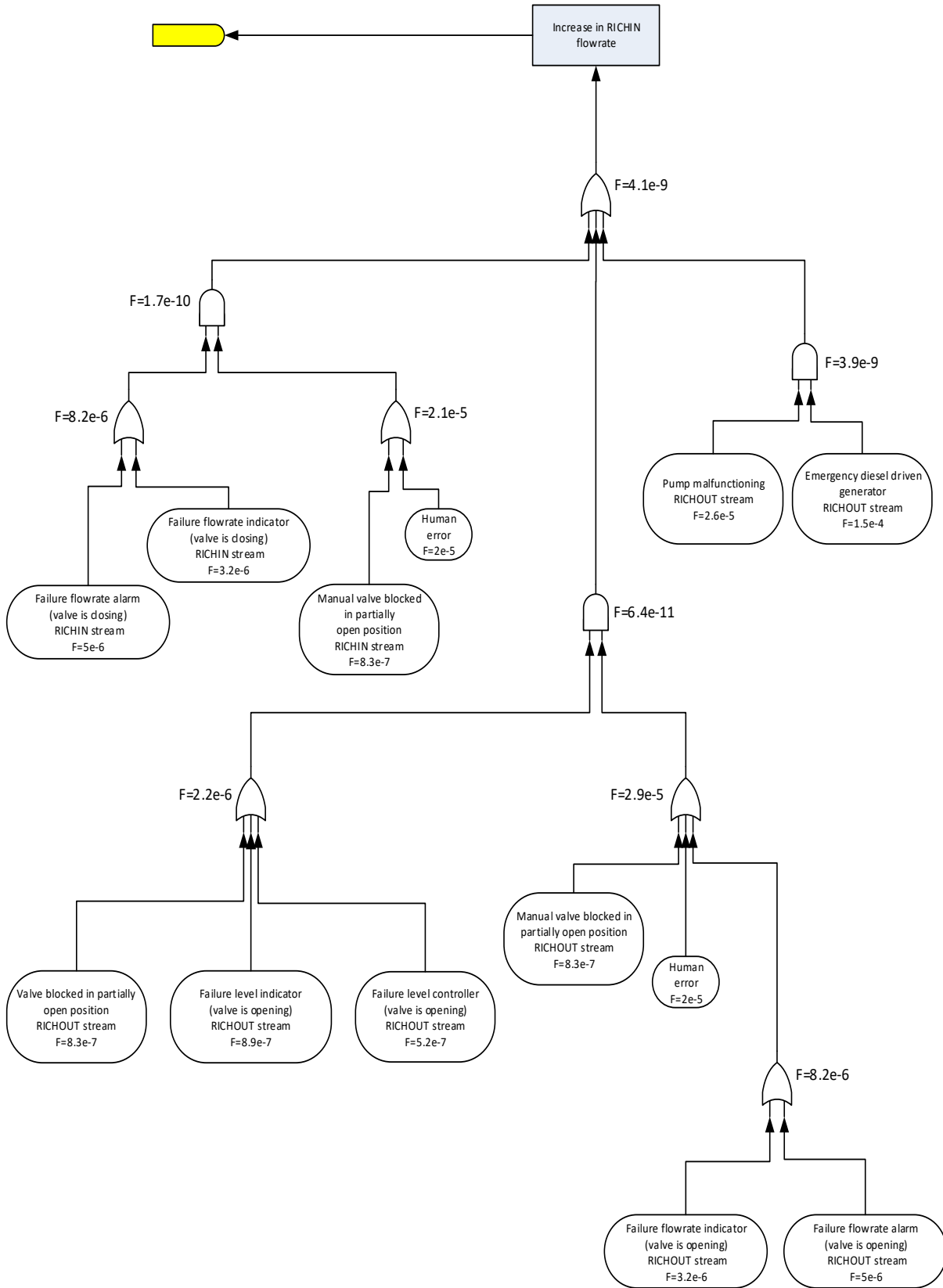


Figure 5.5. Part 2 of modified FTA of a MEA release from a stripping column

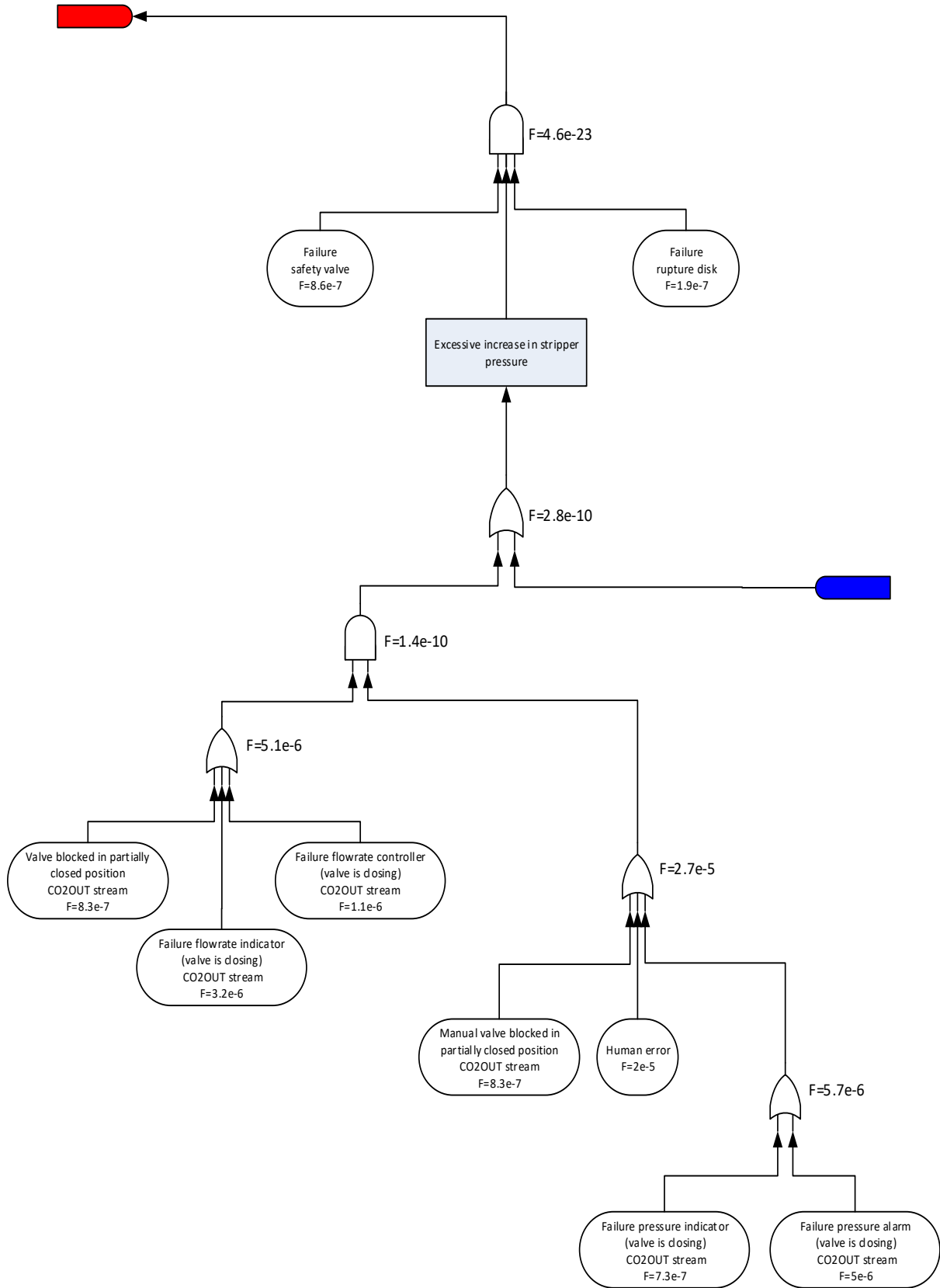


Figure 5.6. Part 3 of modified FTA of a MEA release from a stripping column

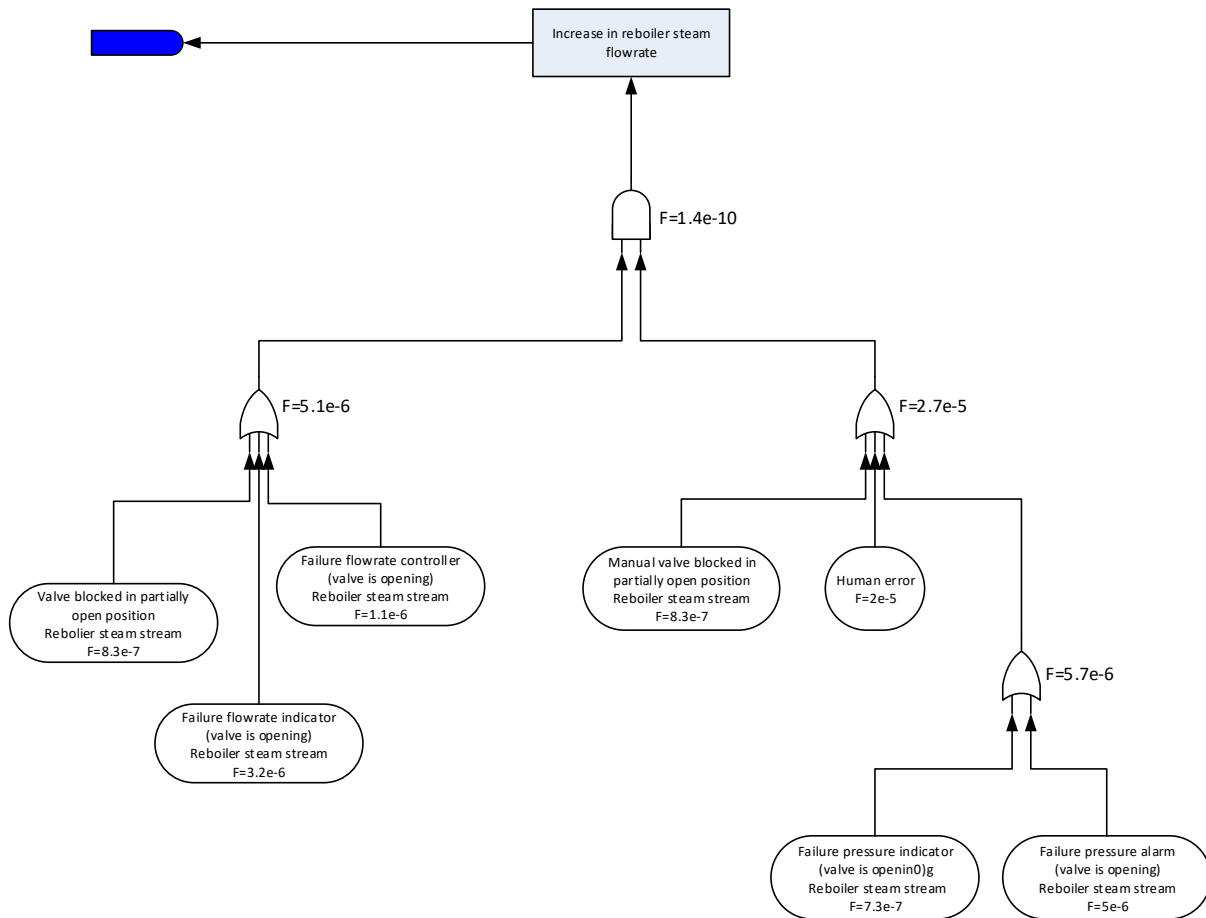


Figure 5.7. Part 4 of modified FTA of a MEA release from a stripping column

As can be seen from the previous figures, the occurrence frequency of the release is decreased a lot from the precedent case: it results $1.75 \cdot 10^{-8}$ events/hours that are equivalent of $1.53 \cdot 10^{-4}$ events/year. A really significant reduction happened, thanks to the improvements inserted: the frequency is more than 2000 times lower than before. The next step, after the occurrence frequency evaluation of the release, is the construction of the ETA in order to individuate all the possible scenarios that can originate. This is displayed in the Figure 5.8 in the following page.

