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Risk Analysis of Sodium Hypochlorite Production Process

Maria Portarapillo, Marica Muscetta*, Almerinda Di Benedetto, Roberto Andreozzi

Università degli studi di Napoli Federico II, Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, P.le V. Tecchio, 80 - 80125, Napoli (IT)
marica.muscetta@unina.it

Sodium hypochlorite poses explosive hazards associated with its complex reactive chemistry. The production process of sodium hypochlorite consists of a first block where the chlorine, caustic soda and hydrogen are produced in an electrolytic cell from brine and a second block where chlorination of caustic soda to form hypochlorite is carried out. This process is characterized by several hazards such as chlorine gas toxicity, explosive hazards due to the presence of hydrogen and chlorine and corrosive hazards. Loss of control of such substances has the potential to cause high-consequence low-probability events. Thus, specific safety measures have to be designed to mitigate risk. In the present work, the risk assessment of the first block of the process is performed, focusing on hydrogen risks. To this end, HAZOP analysis was performed to identify the top events. For each top event, based on properly developed fault trees, the frequency analysis was performed. Eventually, the consequence analysis was carried out by the simulation of phenomena leading to dispersion and consequent ignition of the cloud as function of the distance from the source. Simulations were performed by means of the software PHAST.

1. Introduction

Sodium hypochlorite (NaClO) is a strong oxidizer, a disinfectant, extremely corrosive to metals, strongly alkaline and hypertonic (Tiwari et al., 2018); moreover, sodium hypochlorite is a bleaching agent (Flores et al., 2009). In turn, population growth and its corresponding increases in water consumption coupled with limited freshwater resources, makes water treatment the largest application for bleach, as well as the fastest-growing segment of bleach use (Intratec, 2019). Sodium hypochlorite chemical production is a well-established process in the chemical industry, and the principle behind its operation is also employed for preventing chlorine emissions in chlor-alkali plants (Intratec, 2019). Sodium hypochlorite is typically produced in the chlorine-soda process. The process for chlorine-soda production relies on the utilization of electrolytic membrane cells where hydrogen, chlorine and caustic soda are produced (Albuquerque et al., 2009), and a block in which hypochlorite is produced by chlorination of caustic soda. This process poses several hazards: chlorine gas toxicity, explosive hazards due to the presence of hydrogen and chlorine and corrosive hazards. Loss of control of such substances has the potential to cause high-consequence low-probability events. Recently, two explosions occurred at the Midland Resource Recovery (MRR) facility in Philippi, West Virginia, killing two workers and severely injuring another worker. The CSB determined that the probable cause of these incidents was reaction of unstable chemicals related to the presence of sodium hypochlorite (CSB Report, 2017). In this framework, risk assessment has shown its relevance when dealing with hazardous materials, considered by Pasman as the most dreadful risks (Pasman, 2015). Therefore, to effectively prevent accidents and to properly design safety measures, a risk of the process involving chlorine, hydrogen other than sodium hypochlorite itself evaluation is required. In the present work, the risk assessment of the block of the process dealing with the production of chlorine, hydrogen and caustic soda is performed. To this end, HAZOP analysis was performed to identify the top events. For each top event, the frequency analysis was performed. Eventually, the consequence analysis was carried out by means of simulations through the software PHAST.

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1.1 Process Description

The entire process can be divided into two blocks consisting in the electrolytic cell where the brine solution is produced and the chlorination of caustic soda. The global reaction that takes place within the membrane electrolytic cell is:

$$2NaCl + 2H_2O \rightarrow Cl_2 + H_2 + 2NaOH \qquad Eq(1)$$

As can be seen in the reaction reported in Eq(1), besides the feedstock for hypochlorite production (chlorine gas and caustic soda, Cl_2 and NaOH), there is the formation of explosive gaseous hydrogen. Caustic soda solution obtained reached a concentration value of about 32-35%$_{vol}$ (Chatenet et al., 2000). The hydrogen and caustic soda outgoing from the cathode are separated within a vessel. A part of caustic soda is recycled to the electrolytic cell while the rest is fed to the hypochlorite reactor. The hydrogen is sent to the chimney equipped with a hydraulic seal to avoid ignition and it is inertized by nitrogen. The chlorine gas, outgoing from the anode, is sent to the hypochlorite reactor through vacuum piping. The reaction to produce hypochlorite is reported as in the following:

$$2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O \qquad Eq(2)$$

It is carried out in one or more reactors, where chlorine is fed in counter-current with respect to caustic soda, that is recirculated to the reactor. The reaction is exothermic, and the cooling is necessary to avoid the formation of sodium chlorate. The process is suited to producing both household bleach (5–6 wt.%) and industrial bleach (10–15 wt.%) (Farr et al., 2003). In this work, the risk assessment related to the part of the plant between the electrolytic cell and the chimney was performed, focusing the attention on hydrogen risks.

2. Methods

Firstly, in order to identify the critical areas of the plant for which a detailed safety analysis was necessary, the index method was used (Bonin and Stevenson,1989). On the critical areas a hazards and operability study (HAZOP) (NSW Government Planning, 2008) was carried out, leading to the identification of the top events. For each top event, the frequency analysis was performed based on properly developed fault trees. The top event is traced downward to more basic failures. The underlying technology is the use of a combination of relatively simple logic gates (AND and OR) to synthesize a failure mode of the plant. The top event failure rate or probability was calculated from failure data of more simple events (Lees, 1996). The innovation aspect of this work mainly concerns with simulation of consequences, compared to previous papers (e.g. Binetti and Attias, 2007). The consequence analysis was carried out by the simulation of phenomena such as the dispersion of hydrogen and consequent ignition leading to a flash fire or a jet fire as function of the distance from the source. The simulations were carried out by means of the software PHAST. PHAST provides clear illustration of the outcomes that may result from the hazards on a plant. To better clarify the method phases, Figure 1 shows a flowchart of the risk analysis method used.

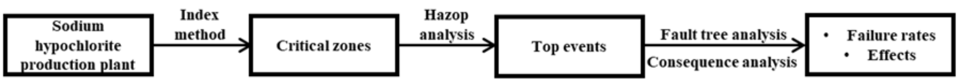

Figure 1: Flowchart of risk analysis method

3. Results

Based on index method analysis, used for screening and setting priorities in the risk analysis, the most critical zone is that between the electrolytic cell and the chimney (G'=18.4) (Bonin and Stevenson,1989). Thus, the HAZOP analysis was carried out on this part of the plant in which hydrogen and chlorine are present. Figure 2 shows a simplified P&ID of the electrolytic cell-hydraulic seal section equipped with instrumentation, based on HAZOP analysis. It can be concluded that top events are the failure of N_2 inerting, the vented H_2 ignition, the failure of the membranes of the electrolytic cells and consequent mixing of H_2 and Cl_2 and the failure of the tubes at high pressure in the H_2 circuit.

3.1 Fault tree analysis

Fault trees have been developed and the frequencies have been calculated or evaluated from literature data (Lees, 1996; Rahman et al., 2010). In the followings the results are discussed for each top event identified.

