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Determining a realistic ranking of the most dangerous process equipment of the ammonia production process: A practical approach

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A R T I C L E   I N F O

A B S T R A C T

OCI Nitrogen seeks to gain knowledge of (leading) indicators regarding the process safety performance of their ammonia production process. The current research determines the most dangerous process equipment by calculating their effects resulting from a loss of containment using DNV GL's Phast™ dispersion model. In this paper, flammable and toxic effects from a release from the main equipment of an ammonia plant have been calculated. Such an encompassing approach, which can be carried out for an entire plant, is innovative and has never been conducted before. By using this model, it has been demonstrated that the effects arising from an event of failure are the largest in process equipment containing pressurized synthesis gas and 'warm' liquid ammonia, meaning the ammonia buffer tanks, ammonia product pumps, and the ammonia separator. Most importantly, this document substantiates that it is possible to rank the most hazardous process equipment of the ammonia production process based on an adverse impact on humans using the calculated effect distance as a starting point for a chance of death of at least 95%. The results from the effect calculations can be used for risk mapping of an entire chemical plant or be employed and applied in a layer of protection analysis (LOPA) to establish risk mitigation measures.

1. Introduction

In 2015, several major process-related accidents occurred at a few site users of Chemelot, a chemical industrial park in Geleen, The Netherlands (OVV, 2018). The increase in the frequency and severity of the accidents caused the Chemelot Board to initiate an external investigation. One of the conclusions was that the potential hazards of the plant and the chemical processes do not receive the necessary attention due to an increased focus on occupational safety (Helsloot et al., 2016). In other words, there is insufficient anticipation of "early warnings" from the chemical processes. The conclusion of Helsloot et al. of a wrong focus is not unknown in the chemical industry: both Hopkins (2000) and Baker (2007) arrived at similar conclusions in their reports on the Esso incident in Longford (Australia) and BP incident in Texas (USA) respectively. Process safety indicators have been in the spotlight for some time (Swuste et al., 2016); HSE (2006), CCPS (2010), Cefic (2016), OGP (2011) and ANSI/API (2010) have subsequently set up guidelines to measure process safety based on indicators. In a special edition of *Safety Science* (volume 47, issue 4, April 2009) these indicators have

been placed more prominently on the science agenda.

OCI, one of Chemelot's largest site users, has faced several serious process safety related accidents, including those at its two ammonia plants. According to an internal investigation they were caused by, among other things, incorrect choice of materials, accelerated wear, incorrect design, and unrecognized risks during work. Although no physical injuries were suffered in any of the incidents, in some cases the ammonia plant had to be shut down for a longer period, these incidents resulted in both hardware damage and a substantial loss of production.

Awaiting the results of the external investigation, OCI started its own investigation in which management asked how process safety can be monitored. The underlying aim of the internal investigation is to be able to take targeted measures at an early stage and stop the development of major accident processes. This paper contains the results of the first phase of the study, and answers the following research question: *Which process equipment have the largest adverse impact on humans in the event of failure?*

The associated sub-questions to be investigated are:

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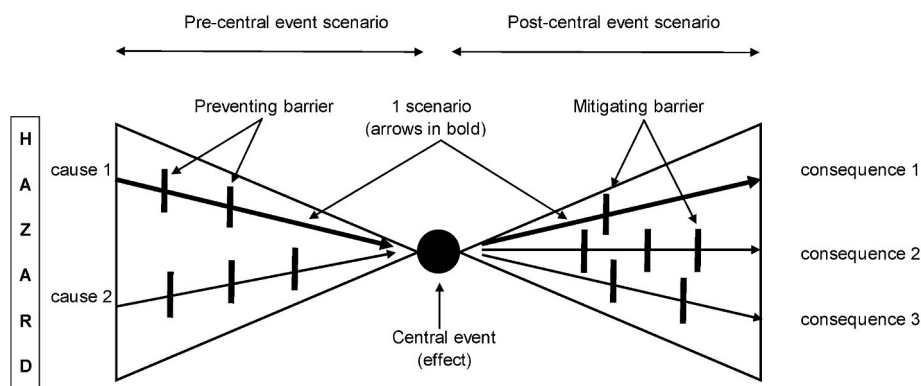   *E-mail address:* peter.schmitz@ocinitrogen.com (P. Schmitz).

Fig. 1. The bowtie model.

Table 1
Relation between hazard, effect and consequence to humans.

Left-hand side of the bowtie	Central event	Right-hand side of the bowtie
The ammonia production process has the following intrinsic hazards: (Over)heated steam, flammable & toxic substances	At a loss of containment, the intrinsic hazards may lead to one of the following effects: Heat radiation or flame contact Overpressure Toxic concentration	The effects may result in one of the following adverse consequences on humans: Burns Internal injury Poisoning

1) Which intrinsic hazards are connected to the ammonia production process?
2) Where in the ammonia production process can an event of failure occur?
3) What adverse impact can the hazards have in the event of failure?
4) How can the adverse impact on humans be measured?

This paper only deals with effects and their calculations, and aims to indicate the most dangerous equipment of the ammonia production process. The likelihood of scenarios which may lead to such effects, is dealt with in another paper (Schmitz, Swuste, Reiniers & Nunen van, 2020).

1.1. Definitions

Since a hazard can manifest itself through a scenario to an effect and subsequently to all kinds of consequences, a link is made to bowties. Bowties are user-friendly for mapping scenarios (Chevreau et al., 2006; De Ruijter and Guldenmund, 2016), and illustrate the relationship between hazard, effect and consequence. The simple, sequential design of bowties is reminiscent of the "Swiss cheese model" of Reason (1990) with the cheese slices as barriers.

Fig. 1 shows the bowtie metaphor and indicates a scenario comprising of two parts, meaning a pre-central event scenario which may take days, weeks, months or even longer to develop, and a post-central event scenario which may unroll quickly into the ultimate consequences: casualties, injuries, damage and/or loss of production (Swuste et al., 2016).

The central event is in the middle of the bowtie and is in a (petro) chemical installation often characterized by an undesired and uncontrolled release of a hazardous substance and/or energy. As it were, a situation arises with an uncontrollable hazard. Hazard is the intrinsic ability or potentiality to cause material damage, casualties and/or injuries. Cockshott (2005) describes hazard as a condition that could potentially lead to injury, and/or damage to property or to the environment. He defines a central event as the initial consequence which

involves the release of a hazard. In this paper Cockshott's initial consequence is freely translated as effect, meaning that the effect is manifested in the central event and can be defined as the primary result of the release of the hazard.

Table 1 shows the relationship between the hazard, effect and consequence to humans. For example, the release of a flammable gas can lead to a jet or flash fire which heat radiation or flame contact may result in severe burns or even fatality. Although some physical properties such as pressure and temperature may be considered as intrinsic hazards, their influence is indirect through the released substances. More pressure leads, for example, to a higher release flow and hence to a larger effect. Consequences have only been considered for humans, and not for the installation or the environment. In contrast to the installation and the environment, humans experience both the effects of a flammable and a toxic release.

1.2. The ammonia production process

The ammonia process uses natural gas, steam, and air as raw materials. The process, shown in Fig. 2, consists of two main parts: 1. The steam reforming, the method for producing hydrogen from natural gas, and 2. The ammonia synthesis loop. The steam reforming is followed by the shift conversion, carbon dioxide removal and methanation steps and is operated at pressures of 25–35 bar. The hydrogen (H_2) is then combined with nitrogen to produce ammonia (NH_3) via the Haber-Bosch process in the synthesis reactor. The numbers in brackets in the text below refer to the process units of Fig. 2.