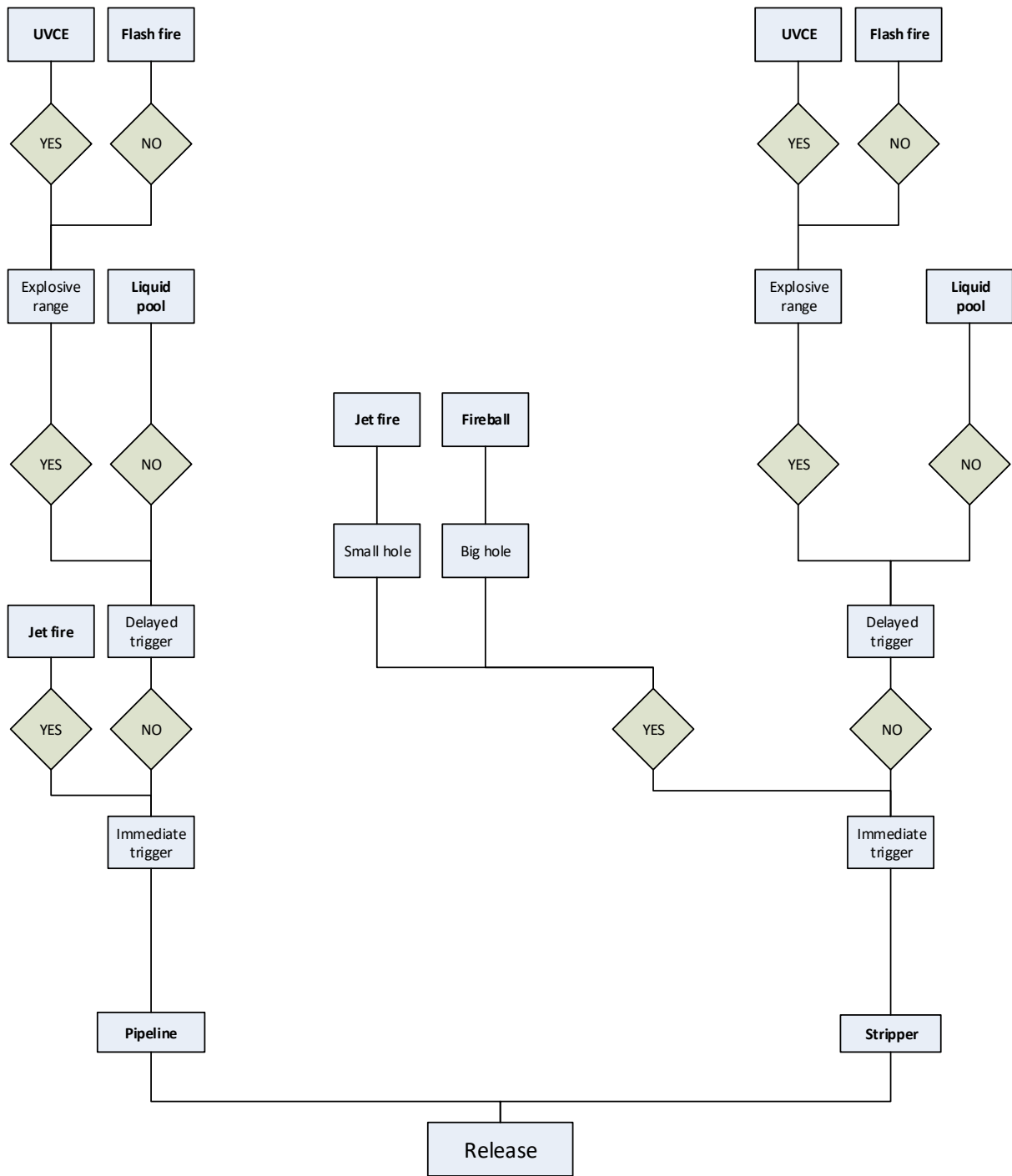


Figure 5.8. ETA of a MEA release from a stripping column

5.3 Aloha[®] simulation of the consequences

Subsequently to the achievement of FTA and ETA reports, it has been run a simulation on a hazard modeling software, which can give details about releases and it generates threat zone estimates for various type of hazards. The simulation details are summarized in the Figure 5.9. The location chosen for the release is the University of Kaiserslautern (Germany), where the pilot plant actually is. The atmospheric data have been set as mean local conditions.

```

SITE DATA:
Location: UNIVERSITY OF KAISERSLAUTERN, GERMANY
Building Air Exchanges Per Hour: 0.63 (unsheltered single storied)
Time: March 30, 2017 0737 hours ST (using computer's clock)

CHEMICAL DATA:
Chemical Name: ETHANOLAMINE
CAS Number: 141-43-5                               Molecular Weight: 61.08 g/mol
PAC-1: 6 ppm           PAC-2: 170 ppm           PAC-3: 1000 ppm
IDLH: 30 ppm           LEL: 30000 ppm           UEL: 131000 ppm
Ambient Boiling Point: 168.5° C
Vapor Pressure at Ambient Temperature: 3.16e-004 atm
Ambient Saturation Concentration: 326 ppm or 0.033%

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)
Wind: 3 meters/second from ESE at 3 meters
Ground Roughness: open country                     Cloud Cover: 5 tenths
Air Temperature: 20° C                             Stability Class: C
No Inversion Height                               Relative Humidity: 70%
  
```

Figure 5.9. Site data, Chemical data and Atmospheric data loaded in Aloha to start the simulation

The study of the consequences is structured in this way: three different temperatures and three different hole sizes are chosen at which the release exhibits. In particular, the temperatures are:

- 120 °C: usually the best practice temperature for the stripping section;
- 268 °C: the maximum temperature to which the Aspen Plus simulation reached the convergence without warnings in the material balances;
- 190 °C: an intermediate value between the previous ones.

The hole diameters instead are taken from the Standard API 581:

- Small: 0.25 in;
- Medium: 1 in;
- Large: 4 in.

Other simulation conditions that have to be specified:

- Every hole is considered on the stripper bottom;
- The MEA amount in the stripper is imposed to be 30 kg, as it is found to be during the process simulation in Aspen Plus;
- The opening on the wall is supposed to be circular;
