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ANDREAH

AMMONIA BASED MEMBRANE REACTOR FOR GREEN HYDROGEN PRODUCTION

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1 EXECUTIVE SUMMARY

1.1 Description of the deliverable content and purpose

Within the framework of the ANDREAH Project, aimed at providing a quantum leap in the development of advanced ammonia decomposition technologies to produce ultra-pure hydrogen (>99.998%) by developing an innovative system based on a Catalytic Membrane Reactor (CMR) for the cracking of Ammonia.

To support the development of appropriate health and safety measures for ANDREA Project, this document constitutes Deliverable D5.2 “Health and Safety Requirements”, prepared under Work Package 5.

The purpose of this report is to present the methodologies adopted and the detailed findings of the Health and Safety Analysis conducted for the ANDREAH Project, with the objective of identifying potential hazards, assessing associated risks, and defining the safety requirements necessary to ensure the safe design, operation, and maintenance of the proposed technology.

The document reports the following task and analysis:

- Health, Safety and Environment (HSE) Philosophy;
- HSE Assessment inspired by HAZard IDentification (HAZID)

The objective of the HSE Philosophy is safeguarding the welfare of employees and the general public.
HSE Philosophy is divided in two main topics, Loss Prevention and Protection.
Loss Prevention is related to the measures aimed to prevent accidents and reduce the risks in the workplace to avoid health and safety damages and property losses caused by accidents. The Protection is related to mitigation of the possible effects in case of accident, avoiding or reducing possible losses in term of safety, environment, asset damage and loss of production.

The objective of the HSE Assessment inspired by HAZID was to identify and evaluate safety hazards. The analysis results are represented by a series of recommendations which take the form of suggested design changes, requirements of verification and additional studies or suggestions for specific operational procedures to be implemented.

For this purpose, a Risk Analysis has been carried out in order to identify the main hazards related to the technologies involved in the Project and to their use in the selected demo phase and to identify possible improvements for each undesirable event or hazard.
This document reports the outcomes of the aforementioned Risk Analysis.

2 INTRODUCTION

2.1 Scope and organization of the document

Within the framework of the ANDREAH Project, one of the foreseen tasks is to develop appropriate safety measures and procedures for securing the safe performance of advanced ammonia decomposition technologies to produce ultra-high hydrogen (>99.998%) by developing an innovative system based on Catalytic Membrane Reactor (CMR) for the Ammonia Cracking, with particular reference to the safety standards (Scope of Work Package 5, Task 5.2).

To address the Health & Safety issues, the following procedure has been applied:

- Preliminary Risk Analysis, aimed at identifying, for each technology involved in the Project, the main hazards only on the basis of the physical and chemical properties of the substances present in the system / process.
- Qualitative Risk Analysis, aimed at identifying the potential hazards related to a system or process and the potential consequences of such event.
- Identification of possible improvements or preventive measures for each undesirable event or hazard.

The HSE analysis has been mainly focused on the definition of guidelines / improvements aimed at minimizing the risks associated to the installation and use of technologies in the demo phase, as well as in any other sites where similar technologies will be replicated.

This task will analyse the ANDREAH processes and technologies in order to develop appropriate safety measures and procedures for securing its safe performances. The analysis will be performed focused on both safety procedures to be taken into account for the validation site, but also guidelines for the scale-up of the system to be integrated at industrial level. Particular attention will be paid to the generation and use of hydrogen as well as to the production and storage of ammonia in order to comply with the requirements in terms of regulatory framework, ATEX and Health and Safety Issues.

3 METHODOLOGY

Risk Analysis is a powerful tool to benchmark the intrinsic safety of a process or an operation against its expected performance, allowing at the same time a quantifiable appraisal of the expected issues towards the human safety and health, the environment, the property and asset, the capacity to continue business. "Risk" is a specific concept, which can be typically defined as the "Combination of the probability of an event and the consequences of the event" and it represents the qualitative and quantitative measure of the combined likelihood of an accidental or unplanned event and the potential consequences of such event.

The Risk Analysis developed in this report will be focused on “major” accidents potentially arising from the operation of the technologies that will be implemented in the ANDREAH Project (prototype), i.e. on those occurrences such as a major emission, fire, or explosion resulting from uncontrolled developments in the course of the operation of any installation, leading to serious danger to human health or the environment.

For this reason, the present Risk Analysis takes into consideration only those events consisting in the release into the atmosphere (loss of containment) of chemicals characterized by flammability and/or toxicity and/or toxicity to the environment. These types of substances could lead, depending on their physical/chemical properties and on the release conditions, to serious consequences for people (e.g. irreversible injuries, fatalities) and/or environment (pollution).

In the framework of ANDREAH Project, the Risk Analysis will be carried out in two steps, described in detail in the next paragraphs:

- HSE Philosophy (see Paragraph 3.1);
- Preliminary (Qualitative) Risk Analysis (see Paragraph 3.2 for the description of the methodological approach).