Process units 1 to 7 are referred to as the steam reforming, the shift conversion, carbon dioxide removal and methanation. The incoming natural gas largely consists of methane (CH_4), but also contains small amounts of sulfur. This is undesirable and sulfur is therefore converted to H_2S and absorbed with the aid of hydrogen and a catalyst (1). In the reformer (2) the desulphurized natural gas is largely converted to CO, CO_2 and hydrogen (H_2) using steam and a catalyst at 825 °C and 35 bars. Air is supplied to the secondary reformer (3), through which nitrogen (N_2) is introduced into the process, which is needed as the second component to make ammonia. The oxygen from the air reacts with some H_2 and increases the secondary reformer's temperature to over 1000 °C, enabling to crack the remaining methane. The CO formed in the cracking process is converted to CO_2 and H_2 in two serial reactors (4 and 5) using steam. To remove the CO_2 from the gas mixture, the process gas is passed through a (physical) scrubber unit (6). The last residues of CO and CO_2 (not converted or washed out) are converted into methane in the methanation (7) using a catalyst and H_2.

The ammonia synthesis loop consists of the process units 8 to 12. In this part of the ammonia production process, the process gas mainly consists of hydrogen and nitrogen, in a ratio of 3 to 1. The synthesis gas is compressed (8) to the synthesis pressure after which the residues of water are removed by adsorption in the molecular sieves (8a). The
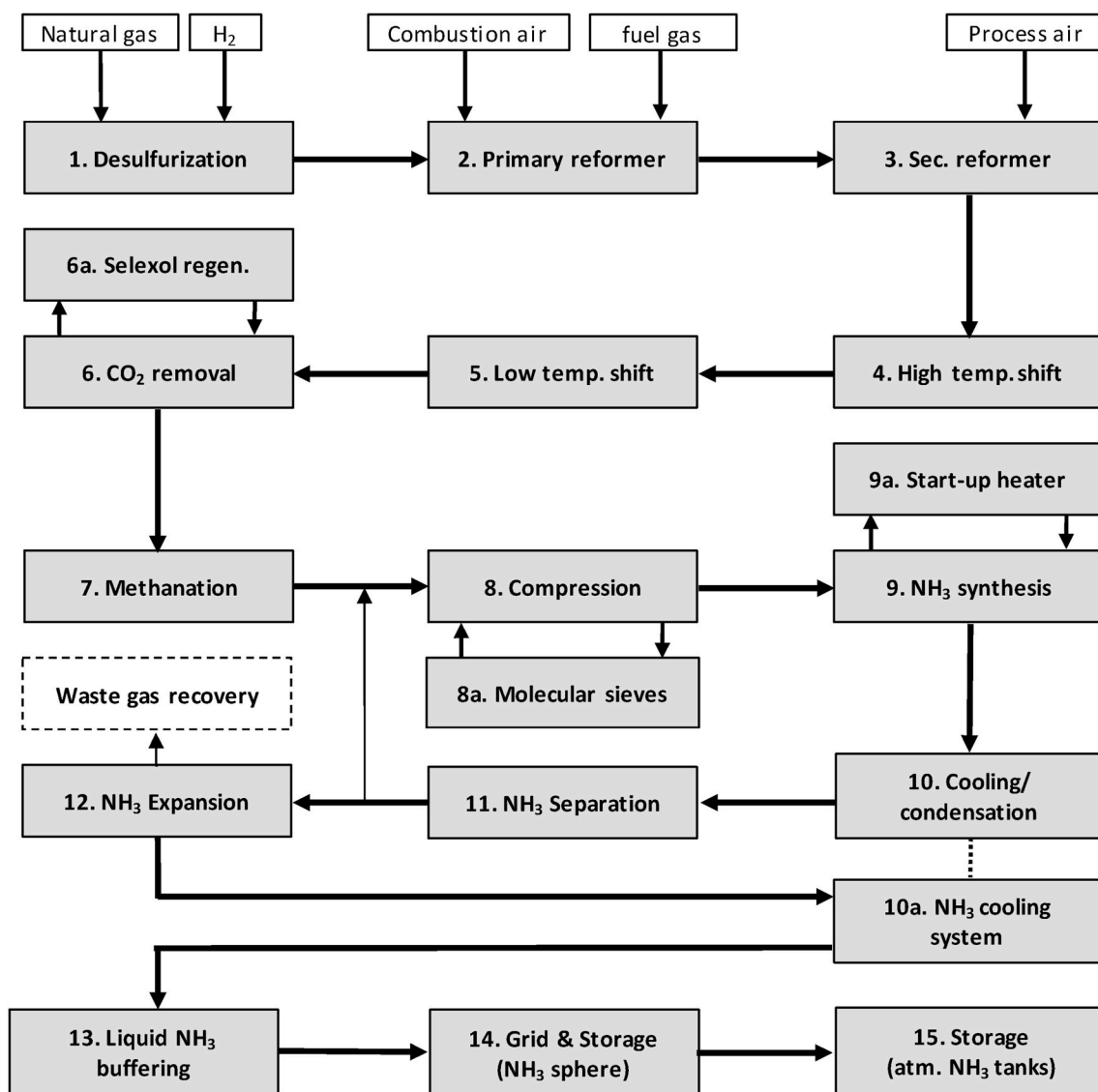
Fig. 2. Overview of the ammonia production process.

reaction to ammonia is according the Haber-Bosch process and takes place in the synthesis reactor (9) in the presence of a catalyst at approx. 200 bar and 515 °C. Since there is insufficient heat in the process in a start-up situation, the start-up heater (9a) is temporarily used to bring the synthesis gas mixture up to its reaction temperature. The ammonia formed is successively cooled (10) and separated in the ammonia separator (11) from the unreacted and inert gases, which are returned to the compressor (8). The liquid ammonia from the ammonia separator (11) is reduced in pressure from 200 bar to approx. 18 bar before entering the expansion vessel (12). The gases released during the ammonia expansion are sent to the waste gas recovery, which is located elsewhere and outside the scope of this study. From the ammonia expansion vessel, the liquid ammonia serves as a coolant (10a) before being sent to the buffer tanks (13) and the ammonia grid (14). Finally, the ammonia is either stored (15) at atmospheric conditions or immediately delivered to the site users (not indicated).

2. Methodology

In this paper various indices have been investigated, most of which have been developed to quickly identify the most significant hazards (in terms of effect) of a (petro)chemical installation. Perhaps the most

commonly used is the Dow Fire & Explosion index (AIChE, 1994a), which calculates an exposure area based on substance, process and installation data from which property damage can be determined. Dow's Chemical Exposure index (AIChE, 1994b) on the other hand, calculates the effect distances due to an airborne amount of a toxic substance and is a simple method for determining relative, acute toxicity hazards in adjacent plants and communities (Marshall and Mundt, 1995). This index is also used for drawing up emergency plans (Mannan, 2004). The Mond index is very similar to Dow's Fire & Explosion index, but is more detailed (Tyler, 1985; Andreasen and Rasmussen, 1990). Unfortunately, the Mond index does not have a separate rating for toxicity. Several indices have been developed for hazard identification, evaluation and inherently safe design purposes: SWeHI, HIRA (FEDI and TDI) and I2SI (Khan and Abassi, 1998; Khan et al., 2001; Khan et al., 2003; Khan and Amyotte, 2004). During the Aramis project a method was also designed for the selection of dangerous equipment (Delvosalle et al., 2006) based on process parameters and substance data. The method developed by Tugnoli and Cozzani (2007) is based on commercial software models and takes into account thermal radiation, overpressure and toxic concentration.

All these indices report a relative risk index on a somewhat arbitrary scale. The numerical index results cannot be compared directly to each

other, although each index provides guidance on the meaning of the numbers it generates (Hendershot, 1997). In this study, the effects have been calculated using the Phast™ software program, which uses standard dispersion models and has an extensive substance database. Phast™ can calculate thermal radiation, concentrations like upper and lower explosion limits, overpressure and toxic concentrations of individual components but also of mixtures, under the predominantly prevailing weather conditions.