- The ground temperature is supposed to be equal to the air temperature.

It has to be recognized also that there is a limit in this simulation: it has been used the same MEA mass contained in the stripper, but it does not take into account that there is not pure MEA but, in the pilot plant, is present a solution of about 30%.

5.3.1 Release temperature of 120°C

5.3.1.1 Case 1a: 120 °C, 0.25 in

Results are displayed in Figure 5.10.

```
Leak from hole in vertical cylindrical tank
Flammable chemical escaping from tank (not burning)
Tank Diameter: 0.2 meters           Tank Length: 3 meters
Tank Volume: 0.094 cubic meters
Tank contains liquid                Internal Temperature: 120° C
Chemical Mass in Tank: 30 kilograms Tank is 34% full
Circular Opening Diameter: 0.25 inches
Opening is 0 meters from tank bottom
Ground Type: Default soil
Ground Temperature: equal to ambient
Max Puddle Diameter: Unknown
Release Duration: ALOHA limited the duration to 1 hour
Max Average Sustained Release Rate: 3.99 grams/min
    (averaged over a minute or more)
Total Amount Released: 197 grams
Note: The chemical escaped as a liquid and formed an evaporating puddle.
The puddle spread to a diameter of 2.7 meters.
```

Figure 5.10. Release simulation results of case 1a (120 °C, 0.25 in) in Aloha

At this temperature, the MEA is liquid. Aloha displayed a message saying that “Threat zone was not drawn because effects of near-field patchiness make dispersion predictions less reliable for short distances”: in this case, Aloha was not able to provide a reliable result because the release was really scarce (the total amount released was only about 197 g at a flowrate of almost 4 g/min).

5.3.1.2 Case 1b: 120 °C, 1 in

Results are displayed in Figure 5.11.

```

Leak from hole in vertical cylindrical tank
Flammable chemical escaping from tank (not burning)
Tank Diameter: 0.2 meters           Tank Length: 3 meters
Tank Volume: 0.094 cubic meters
Tank contains liquid                Internal Temperature: 120° C
Chemical Mass in Tank: 30 kilograms Tank is 34% full
Circular Opening Diameter: 1 inches
Opening is 0 meters from tank bottom
Ground Type: Default soil
Ground Temperature: equal to ambient
Max Puddle Diameter: Unknown
Release Duration: ALOHA limited the duration to 1 hour
Max Average Sustained Release Rate: 49.4 grams/min
    (averaged over a minute or more)
Total Amount Released: 245 grams
Note: The chemical escaped as a liquid and formed an evaporating puddle.
The puddle spread to a diameter of 2.8 meters.