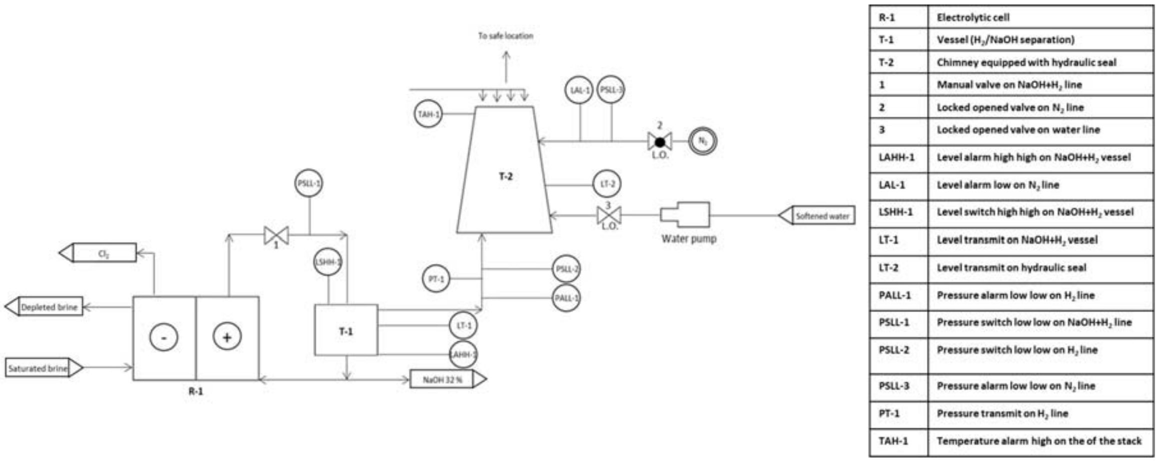

Figure 2: Simplified P&ID of the electrolytic cell-hydraulic seal section equipped with instrumentation, based on HAZOP analysis

3.1.1 Failure of N_2 inerting (Event 1)

H_2 is fed to the chimney and it flows through liquid water to avoid H_2 ignition in the chimney. N_2 is fed to the chimney via gas cylinders. Generally, two gas cylinder sets are present, equipped with an auto change-over system to automatically switch from one set to the other. The switch is activated when the pressure of the cylinders of one set reaches a low limiting value. Before the system is activated, the alarm sounds to alert operators. In the lines, two manual valves are present to connect/exclude the cylinders. In the case of accidental closure of the cylinders, the inerting process would fail. In Figure 3, the fault tree is shown. For each basic event, the failure rate has been evaluated from literature data (Lees, 1996; ESP-RIFTS, 2019). In Table 1 the data are given. In Table 1, λ is the failure rate (event/millions of hours) and q is the failure probability of component. Considering a typical bathtub failure rate curve, λ can be assumed approximately constant over the midlife of the components. The average frequency evaluated from these data for 3 years of plant operation of 25000 hr is equal to 7.5·E-2 events/year.

3.1.2 Released H_2 ignition (Event 2)

In the case of failure of the inerting process, the released H_2 could ignite. The frequency of this event is related to the ignition probability and it has been evaluated from literature data (Kletz, 1977). It is equal to 1.0·E-1 events/year.

3.1.3 Fail of the membranes of the electrolytic cells and consequent mixing of H_2 and Cl_2 and fail of the tubes at high pressure in the H_2 circuit (Events 3-4)

The failure of the tubes at higher pressure in the hydrogen circuit as well as the failure of the membranes of the electrolytic cells and consequent mixing of H_2 and Cl_2 event may be directly arising from a high pressure in hydrogen line, which is the top event considered in the fault tree. In order to evaluate the failure frequency, the related fault tree was developed. In Table 2, both basic events and failure rates are given. From the calculation of the frequency over 3 years, a frequency value equal to 2.5·E-2 events/year was found.
All the events have been classified in terms of findings level by assuming as reference the frequency threshold value 1E-6 events/year. On the basis of frequency classes incidental events, the events 1-2 belong to the HIGH risk level class (frequency 0.03-1) while events 3-4 to the MEDIUM one (frequency 0.001-0.03) (Calabrese, 2008).

Table 1: Failure rates of the first top event

Event	Failure type	λ·E-6 [EV/h]	q	References
1	Manual valve (2) wrongly closed	6-12	-	(Lees, 1996)
2	Not working auto-changeover	1.20	-	(Wang, 2013)
3	Not working alarm	2.00	-	(Moss, 1988)
4	Non-intervention of operators	-	1E-3-1E-2	(Lees, 1996)