This research has been performed following four steps, which are described in the sections below:

1) Selecting the main process equipment;
2) Collecting the associated process data;
3) Drawing up the starting points;
4) Calculating the effects using Phast™.

2.1. Step 1: Selecting the main process equipment

The hazards of the ammonia production process are very diverse in nature. The natural gas, the cracked gas from the steam reforming and the synthesis gas pose a fire and an explosion hazard. Ammonia, and several other substances in the process, such as CO and CO_2, are toxic. In addition, the ammonia production process produces steam at all kinds of pressures and temperatures, which not only entails a (physical) explosion risk but also a risk of burns in the event of a release.

An ammonia plant consists of many process equipment (vessels, reactors, heat exchangers, etc.) and pipes. In order to estimate where the hazards of the ammonia process are located and how these hazards relate to each other, the ammonia production process has been divided into smaller parts than the process units indicated in Fig. 2. In this research 64 process equipment have been selected to be significant and representative for the ammonia production process. The pipework is excluded because its effects can be traced back to the process equipment connected to it.

The ammonia production process is connected to a grid which exports the produced ammonia to the site users and the two atmospheric storage tanks. The boundaries of the ammonia production process to be investigated are limited from the imported natural gas to the export of the produced ammonia into the grid. The grid as well as the atmospheric storage tanks and loading facilities are outside the scope of this research, indicated as process unit 14 and 15 in Fig. 2 respectively.

2.2. Step 2: Collecting the necessary process data

Clearly, process pressures, temperatures and substances are influencial parameters for determining the effect radii. In addition, the height of the release is of influence as is the contained quantity, where ammonia is concerned. The total release depends not only on the (automated) controls of the ammonia production process, but also on the response time of the control room operators. This particularly affects in case of ammonia where the source duration strongly determines the effect radius. The issue of the response time was presented to several control room operators and from the interviews it appeared that in the event of an operational abnormality, they first try and keep the ammonia production process running rather than focusing on the possibility of a calamity. This is understandable because a shutdown of the ammonia production process may entail a disturbance of the ammonia supply to the site users. Only when the control room operators see an emerging risk, they will shut down the ammonia production process as quickly as possible, taking it to a predefined, safe state. In consultation with the control room operators the response time has been set at 5 min, assuming the safeguarding system does not automatically intervene prematurely. In the worst case it takes 5 min before the main pumps and compressors are being stopped, the ammonia process has been isolated into so-called containment systems and is being depressurized using the flares.

In Dow's Chemical Exposure Index Guide (AIChE, 1994a, b), the release time of toxic scenarios is set at 5 min. The Dutch guideline for risk calculations, Bevi (RIVM, 2015) and the purple book (VROM, 2005b) use different response times for the calculation of quantitative risk assessments, and distinguish between different containment systems. The containment system closest to the situation of the ammonia plants is a semi-automatic containment system, meaning that a leak is automatically detected and reported in a continuously staffed control room, and where the control room operator activates the shutdown system after validation by pushing a button. The response time of a semi-automatic containment system is 10 min. This length of time is not considered realistic and as indicated above the response time to manually activate the shutdown system has been determined at 5 min. As the response time is only relevant in case of ammonia and given the large size of such a release, this will inevitably lead to rapid detection from the controlled process and from local observations (odor, noise) by the control room and field operators respectively. Hence, little time is needed to validate such an event.

By isolating the ammonia production process there is no more flow of liquid and gas between the containment systems. However, this is still possible between the process equipment within one containment system. In general, gases can move freely through a containment system whereas liquids can not, as most liquid flows are controlled by valves or pumps.

2.3. Step 3: Drawing up the starting points

To guarantee that data is handled in the same way and that accepted criteria are used as an input of the dispersion calculations, a few starting points have been formulated. As indicated in section 1.1 only consequences on humans have been considered whereas consequential damage and production outage have been ignored. The toxic concentration, heat radiation, flame contact and overpressure scenarios have been calculated at a height of 1 m as most employees present in the plant are at ground level (RIVM, 2015; Tugnoli and Cozzani, 2007). The synthesis gas and ammonia compressors are in a building at a height of 8 m. Since there is a reasonable chance of operators and mechanics being present at a height of 8 m, the calculations assume that these compressors are located on ground level and in the open air.

The calculated effects are shown as radii within which there is a chance of death of at least 95% which is much higher than what Tugnoli and Cozzani (2007), Khan and Abassi (1998), and Khan et al. (2001) have chosen (1%, 50% and 50% respectively). The largest distance from the source is used as a measure of the size of the effect. In this way, the effects of the different process equipment as a result of an uncontrolled release can be compared with each other, whether it concerns a heat radiation, a flame contact, a toxic cloud or an overpressure scenario.

For the calculations of the 64 main process equipment of the ammonia production process, a free outflow has been assumed through a round 50 mm hole located at the bottom of the equipment. This diameter size is an accepted practice in the chemical industry and based on an average diameter of flanges and pipe fittings welded to equipment for piping, valves and instrumentation. In addition, the direction of the outflow has been taken horizontal (RIVM, 2015).

For the liquid filled vessels, the degree of filling is in accordance with normal operation and set at 50%. As gases can move freely through an isolated containment system, all gaseous components of an isolated containment system will flow out. In contrast, liquid flows inside a containment system need to be assessed case-by-case to establish the subsequent delivery from adjacent equipment because liquid flows are controlled by valves and pumps. Since the hole is at the bottom, the liquid inside a process equipment will flow out completely.

In the event of a calamity, the ammonia production process is taken to a safe state, either automatically by the safeguarding system or manually by the operating staff, meaning that several predefined valves
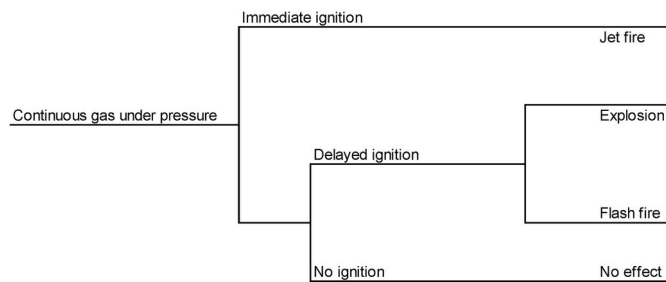
Fig. 3. Event tree for continuous release of a flammable gas (RIVM, 2015).

are closed so that the containment systems are isolated from each other. Seven containment systems have been defined with reference to the process units of Fig. 2: 1 to 5; 6 and 6a; 7; 8 and 8a; 9 to 11 (without 10a); 10a and 12; and 13.

A probit relationship shows the relationship between the concentration of a substance, the exposure time and the effect on humans. A probit relationship for a toxic substance can be used for any combination of concentration and exposure time to estimate the percentage of people who decease from exposure to the substance. For the toxic effects of ammonia, the probit relationship $Pr = -16.21 + \ln(\int C^2 \times dt)$ has been used, where C is the concentration in parts per million (ppm) and t is the exposure time in minutes (RIVM, 2015). The exposure time for the persons present in the affected area is equal to the duration of the release, unless there is significant pool evaporation. In such a case, the additional exposure time has been estimated using the dynamic exposure images of Phast™. The concentration can be calculated based on the total exposure time using the above probit relationship. The concentration being entered for the calculation of the toxic radii is based on a chance of death of 95%, assuming no chance of escape from the toxic cloud in the affected area.