```

Figure 5.11. Release simulation results of case 1b (120 °C, 1 in) in Aloha

Results are analogous of the previous one. Also this time Aloha was not able to provide a reliable result because the release was really small (the total amount released was only about 245 g at a flowrate of almost 50 g/min).

5.3.1.3 Case 1c: 120 °C, 4 in

Results are displayed in Figure 5.12.

```

Leak from hole in vertical cylindrical tank
Flammable chemical escaping from tank (not burning)
Tank Diameter: 0.2 meters           Tank Length: 3 meters
Tank Volume: 0.094 cubic meters
Tank contains liquid                Internal Temperature: 120° C
Chemical Mass in Tank: 30 kilograms Tank is 34% full
Circular Opening Diameter: 4 inches
Opening is 0 meters from tank bottom
Ground Type: Default soil
Ground Temperature: equal to ambient
Max Puddle Diameter: Unknown
Release Duration: ALOHA limited the duration to 1 hour
Max Average Sustained Release Rate: 154 grams/min
    (averaged over a minute or more)
Total Amount Released: 330 grams
Note: The chemical escaped as a liquid and formed an evaporating puddle.
The puddle spread to a diameter of 2.9 meters.

```

Figure 5.12. Release simulation results of case 1c (120 °C, 4 in) in Aloha

Results are analogous of the previous one. Also this time Aloha was not able to provide a reliable result because the release was really small (the total amount released was only about 330 g at a flowrate of almost 154 g/min).

5.3.2 Release temperature of 190°C

5.3.2.1 Case 2a: 190 °C, 0.25 in

Results are displayed in Figure 5.13.

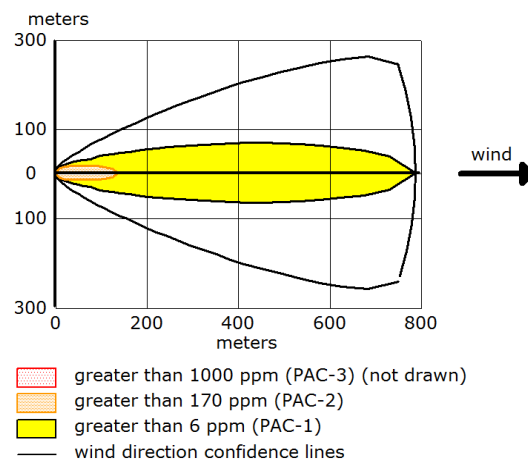


Figure 5.13. Plot of release simulation of case 2a (190 °C, 0.25 in) in Aloha

All the MEA contained in the stripper has been released at a flowrate of 14.8 kg/min. It can be seen from the plot that a plume of gaseous MEA is forming: in fact, in this case the release temperature is a bit higher than the MEA boiling temperature (168.8°C).

5.3.2.2 Case 2b: 190 °C, 1 in

Results are displayed in Figure 5.14.

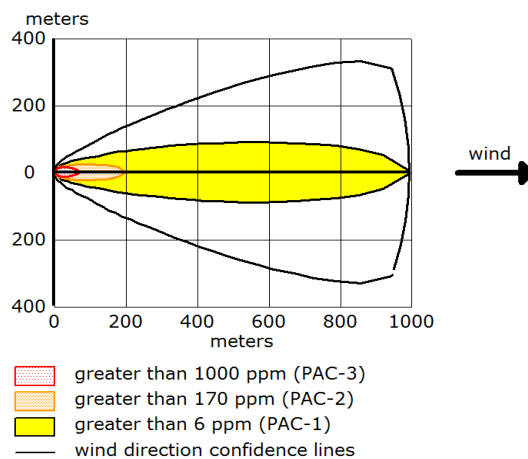


Figure 5.14. Plot of release simulation of case 2b (190 °C, 1 in) in Aloha

Results are analogous of the previous one: obviously, the release flowrate and the area involved are bigger and consequent health risks too (appearance of the red zone in the plot).

5.3.2.3 Case 2c: 190 °C, 4 in

Results are displayed in Figure 5.15.

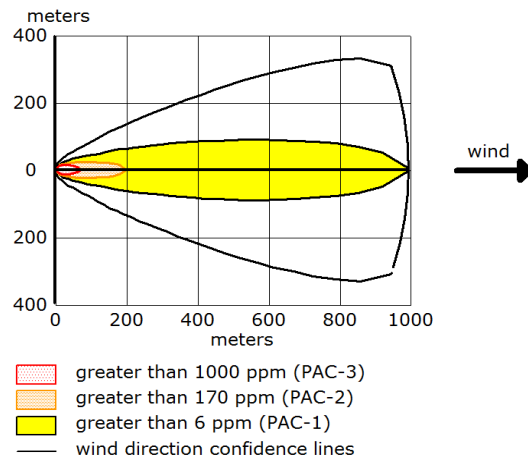


Figure 5.15. Plot of release simulation of case 2c (190 °C, 4 in) in Aloha

Results seem to be perfectly identical of the previous case: probably the system have reached a sort of asymptote in terms of release flowrate.