Figure 3: N_2 inerting failure fault tree

Table 2: Failure rates of the mixing of H_2 and Cl_2 top event

Event	Failure type	λ·E-6 [EV/h]	q	References
1	Not working LT-1	17.1	-	(Moss, 1988)
2	Not working alarms	2.00	-	(Moss, 1988)
3	Inefficient operators intervention	-	1E-3-1E-2	(Lees, 1996)
4	Not working LSHH-1	11.4	-	(Moss, 1988)
5	Failed interruption of power supply to the cell	1.45	-	(Moss, 1988)
6	Faulty electricity release button	1.03	-	(Moss, 1988)
7	Wrong identification of the water line	0.034	-	(Lees, 1996)
8	Winterization	-	0.25	(ESP-RIFTS, 2019)
9	Identification system failure	11.4	-	(ESP-RIFTS, 2019)
10	PT-1 failure	14	-	(Moss, 1988)
11	LT-2 failure	34.2	-	(Moss, 1988)
12	Signal failure	2	-	(Moss, 1988)

3.2 Consequences

Each consequences simulation was carried out through PHAST. The following simulation conditions were set: ambient temperature at 20 °C, 77 % of relative humidity and wind velocity equal to 2 m/s. Each top event was simulated with two atmospheric stability classes (according to Pasquill classification): class D is typical of morning while class F is typical of night conditions (very stable) (American Institute of Chemical Engineers - CCPS, 2000).

3.2.1 H_2 ignition from the hydraulic seal

The ignition of the released H_2 from the hydraulic seal may give rise to a jet-fire or to a flash fire. In the case of delayed ignition, a flash fire is expected. The areas with fuel concentration equal to the flammability limit (LFL) and LFL/2 were calculated. In order to identify these conditions, the gas dispersion into the atmosphere has to be simulated. The first simulation was carried out with hydrogen (30 kg/h), release temperature 60 °C, release pressure 0.02 bar, efflux diameter 0.3 m, height of release point 18 m (chimney) and effluent flow rate 370 m^3/h (continuous release). In Figure 4 (a and b), the H_2 concentration iso-curves at 20000 ppm (LFL/2) and 40000 ppm (LFL) are shown for both stability classes. The flammable zone in the case of class F is larger than in the case of class D. This is due to the stability of the atmosphere; the mixing process is mainly controlled by diffusion. In Table 3 the results are summarised. In the case of jet-fire, radiation fluxes are not found on the ground. The ground concentration is very affected by the release height: indeed, as it increases, the ground concentration decreases, and LFL is not reached. At the release height, reversible damages (3 kW/m^2) can be found at 6 m away. The same simulations were performed by assuming the presence of N_2 flux as inerting (hydrogen 370 m^3/h, nitrogen 3300 m^3/h; release temperature 60°C, release pressure 0.02 bar, efflux diameter 0.3 m, height of release point 18 m; effluent flow rate 370 m^3/h). By comparing with the previous results, it comes out that in the presence of a high N_2 flow rate, the dimensions of the flammable zones increase with respect to the case of N_2 absence. This result is related to the entertainment of the H_2

upstream due to the N_2 flow. The results are summarised in Table 4. Also in this case, radiation fluxes are not found on the ground. At the release height, reversible damages (3 kW/m^2) can be found at 21 m away.

3.2.2 High pressure H_2 circuit

Both the electrolytic membrane rupture and the H_2 leakage due to the flexible tube rupture may be caused by an overpressure in the hydrogen circuit. In this section, the simulation of a flexible tube rupture and the consequent release of hydrogen is shown. Both jet fire and flash fire have been simulated. The electrolyser is positioned at 3-meter height and H_2 exits from 50 small tubes. Each tube has a diameter equal to 40 mm (hydrogen 30 kg/h, release temperature 90 °C, release pressure 0.05 barg, efflux diameter 0.04 m, release height 3 m; stability class F). Results of the simulations are shown in Figure 4c and summarised in Table 5. Also in this case, radiation fluxes are not found on the ground.