Fig. 3 shows the consequences from a continuous release of a flammable gas. A direct ignition leads to a jet fire, whereas a delayed ignition leads to a flash fire or an explosion (RIVM, 2015). For heat radiation in case of a jet fire, the following probit relationship has been assumed: $Pr = -36.38 + 2.56 \ln(\int Q^{4/3} \times dt)$, where Q is the heat radiation in W/m2 and t the exposure time in seconds (RIVM, 2015). The radii of 35 kW/m^2 have been calculated for heat radiation due to jet fires. An exposure time of 20 s within the 35 kW/m^2 radius will inevitably lead to death, assuming 20 s will not be enough time to escape from the affected area.

The main body parts that can be directly damaged by a pressure wave resulting from a blast or an explosion are the ears and lungs (HSE, s.d.). In addition, explosions can also be associated with other injuries caused by projectiles and flying objects, physical displacement or inhalation of hot and toxic gases (Owers et al., 2011; Zuckerman, 1940; Mannan, 2004; VROM, 2005a). The chance of injuries from the latter group increases proportionally as one is closer to the explosion (Dussault et al., 2014). For overpressure-related personal injury, the HSE uses the probit relationship: $Y = 5.13 + 1.37 \ln(P)$, where P is the overpressure in bar (HSE, s.d.). The probit relationship shows that exposure to an overpressure of 0.9 bar results in a 50% chance of death. Mannan (2004) refers to Eisenberg et al., who determined a 50% chance of death at 1.4 bar overpressure based on serious lung bleeding. APPEA (HSE, s.d.) applies 0.7 bar as 100% fatal for both indoor locations and unprotected structures, whereas the Dutch guideline for risk calculations (RIVM, 2015) puts the site-specific risk at 1 for an overpressure higher than 0.3 bar. Owers et al. (2011) state that the chance of death is 50% at 9 barg, but this would only concern primary effects, meaning the interaction from the blast wave with the body. In fact, much higher pressure levels (up to tens of bars) are reported to which people can still be exposed, where it is assumed that not the overpressure but other explosion effects usually result in a much higher chance of death (HSE, s.d.; Zipf & Cashdollar, s.d.; Mannan, 2004; VROM, 2005a). Lethality only occurs with high overpressures and long duration of the pressure wave (VROM,

2005a). It must be concluded that the values reported in the literature differ considerably from each other and that it is not always clear which explosion effects and which injuries have been included in the chance of death. For this research it is assumed that an overpressure of 0.9 bar from an explosion results in a chance of death more than 95%. Besides the direct consequences for the ears and lungs, other injuries have also been considered. Finally, it should be noted that the actual overpressure exerted on humans by the blast wave, due to reflection and circulation, may be greater than the calculated overpressure (VROM, 2005a).

When calculating the pressure effects resulting from an explosion, the growth and displacement of the cloud, as well as the moment of ignition, has been considered carefully. The latter is set in Phast™ in such a way that the resulting pressure wave reaches a maximum distance from the point of release. The distance from the overpressure radius to the point of release has been taken as a measure of the magnitude of the overpressure effect. It is assumed there is no chance of escape from the affected area in case of an explosion.

A release of a continuous pressurized gas may also lead to a flash fire, meaning a rapid combustion without significant overpressures. A flash fire can only occur when the explosive cloud is not confined nor hindered by obstacles. Persons within the ignited cloud will be seriously burned by direct flame contact. In most cases, the size of the burned skin surface is so large that those exposed will decease. As an estimate of the extent of personal injury from a flash fire, it seems reasonable to assume that all persons within the cloud at the time of ignition will be fatally affected. Due to the short exposure time, the extent of personal injury outside the cloud will be relatively small. The lower explosion limit defines the size of the explosive cloud and is used as a measure of the effect (VROM, 2005a).

Flash fires are particularly dangerous in confined areas, as even a relatively small fire can consume enough oxygen and produce enough smoke to cause death of the persons present. But as the flash fires will occur in the open, asphyxiation and smoke inhalation have not been considered.

In the containment system 9 to 11 and excluding 10a (see Fig. 2) the composition of the substances can be both flammable and toxic. The flammable and toxic gases can move freely through the containment system, which leads to different effects in the event of an equipment failure. For the calculation of the jet fire, flash fire and explosion effects, a gas composition is assumed as it is present in the equipment during normal operation. Exposure to a heat radiation, flame contact and an overpressure is already fatal when the release is of a short duration. This is different for exposure to ammonia as only longer durations prove to be fatal. Therefore, the entire gas mass (of 8500 kg) and the release duration does play a prominent role in the calculation of the effects of a toxic ammonia release. The duration of the release determines the exposure time and thus the ammonia concentration for a chance of death of at least 95%. In view of the longer release duration, the gas composition of the total containment system has been averaged in order to make a better estimate of the flow rate of the release and hence the release duration and exposure time.

In the containment system 10a and 12 (see Fig. 2) there is a subsequent supply of liquid ammonia from other equipment in the containment system. If the release rate shows a cascading variation, each variation is calculated considering its release rate and duration. The calculated effect radii are then placed in time to determine the maximum effect distance.

2.4. Step 4: Calculating the effects using Phast™

Phast™ version 7.21 has been used for the dispersion calculations. The calculation model can be used to analyze and quantify situations in which potential consequences may occur to people, the environment and installations (DNV GL, 2014). The calculations assume that the process equipment are located in a free space without being surrounded by other equipment. Next to process data and substance properties,

Table 2
Input data for the Phast™ calculations.

Process unit	Equipment (TS – Tube Side, SS – Shell Side)	Central event	Pressure (bar g)	Temp. (°C)	Height (m)	Composition (mol %)							Mass gaseous NH3 (kg)	Mass liquid NH3 (kg)	Subsequent supply (kg/h)
						CH4	CO2	CO	H2	N2	H2O	NH3			
1	Desulfurization	Jetfire/ expl/fl. fire	38	320	3	83.8	1.4	0	3.5	4	0				
2	Reformer (TS)	Jetfire/ expl/fl. fire	38	800	3	11.9	3.6	2.8	21.2	0.8	59.1				
3	Secondary reformer	Jetfire/ expl/fl. fire	37	950	3	2.7	4.9	7.1	32.5	14.6	37.1				
3	Waste gas heat boiler	Jetfire/ expl/fl. fire	37	620	4	0.2	4.9	10.1	35.2	14.2	37.1				
4	High temperature shift	Jetfire/ expl/fl. fire	35	360	3	0.2	8.0	6.1	38.3	14.2	34.0				
5	Low temperature shift	Jetfire/ expl/fl. fire	33.5	240	3	0.2	12.0	1.1	42.3	14.2	30.0				
6	CO2 absorber	Jetfire/ expl/fl. fire	31.7	−1	4.5	0.2	10.1	0.3	67.1	22.0	0				
6	Separator downstream CO2 absorber	Jetfire/ expl/fl. fire	31	−1	1	0.3	0.1	0.3	74.6	24.4	0				
7	Methanation	Jetfire/ expl/fl. fire	30	270	4	0.5	0.1	0.1	74.2	24.5	0.3				
7	Synthesis gas cooler (SS)	Jetfire/ expl/fl. fire	30	30	2	0.7	0	0	73.9	24.6	0.5				
8	Synthesis gas compressor	Jetfire/ expl/fl. fire	200	40	1	0.7	0	0	73.9	24.6	0.5				
8a	Molecular sieves	Jetfire/ expl/fl. fire	72	5	3	0.7	0	0	73.9	24.6	0.5				
9	Syngas heat exchanger (TS)	Jetfire/ expl/fl. fire	200	31	3	8.9			63.7	21.2		1.3			
9	Syngas heat exchanger (TS)	Tox. cloud	200	31	3	9.5			57.5	21.5		8.5	8500		
9	Synthesis reactor	Jetfire/ expl/fl. fire	200	450	1	9.5			57.5	21.5		8.5			
9	Synthesis reactor	Tox. cloud	200	450	1	9.5			57.5	21.5		8.5	8500		
10	Synloop waste heat boiler (TS)	Jetfire/ expl/fl. fire	200	300	1.5	10.1			51.6	17.3		15.5			
10	Synloop waste heat boiler (TS)	Tox. cloud	200	300	1.5	9.5			57.5	21.5		8.5	8500		
10	Syngas heat exchanger (SS)	Jetfire/ expl/fl. fire	200	175	3	10.1			51.6	17.3		15.5			
10	Syngas heat exchanger (SS)	Tox. cloud	200	175	3	9.5			57.5	21.5		8.5	8500		
10	NH3 converter effluent chiller (TS)	Jetfire/ expl/fl. fire	200	−25	3	11.3			58.0	19.0		5.7			
10	NH3 converter effluent chiller (TS)	Tox. cloud	200	−25	3	9.5			57.5	21.5		8.5	8500		
11	Ammonia separator	Jetfire/ expl/fl. fire	200	−25	1	11.8			60.4	19.9		1.7			
11	Ammonia separator	Tox. cloud	200	−25	1	9.5			57.5	21.5		8.5	8500	1500	
12	Ammonia expansion vessel	Jetfire/ expl/fl. fire	18	−22	5	23.5			42.3	15.8		11.1			
12			18	−22	5	23.5			42.3	15.8		11.1		2300	68,000