5.3.3 Release temperature of 268°C

5.3.3.1 Case 3a: 268 °C, 0.25 in

Results are displayed in Figure 5.16.

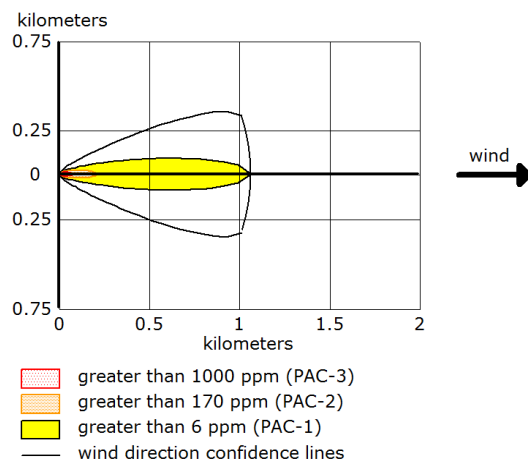


Figure 5.16. Plot of release simulation of case 3a (268 °C, 0.25 in) in Aloha

Results are analogous of the previous one: obviously, the release flowrate and the area involved are bigger and consequent health risks too thanks to the higher temperature.

5.3.3.2 Case 3b: 268 °C, 1 in

Results are displayed in Figure 5.17.

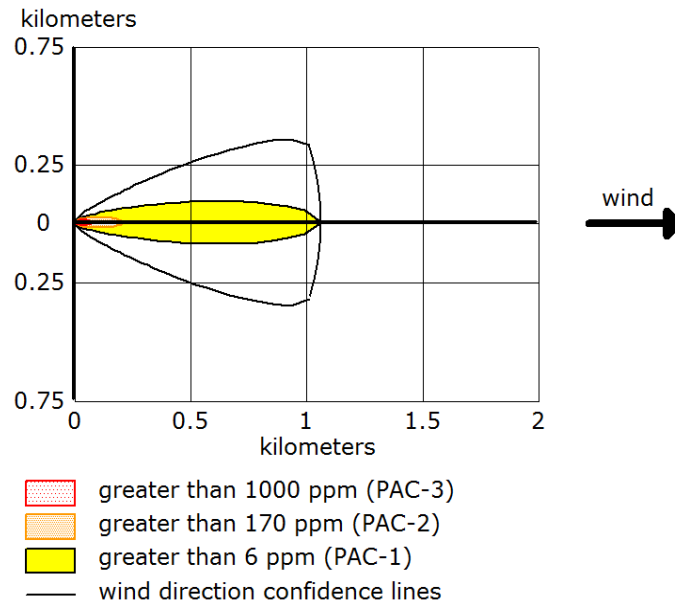


Figure 5.17. Plot of release simulation of case 3b (268 °C, 1 in) in Aloha

Results seem to be perfectly identical of the previous case: probably the system have reached a sort of asymptote in terms of release flowrate.

5.3.3.3 Case 3c: 268 °C, 4 in

Results are displayed in Figure 5.18.

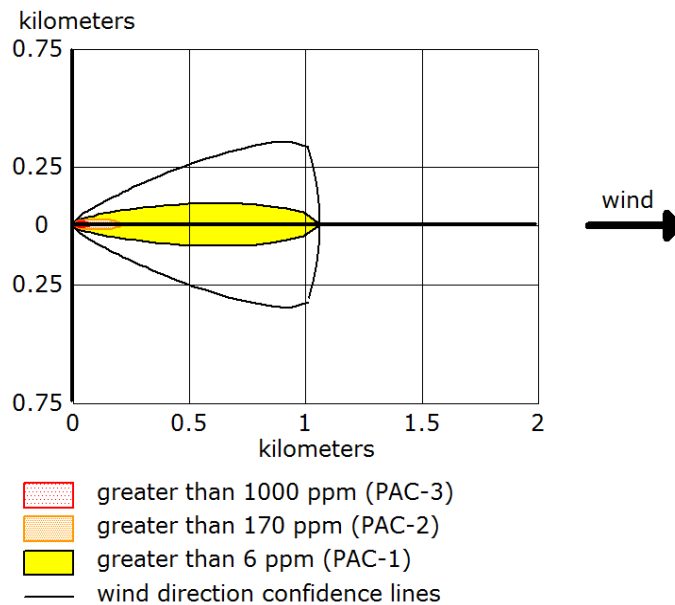


Figure 5.18. Plot of release simulation of case 3c (268 °C, 4 in) in Aloha

Results seem to be perfectly identical of the previous case: probably the system have reached a sort of asymptote in terms of release flowrate.

Conclusions

In this century, the attention for the environment is becoming always more and more effective. There are a lot of ways to reduce the CO₂ emissions in the atmosphere, in order to try to reduce the greenhouse effects. In this work, the focus has been on the Carbon Capture and Storage technology, in particular on the capture section: the goal was to support the advancement of the known best practices in this field.