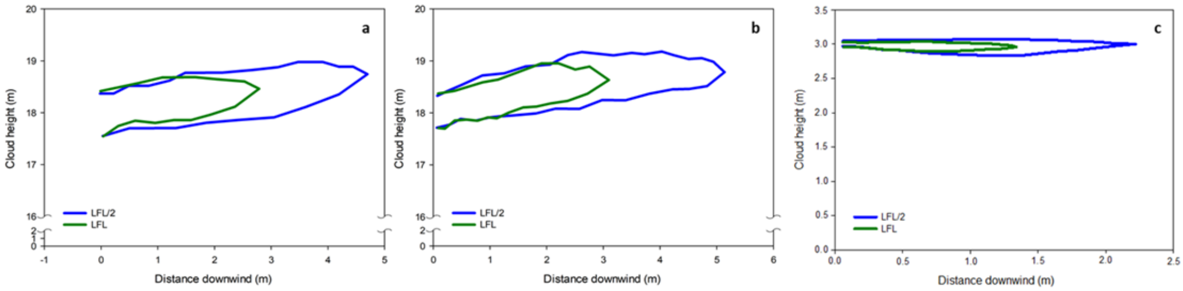

Figure 4: (a, b) Flash fire, hydrogen to the chimney, class D (a) and F (b). (c) Flash fire, H_2 leakage due to the flexible tube rupture, class F

Table 3: Summary of results in terms of accidental scenarios for hydrogen to the chimney

Accidental scenario	Threshold parameter	Damage distance (m)	
Flash fire	LFL (40000 ppm)	2.8 m at 18.4 m (D)	3.1 m at 18.6 m (F)
	LFL/2 (20000 ppm)	4.7 m at 18.7 m (D)	5.1 m at 18.8 m (F)
	Flame length (m)	5.13 at 18 m height	
JET FIRE Radiation on the ground (kW/m^2)	12.5	Not found	
	7	Not found	
	5	Not found	
	3	Not found	
JET FIRE Radiation at 18 m height (kW/m^2)	3	6 (D)	6 (F)

Table 4: Summary of results in terms of accidental scenarios for hydrogen to the chimney, with nitrogen

Accidental scenario	Threshold parameter	Damage distance (m)	
Flash fire	LFL (67140 ppm)	4 m at 19.4 m (D)	4.6 m at 19.6 m (F)
	LFL/2 (33570 ppm)	6.9 m at 20.1 m (D)	7.7 m at 19.9 m (F)
JET FIRE Radiation on the ground (kW/m^2)	Flame length (m)	20 at 18 m height	
JET FIRE Radiation at 18 m height (kW/m^2)	3	21 (D)	21 (F)

Table 5: Summary of results in terms of accidental scenarios for H_2 leakage due to the flexible tube rupture

Accidental scenario	Threshold parameter	Damage distance (m)
Flash fire	LFL (40000 ppm)	1.3 m at 3 (F)
	LFL/2 (20000 ppm)	2.2 m at 3 m (F)

4. Conclusions

In this work, the quantitative risk assessment of the hypochlorite production process was carried out. On the basis of HAZOP and fault trees analysis, each top event was assigned to a risk level class. The consequence analysis was carried out for each event, considering the dispersion and the ignition of the released H_2 from the chimney and the high pressure in H_2 circuit with a tube rupture. The ignition of the released H_2 from the chimney may give rise to a jet-fire or to a flash fire at the release height while the ground concentration is always lower than LFL/2. It depends on the very stable conditions chosen for these simulations that lead to the least amount of turbulent mixing. Indeed, in each simulation the flammable zone in class F (night and stable condition) is larger than in the case of class D (morning condition) due to the lower degree of turbulence. In addition, the radiation damages in case of jet fire occurrence are not found on the ground for both the release heights. The simulation with nitrogen showed the capability of nitrogen to entrain the hydrogen, increasing the extension of the cloud. Moreover, consequences analysis in case of H_2 leakage due to the flexible tube rupture was carried out, showing damages for flash fire close to the dispersion source. Dispersion and consequence calculation have to be performed for this process, providing an estimate of the area affected by possible damages and guidelines for design features close to the critical zones. In future works, the risk analysis should be extended removing the simplifying assumption of λ constancy.

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