(continued on next page)

Table 2 (*continued*)

Process unit	Equipment (TS – Tube Side, SS – Shell Side)	Central event	Pressure (bar g)	Temp. (°C)	Height (m)	Composition (mol %)							Mass gaseous NH3 (kg)	Mass liquid NH3 (kg)	Subsequent supply (kg/h)
						CH4	CO2	CO	H2	N2	H2O	NH3			
10a	Ammonia expansion vessel NH3 converter effluent chiller A (SS)	Tox. Cloud Tox. cloud	5.2	10	3									5650	68,000
10a	NH3 converter effluent chiller B (SS)	Tox. cloud	2.3	−7	3									4600	0
10a	NH3 converter effluent chiller C (SS)	Tox. cloud	0.8	−21	3									4200	0
10a	NH3 converter effluent chiller D (SS)	Tox. cloud	0.1	−32	3									2200	0
10a	Ammonia compressor	Tox. cloud	9.3	105	1										50,000
10a	Ammonia condenser	Tox. cloud	9	25	9									5	50,000
10a	Ammonia collection vessel	Tox. cloud	9	25	5									2200	50,000
10a	Ammonia product pumps	Tox. cloud	17	10	1									3700	68,000
13	Ammonia buffertanks	Tox. cloud	16	10	1.5									32,200	0

weather conditions and wind speed are influential. The calculations are based on the average weather conditions as recorded in the weather service database of Maastricht Aachen airport. The most common weather type is D ("pasquill stability D, neutral little sun and high wind or overcast/windy night") with a wind speed of 5 m/s. The average temperature is assumed to be 10 °C.

3. Results

A selection of the 64 most relevant process equipment of the ammonia production process is shown in Tables 2 and 3. The selection is based on expert opinion, and an average cross-section of an ammonia plant comprising the most recognizable equipment has been considered. Table 2 contains input data such as the process pressure and temperature and the height at which the content is being released. It also lists the most relevant substances of the gas composition, and the mass of the gaseous and liquid ammonia. And finally, for some of the process equipment, the subsequent supply of ammonia from other process equipment of the containment system is recorded.

Table 3 shows the calculated effect distances, which are the horizontal distances from the source to the effect radius at a height of 1 m. Table 3 also lists the calculated release rates and their duration. The release durations leading to heat radiation, flame contact and overpressure effects are much longer than 20 s and have not been calculated in more detail. The exposure time inevitably leads to a chance of death of at least 95% in case of a jet fire of 35 kW/m^2. In case of an (unignited) gas cloud the duration is long enough to become stable and to reach its maximum size before it is ignited in a delayed time. The last column records the concentrations of ammonia that correspond to the exposure time. If there is a varying release rate due to a subsequent delivery, both the concentration of the first and of the total release duration are given.

Fig. 4 shows the 35 kW/m^2 radius of the synthesis reactor (step 9 in Fig. 2) as a top view at 1 m height. The point of release is in the middle of the Y-axis. The synthesis reactor has a pressure of 200 bar and a temperature of 450 °C in normal operation. The gas consists of hydrogen and nitrogen in a ratio of 3 to 1 with approximately 9.5% methane. The release rate is 31.3 kg/s, which results in a jet fire when immediately ignited. The maximum distance of the 35 kW/m^2 radius at 1 m height from the point of release is 55 m. Fig. 5 shows the course of the heat

radiation from the point of the release as a side view at 1 m height. The heat radiation is more than 35 kW/m^2 between 16 and 55 m. The maximum heat radiation is over 100 kW/m^2 in the center of the jet fire.

Fig. 6 shows a side view of the gas cloud released from the separator downstream the CO$_2$ absorber (step 6 of Fig. 2). The size of the gas cloud is limited by its lower explosion limit of 53,200 ppm which is assumed to be the size of the flash fire. The maximum distance to the source is just over 35 m.

A gas release at the molecular sieves (step 8a of Fig. 2) can also lead to a jet fire, a flash fire or an explosion due to respectively an immediate or delayed ignition. Fig. 7 shows the 0.9 bar overpressure radius at ground level with a maximum distance of 19 m from the point of release, with the ignition source in the middle of the explosion at 15 m from the point of release. The effect radius at 1 m height has been calculated assuming the explosion to be spherical and its center on ground level. The moment of ignition is set in Phast™ as delayed, meaning the explosive cloud is ignited after 11 s after its first release when it has stabilized within its explosive limits. This delayed explosion scenario is assumed to be worst case.

Fig. 8 shows a side view of a toxic cloud released from the (shell of the) ammonia converter effluent chiller A (step 10 of Fig. 2). The chiller's shell side contains 5650 kg of saturated ammonia at 10 °C at an equilibrium pressure of 5.2 bar gauge, which is released at the bottom of the equipment at a height of 3 m. There will also be a subsequent delivery of 68 tons/hr ammonia for 300 s, meaning the control room response time. The total amount of ammonia is released at a flow rate of 33.8 kg/s for 336 s. No pool is formed so the exposure time is equal to the release duration. For a 95% chance of death, the ammonia concentration at an exposure time of 336 s is 38,800 ppm. The effect radius at 1 m height for this concentration is 84 m. The 38,800 ppm radius stabilizes after 9 s and continues until the chiller has emptied after 336 s.

Fig. 9 shows the calculated effects in a bar graph in which the main equipment is put in the order of the ammonia production process. The numbers behind the equipment correspond to the process units in Fig. 2. The largest effects of the ammonia production process due to the release of flammable gases are to be expected in the process part with the highest pressures: from compression to ammonia separation. The largest toxic effects regarding the release of ammonia can be found at the ammonia product pumps and the buffer tanks.

Table 3
Output data from Phast™.