Initially a historical analysis of the industrial accidents regarding the substances that can be used in the capture section of a CCS plant has been done, with the result that the manipulation of monoethanolamine, one of the solvents between the chemical absorption processes, is probable more critical than other capture process.

Afterwards, an Aspen Plus simulation on a pilot plant operating a carbon capture process with MEA, permitted the identification of the main critical part of the plant that has been verified to be the stripping column. That has been obtained by running several simulations with a continuous increase in the flue gas temperature, until 268°C has been reached: this value is important because issues arose in the material balances, in particular the charge balance has not been respected anymore up from this point, right in the stripper.

After these considerations, a risk analysis, which has been performed in this thesis, has brought a lot of different improvements, in particular through the Hazop. From this technique resulted that there was the need of a lot of improvements, like the installation of pressure, flowrate and temperature alarms, manual valves, control systems, emergency generators, addition of by-pass streams, writing an emergency plan and the prediction of an emergency shut down of the plant. This was the list of all the countermeasures the pilot plant needed to overcome all possible malfunctioning, equipment failures and, in general, process alterations from the ordinary operations, with the aim of reduce the occurrence frequency of a MEA release; that has been verified with the help of the Fault Tree Analysis done before and after that the modifications have been carried out. This brought to a reduction of more than 2000 times of the frequency of the MEA release: precisely the first FTA had a frequency of 0.36 events/year and the modified one reached $1.53 \cdot 10^{-4}$ events/year. It is also strongly suggested to carry out the risk analysis in parallel with the process design because there is not so much experience with this technology, so the predictive part is extremely important and have to be really accurate.

To conclude this thesis, it has been performed a simulation with Aloha, a hazard modeling program, to graphically represent a MEA release between different conditions both in terms of temperature and in terms of hole diameters in the stripper. It resulted that by increasing the temperature and the hole size the seriousness of the release is intensified, with an enlarged spread of the substance.

Appendix

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ORGANICS

MATERIAL SAFETY DATA SHEET Ethanolamine

Section 1 - Chemical Product and Company Identification

MSDS Name:	Ethanolamine
Catalog Numbers:	14958-0000, 14958-0010, 14958-0025, 14958-0200, 14958-0250
Synonyms:	2-Aminoethanol
Company Identification:	Acros Organics BVBA Janssen Pharmaceuticaaan 3a 2440 Geel, Belgium
Company Identification: (USA)	Acros Organics One Reagent Lane Fair Lawn, NJ 07410
For information in the US, call:	800-ACROS-01
For information in Europe, call:	+32 14 57 52 11
Emergency Number, Europe:	+32 14 57 52 99
Emergency Number US:	201-796-7100
CHEMTREC Phone Number, US:	800-424-9300
CHEMTREC Phone Number, Europe:	703-527-3887

Section 2 - Composition, Information on Ingredients

CAS#	Chemical Name:	%	EINECS#
141-43-5	Ethanolamine	99%	205-483-3

Hazard Symbols: C



Risk Phrases: 20/21/22 34

Section 3 - Hazards Identification

EMERGENCY OVERVIEW

Harmful by inhalation, in contact with skin and if swallowed. Causes burns.

Potential Health Effects

Eye:	Causes eye burns.
Skin:	Harmful if absorbed through the skin. Causes skin burns.
Ingestion:	Harmful if swallowed. Causes gastrointestinal tract burns.
Inhalation:	Harmful if inhaled. Causes chemical burns to the respiratory tract.
Chronic:	

Section 4 - First Aid Measures

Eyes:	Flush eyes with plenty of water for at least 15 minutes, occasionally lifting the upper and lower eyelids. Get medical aid immediately.
Skin:	Get medical aid immediately. Flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes.
Ingestion:	Get medical aid immediately. Wash mouth out with water.
Inhalation:	Get medical aid immediately. Remove from exposure and move to fresh air immediately. If not breathing, give artificial respiration. If breathing is difficult, give oxygen.

Notes to Physician:

Section 5 - Fire Fighting Measures

General Information:	As in any fire, wear a self-contained breathing apparatus in pressure-demand, MSHA/NIOSH (approved or equivalent), and full protective gear. Will burn if involved in a fire. Combustible liquid.
Extinguishing Media:	In case of fire, use water, dry chemical, chemical foam, or alcohol-resistant foam.

Section 6 - Accidental Release Measures

General Information:	Use proper personal protective equipment as indicated in Section 8.
Spills/Leaks:	Absorb spill with inert material (e.g. vermiculite, sand or earth), then place in suitable container.

Section 7 - Handling and Storage

Handling:	Avoid breathing dust, vapor, mist, or gas. Avoid contact with skin and eyes.
Storage:	Store in a cool, dry place. Store in a tightly closed container. Store under nitrogen.

Section 8 - Exposure Controls, Personal Protection

Engineering Controls:

Facilities storing or utilizing this material should be equipped with an eyewash facility and a safety shower. Use adequate ventilation to keep airborne concentrations low.

Exposure Limits

CAS# 141-43-5:

United Kingdom, WEL - TWA: 3 ppm TWA; 7.6 mg/m³ TWA United Kingdom, WEL - STEL: 6 ppm STEL; 15 mg/m³ STEL
 United States OSHA: 3 ppm TWA; 6 mg/m³ TWA
 Belgium - TWA: 3 ppm VLE; 7.6 mg/m³ VLE Belgium - STEL: 6 ppm VLE; 15 mg/m³ VLE
 France - VME: 3 ppm VME; 8 mg/m³ VME
 Germany: 2 ppm TWA; 5.1 mg/m³ TWA Germany: skin notation
 Japan: 3 ppm OEL; 7.5 mg/m³ OEL
 Malaysia: 3 ppm TWA; 7.5 mg/m³ TWA
 Netherlands: 3 ppm STEL; 7.6 mg/m³ STEL Netherlands: 1 ppm MAC; 2.5 mg/m³ MAC
 Spain: 3 ppm VLA-ED; 7.5 mg/m³ VLA-ED Spain: 6 ppm VLA-EC; 15 mg/m³ VLA-EC

Personal Protective Equipment

Eyes:	Wear chemical splash goggles.
Skin:	Wear appropriate protective gloves to prevent skin exposure.
Clothing:	Wear appropriate protective clothing to prevent skin exposure.
Respirators:	Follow the OSHA respirator regulations found in 29 CFR 1910.134 or European Standard EN 149. Use a NIOSH/MSHA or European Standard EN 149 approved respirator if exposure limits are exceeded or if irritation or other symptoms are experienced.

Section 9 - Physical and Chemical Properties

Physical State: Clear liquid
Color: APHA: 15 max
Odor: ammonia-like
pH: Not available
Vapor Pressure: 0.48mmHg @20 deg C
Viscosity: 24 cP @20 deg C
Boiling Point: 170 deg C @760mmHg (338.00°F)
Freezing/Melting Point: 10.3 deg C (50.54°F)
Autoignition Temperature: 450 deg C (842.00 deg F)
Flash Point: 85 deg C (185.00 deg F)
Explosion Limits: Lower: 5.5 Vol %
Explosion Limits: Upper: 17 Vol %
Decomposition Temperature: Not available
Solubility in water: Miscible
Specific Gravity/Density: 1.012
Molecular Formula: C2H7NO
Molecular Weight: 61.08

Section 10 - Stability and Reactivity

Chemical Stability: Stable under normal temperatures and pressures. Air sensitive. Hygroscopic: absorbs moisture or water from the air.
Conditions to Avoid: Incompatible materials, light, exposure to air, exposure to moist air or water.
Incompatibilities with Other Materials: Oxidizing agents, acids, acid chlorides, aluminum, anhydrides, copper, galvanized iron.
Hazardous Decomposition Products: Nitrogen oxides, carbon monoxide, carbon dioxide.
Hazardous Polymerization: Has not been reported.

Section 11 - Toxicological Information

RTECS#: CAS# 141-43-5: KJ5775000
LD50/LC50: RTECS:
CAS# 141-43-5: Draize test, rabbit, eye: 250 ug Severe;
 Oral, mouse: LD50 = 700 mg/kg;
 Oral, rabbit: LD50 = 1 gm/kg;
 Oral, rat: LD50 = 1720 mg/kg;
 Skin, rabbit: LD50 = 1 mL/kg;
 .
Carcinogenicity: Ethanolamine - Not listed as a carcinogen by ACGIH, IARC, NTP, or CA Prop 65.
Other: See actual entry in RTECS for complete information.

Section 12 - Ecological Information

Ecotoxicity: Not available

Section 13 - Disposal Considerations

Dispose of in a manner consistent with federal, state, and local regulations.

Section 14 - Transport Information

	IATA	IMO	RID/ADR
Shipping Name:	ETHANOLAMINE	ETHANOLAMINE	ETHANOLAMINE

Hazard Class:	8	8	8
UN Number:	2491	2491	2491
Packing Group:	III	III	III

Section 15 - Regulatory Information

European/International Regulations

European Labeling in Accordance with EC Directives

Hazard Symbols: C

Risk Phrases:

R 20/21/22 Harmful by inhalation, in contact with skin and if swallowed.

R 34 Causes burns.

Safety Phrases:

S 26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

S 36/37/39 Wear suitable protective clothing, gloves and eye/face protection.

S 45 In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

WGK (Water Danger/Protection)

CAS# 141-43-5: 1

Canada

CAS# 141-43-5 is listed on Canada's DSL List

US Federal

TSCA

CAS# 141-43-5 is listed on the TSCA Inventory.

Section 16 - Other Information

MSDS Creation Date: 7/16/1996

Revision #2 Date 5/30/2005

Revisions were made in Sections: General revision.

The information above is believed to be accurate and represents the best information currently available to us. However, we make no warranty of merchantability or any other warranty, express or implied, with respect to such information, and we assume no liability resulting from its use. Users should make their own investigations to determine the suitability of the information for their particular purposes. In no event shall the company be liable for any claims, losses, or damages of any third party or for lost profits or any special, indirect, incidental, consequential, or exemplary damages howsoever arising, even if the company has been advised of the possibility of such damages.

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