Process unit	Equipment (TS – Tube Side, SS – Shell Side)	Central event	Effect radius (m)	Flow rate (kg/h)	Source duration (s)	Concentration at chance of death ≥ 95% (ppm)
1	Desulfurization	Jetfire/expl/fl. fire	32/8/0	8.16	>20	
2	Reformer (TS)	Jetfire/expl/fl. fire	0/0/0	6.42	>20	
3	Secondary reformer	Jetfire/expl/fl. fire	0/0/0	6.39	>20	
3	Waste gas heat boiler	Jetfire/expl/fl. fire	0/0/0	6.41	>20	
4	High temperature shift	Jetfire/expl/fl. fire	0/0/0	7.23	>20	
5	Low temperature shift	Jetfire/expl/fl. fire	0/0/0	7.70	>20	
6	CO_2 absorber	Jetfire/expl/fl. fire	0/12/0	8.79	>20	
6	Separator downstream CO_2 absorber	Jetfire/expl/fl. fire	30/19/35	7.21	>20	
7	Methanation	Jetfire/expl/fl. fire	0/7/0	4.95	>20	
7	Synthesis gas cooler (SS)	Jetfire/expl/fl. fire	22/13/20	6.62	>20	
8	Synthesis gas compressor	Jetfire/expl/fl. fire	61/49/71	41.3	>20	
8a	Molecular sieves	Jetfire/expl/fl. fire	34/19/21	16.3	>20	
9	Syngas heat exchanger (TS)	Jetfire/expl/fl. fire	61/37/49	47.8	>20	
9	Syngas heat exchanger (TS)	Tox. cloud	2	49.6	171	53,000
9	Synthesis reactor	Jetfire/expl/fl. fire	55/26/38	31.3	>20	
9	Synthesis reactor	Tox. cloud	2	31.3	271	41,100
10	Synloop waste heat boiler (TS)	Jetfire/expl/fl. fire	57/26/37	37	>20	
10	Synloop waste heat boiler(TS)	Tox. cloud	2	37	230	46,000
10	Syngas heat exchanger (SS)	Jetfire/expl/fl. fire	57/20/21	42	>20	
10	Syngas heat exchanger (SS)	Tox. cloud	2	40	212	49,000
10	NH3 converter effluent chiller (TS)	Jetfire/expl/fl. fire	66/38/52	57	>20	
10	NH3 converter effluent chiller (TS)	Tox. cloud	2	57	148	58,000
11	Ammonia separator	Jetfire/expl/fl. fire	68/55/86	55.9	>20	
11	Ammonia separator	Tox. cloud	34	218–56.4	7–150	270,000–57,000
12	Ammonia expansion vessel	Jetfire/expl/fl. fire	0/7/0	4.1	>20	
12	Ammonia expansion vessel	Tox. Cloud	34	65–19	50–250	101,000–41,000
10a	NH3 converter effluent chiller A (SS)	Tox. cloud	84	33.8	336	38,800
10a	NH3 converter effluent chiller B (SS)	Tox. cloud	51	22.9	200	50,000
10a	NH3 converter effluent chiller C (SS)	Tox. cloud	41	13.7	307	41,000
10a	NH3 converter effluent chiller D (SS)	Tox. cloud	14	4.9	449	33,600
10a	Ammonia compressor	Tox. cloud	11	2.8	300	41,000
10a	Ammonia condenser	Tox. cloud	0	13.9	300	41,000
10a	Ammonia collection vessel	Tox. cloud	27	43.8–13.9	74–226	83,000–41,000
10a	Ammonia product pumps	Tox. cloud	128	61	300	41,000
13	Ammonia buffertanks	Tox. cloud	156	59	542	30,500

It should be noted that where process equipment does not show any effect, it does not mean that there are no effects. However, the effects do not meet the criterion whereby the chance of death is at least 95% at a height of 1 m.

4. Discussion

In the toxic scenarios, the release duration largely determines the size of the effect. The release duration for those scenarios with a subsequent delivery of ammonia from another process equipment in their containment system (process units 10a and 12, see Fig. 2), is depending on the response time of the control room operator to shut down the plant. In consultation with control room operators, a response time of 5 min has been chosen, based on rapid detection, both from process data and from local observations (odor, noise) in combination with a simple intervention. A longer reaction time of for example 10 min, would increase the toxic radii somewhat, but would not significantly change the overall conclusion.

The effects have been calculated with a chance of death of at least 95% and this is much higher than was found in other papers and guidelines. Due to the choice of such a high chance of death, all persons in the effect radius will not be able to flee or avoid the hazard and will,
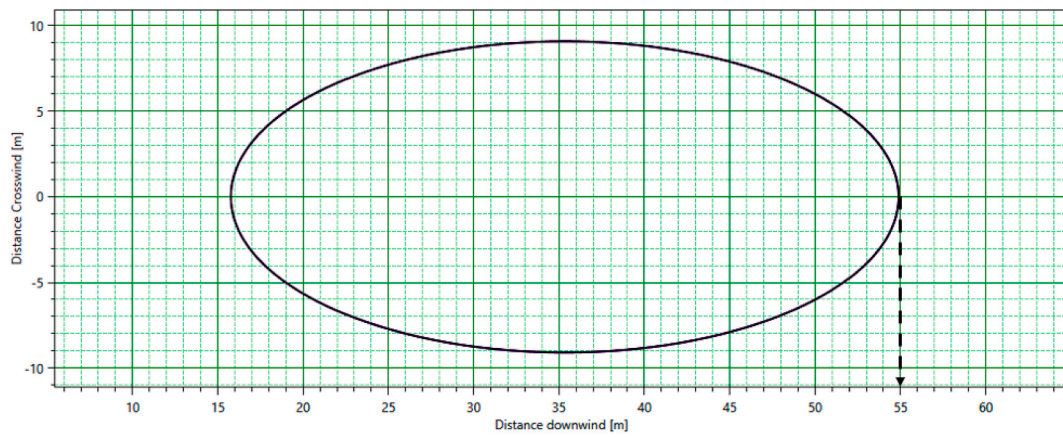
Fig. 4. Top view at 1 m height of the 35 kW/m^2 radius of the synthesis reactor as a function of the distance from the point of release.
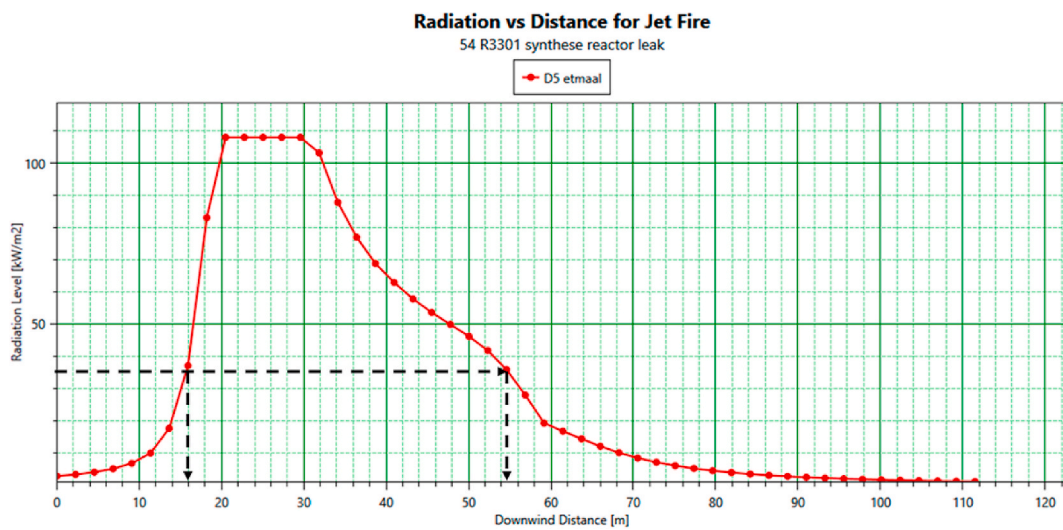

Fig. 5. Side view at 1 m height of the heat radiation of the synthesis reactor as a function of the distance from the point of release.
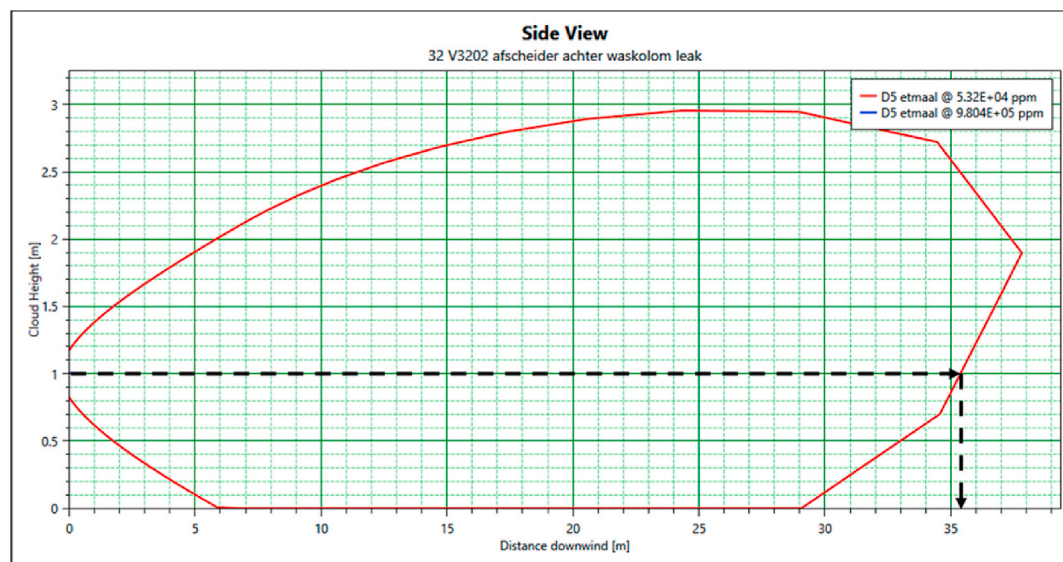

Fig. 6. Side view of the flammable gas cloud of the separator downstream the CO_2 absorber as a function of the distance from the point of release.

Late Explosion Worst Case Radii
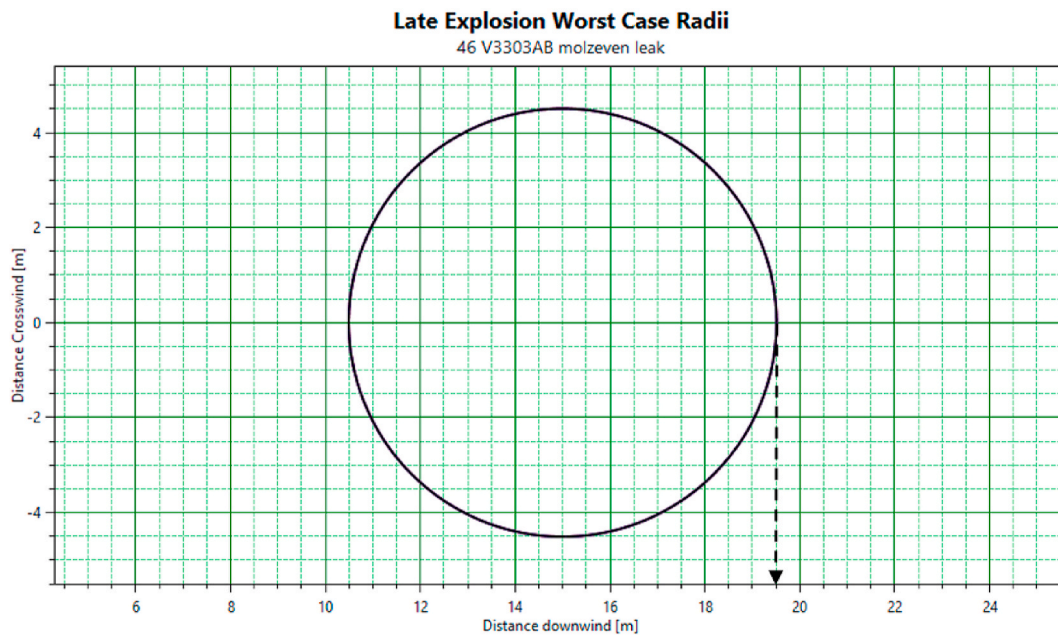46 V3303AB molzeven leak

Fig. 7. Top view of the 0.9 bar overpressure radius at ground level of the molecular sieves as a function of the distance from the point of release.
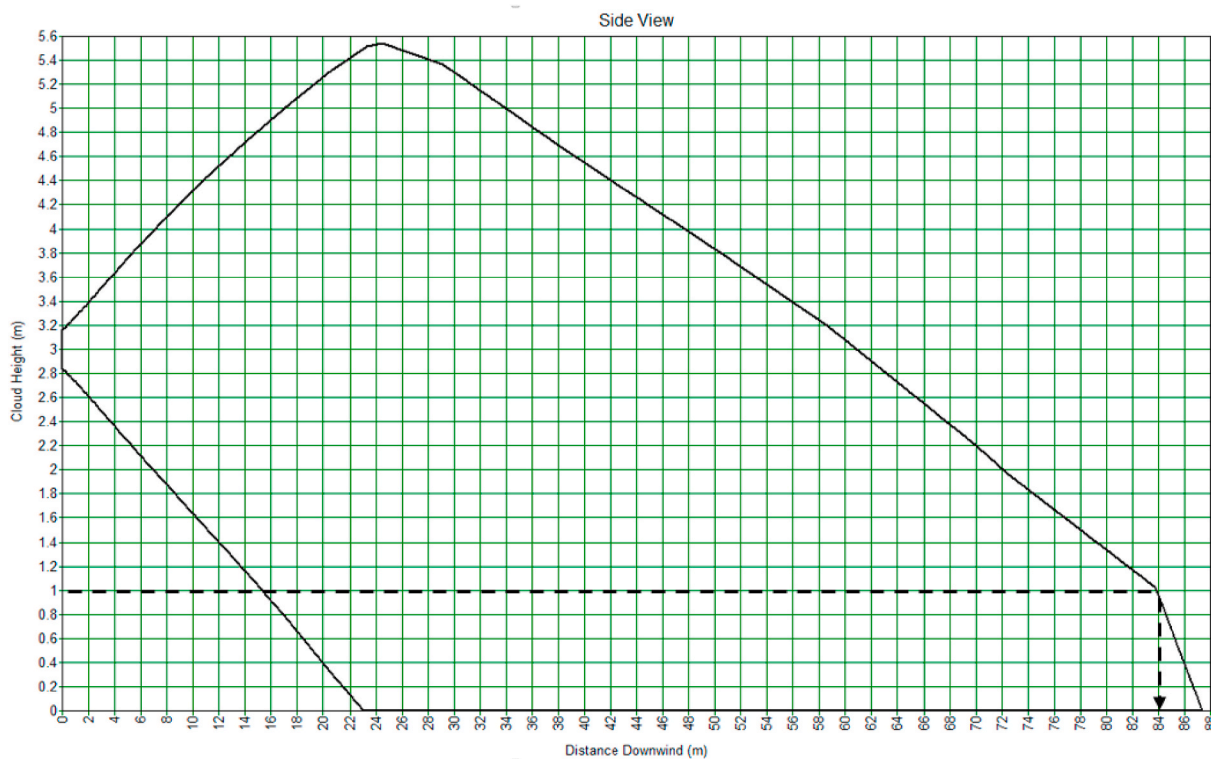
Side View

Fig. 8. Side view of 38,800 ppm ammonia radius of the ammonia convertor effluent chiller A (shell side) as a function of the distance from the point of release.

regardless of their physical condition, be immediately affected and will most certainly decease. The probit relationship of ammonia shows an asymptotic approximation of the concentration to one million ppm with an increasing chance of death. The choice of 95% chance of death is arbitrary to the extent that a greater chance leads to too high concentrations and too small effect radii. The toxic effects could therefore be underestimated.

The overpressure of 0.9 bar at which it is very likely to decease from the blast pressure could be questioned as standards, guidelines and

scientific studies reveal a large variety of values. However, where the HSE, s.d. probit relationship establishes a chance of death of 50% for 0.9 bar based on primary effects (lung damage), a more than 95% chance of death considering the secondary, tertiary and even quaternary effects appears to be justified. Even more because there is a possibility that in a confined process installation the actual overpressure exerted on people is higher than the calculated overpressure due to reflection and turbulences.

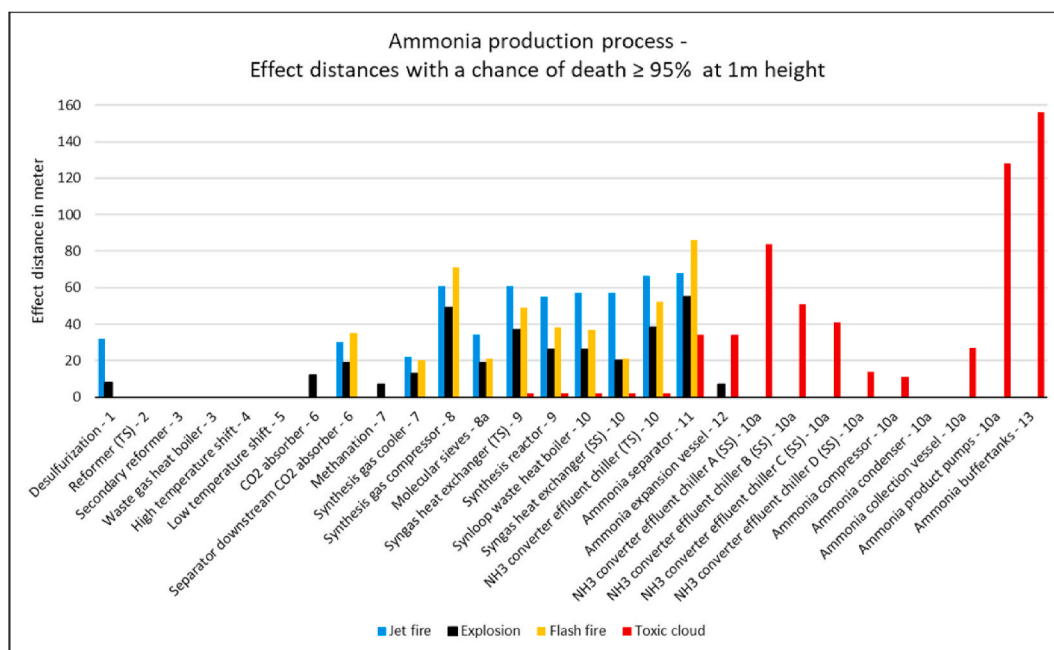Phast™ has been provided to the authors as a good dispersion

Fig. 9. Overview of the effect distances for the main equipment of the ammonia production process with a chance of death of at least 95%.

calculation model for this purpose. However, it could have been any other. Like all models, the Phast™ calculation model has several limitations that must be considered. Some of meaning are mentioned below:

- Any structures, buildings, and the like are not included in the calculations. This is not possible in Phast™ unless these data are entered manually.
- The hazards of most mixtures are determined by the individual components, meaning that the absorption of ammonia by moisture in the outside air is not considered.
- Phast™ can calculate with changing compositions, but only as a step disturbance and not according to a (predefined) curve. This is especially relevant for toxic effects with longer exposure times where the released gas' composition changes. To overcome this, toxic effects were calculated using average compositions of the released gas.
- Phast™ calculates dispersions as if equipment is located in a free space. So, caution is appropriate when equipment is located indoor or in confined spaces.
- When used in batch plants, attention should be paid to the choice of process conditions as they may vary.

Flammable, explosive and toxic clouds progress in a specific direction, meaning they are determined by the location of the release (jet fires) or by the prevailing wind (toxic clouds). This is different for flash fires and explosions: both the flames and the overpressure radius develop in all directions from the center of the explosion. Flash fires and explosions therefore cover a larger area, which makes them more dangerous than the other two. However, this phenomenon has not been considered as the distance has been chosen as a measure of the size of the effect.

Regarding flash fire effects it is assumed that everyone in the flammable cloud will decease. This assumption is somewhat conservative as field operators and mechanics wear protective clothing made of fire-retardant materials, which significantly reduce or prevent thermal injury in the body areas that are covered by the fire-retardant material.

In the overpressure and heat radiation scenarios no account has been taken of secondary effects by domino scenarios although they may be possible (Reniers and Cozzani, 2013). Secondary effects can be determined in a next step using Phast™ by calculating overpressure and heat radiation levels at which consequential damage may occur to adjacent process equipment. Secondary effects should then be attributed to the initially failed process equipment. However, it should be noted that the chance of death may be substantially lower from domino scenarios as they take some time to develop, meaning that the chance of escaping from the affected area is much larger. It is expected that these calculations will most likely not substantially contribute to the results of this research.

It can be deduced from Fig. 9 that:

- The largest effect distances are attributable to ammonia;
- The effects of heat radiation, flame contact and overpressure are approximately the same;
- The heat radiation and overpressure effects up to and including the CO_2 absorber (step 6 of Fig. 2) are less than 35 kW/m^2 and 0.9 bar respectively at ground level. The inert gases present (CO_2, N_2 and water) absorb so much energy that they significantly reduce the effects;
- Process pressure is decisive regarding the overpressure, flame contact and heat radiation effects;
- The hold-up of saturated ammonia and the subsequent delivery contribute to the release duration, and thus to the effect radii;
- The higher the temperature of the saturated ammonia, the larger the effect radii.

5. Conclusions

In this paper, flammable and toxic effects from a release from the main equipment of an ammonia plant have been calculated. Such an encompassing approach, which can be carried out for an entire plant, is innovative and has never been conducted before. The calculations show that the ammonia production process comprises several intrinsic hazards related to the presence of steam, flammable gas and ammonia. A release of a hazardous substance can give rise to burns, internal injury or poisoning from exposure to heat radiation, flames, overpressure or toxic concentration respectively. In the front end of the ammonia production process loss of containment scenarios may lead to heat radiation from jet fires, flame contact from flash fires or to overpressure from explosions due to the presence of flammable components. In the back end there is

also ammonia present which release may lead to high toxic concentration levels resulting in poisoning. Releases of steam have not been considered as their effects are much smaller than those from jet or flash fires. The largest adverse impact on humans in the event of failure can be expected from the compression to the ammonia separation (exposure to heat radiation, flame contact and overpressure) and from the ammonia product pumps and the buffer tanks (exposure to a toxic ammonia concentration). In general, it can be concluded that pressure, temperature and mass are of meaning in that when they increase, the effects and hence the adverse impact on humans become larger.

Effects have been calculated for a chance of death of at least 95%. This results in effect radii from which maximum distances from the point of release can be determined. By taking the maximum distance as a (relative) measure, the effects of a release of both flammable and toxic substances can be compared. If the central event cannot be avoided, there is a 1 to 1 relationship between the central event and the consequences of burns, internal injury, and poisoning resulting in death. The method in this paper enables to measure the adverse impact on humans from a release of hazardous substances from any process equipment. Hence, this paper provides a relative ranking of equipment and does not claim to provide absolute results, but it leads to an understanding of the relative position of equipment with respect to their dangerousness.

The effect calculation results can be used for risk mapping of an entire chemical plant or be employed and applied in a layer of protection analysis (LOPA) to establish risk mitigation measures. The results from this research provided new insights for OCI Nitrogen into the current method of equipment classification and the investment in preventive measures. A path forward for future process safety research can be the link of the equipment ranking results with barrier management and as such, further optimization of safety investments.

Author statement

Peter Schmitz: Conceptualization, Methodology, Writing – original draft. Genserik Reiniers: Conceptualization, Supervision, Writing – review & editing. Paul Swuste: Conceptualization, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial i nterests or personal relationships that could have appeared to influence the work reported in this paper.

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