3.1 HSE Philosophy

Scope of the section is to describe the general HSE Philosophy of the ANDREAH Project System Safeguarding the welfare of employees and the general public is an obligation for each Company. Moreover, good management practices needed to ensure safe operation also ensure efficient operation.

HSE Philosophy is divided in two main topics, Loss Prevention and Protection.
Loss Prevention is related to the measures aimed to prevent accidents and reduce the risks in the workplace to avoid health and safety damages and property losses caused by accidents.

In ANDREAH Project system operation, in addition to occupational hazards related to the working environment, there are specific major hazards related to the presence and handling of flammable substances and flammable gas.
These hazards must be taken into account and the risks associated to these hazards shall be reduced to acceptable levels through the application of engineering best practices, codes and standards.
Loss Prevention during process design is developed by following steps:

- Identification of the Hazards that can be faced in the plant/facility;
- Management of the Hazards identified, to prevent the occurrence of them.

The Protection is related to mitigation of the possible effects in case of accident, avoiding or reducing possible losses in term of safety, environment, asset damage and loss of production.
This document summarizes the philosophies and criteria to be followed in the design in order to:

- Minimize the occurrence of potential hazards;
- Minimize the consequences of an accidental event, providing safety devices to detect, isolate and control accidental releases of flammable gases;

- Ensure a safe working environment for personnel.

The basic Loss Prevention approach to eliminate or prevent hazards can be summarised as follows:

- Identify potential hazards leading to loss of containment for random causes, such as inspection, anticorrosion measures, etc;
- Control of the process: prevention of dangerous deviations of process variables (pressure, temperature, flow, etc.) by provision of automatic process control system and emergency control system.

The basic Protection approach to minimize the losses can be summarised as follows:

- Limitation of inventory that can be released in case of process losses;
- Mitigation of consequences in case of loss of containment.

The following hierarchical approach shall be applied to the management of risk for this project:

- Identification of hazards and risk evaluation;
- Elimination and minimization of hazards by design (inherently safe design);
- Prevention (reduction of likelihood);
- Detection (transmission of information to control point);
- Control (limitation of scale, intensity, duration and escalation);
- Mitigation of consequences (protection from effects) and
- Evacuation (safe escape of personnel).

3.1.1 Identification of Hazards and Hazards Assessment Studies

All hazards related to the ANDREAH system operations shall be identified during design development. They mainly depend on the type of hazardous substances present, the operating conditions of them and system layout.
These hazards identified must be considered during engineering design phase of the demo plant and the risks associated to these hazards shall be reduced to acceptable levels through the application of engineering best practices, codes and standards.
During this phase, the design of the system must consider and implement all the additional risk prevention actions and mitigation measures inspired in the HAZard IDentification (HAZID) Study.

3.2 Preliminary risk analysis

3.2.1 Objectives

In order to focus the efforts of the subsequent Qualitative Risk Assessment on real major hazard related to the technology, a preliminary (qualitative) risk analysis will be carried out, aimed at identifying the main hazards only on the basis of the physical and chemical properties of the substances present in the system / process.

3.2.2 Scope and limitations

The preliminary risk analysis will be performed for the ANDREAH Project.

3.2.3 Methodology assumption and criteria

The preliminary identification of the main hazards related to the technology will be carried out through the following steps:

1. Identification of the substances processed in the system under analysis;
2. Identification of the main hazards related to each substance, based on material classification according to Regulation 1272/2008/CE;
3. Definition of potential adverse effects on people or environment.

For this preliminary analysis, the main hazardous properties that will be investigated are the

following:

- Toxicity:
- IDLH, Immediately Dangerous to Life and Health: an atmospheric concentration of any toxic, corrosive or asphyxiant substance that poses an immediate threat to life or would cause irreversible or delayed adverse health effects or would interfere with an individual's ability to escape from a dangerous atmosphere;
- LC50, Lethal Concentration 50: concentration of a material in air that is lethal for 50% of the subjects in case of exposure for 30 minutes;
- LOC, Level Of Concern: concentrations of an extremely hazardous substance in air above which there may be serious irreversible health effects or death as a result of a single exposure for a relatively short period of time (1/10 of NIOSH IDLH levels);
- Flammability;
- LFL, Lower Flammable Limit: the concentration of a flammable gas in air below which there is insufficient amount of gas to support and propagate combustion;
- UFL, Upper Flammable Limit: the concentration of a flammable gas in air above which there is insufficient amount of oxygen to support and propagate combustion;
- Toxicity for the environment.

Depending on the hazardous properties of the materials, the following accidental scenarios could occur:

- Jet Fire: a fire type resulting from the discharge of liquid, vapour, or gas into free space from an orifice, the momentum of which induces the surrounding atmosphere to mix with the discharged material;
- Pool Fire: the combustion of material evaporating from a layer of liquid at the base of the fire;
- Flash Fire: a fire that spreads by means of a flame front rapidly through a diffuse fuel, such as a dust, gas, or the vapours of an ignitable liquid, without the production of damaging pressure;
- Explosion (confined or unconfined): a release of energy that causes a pressure discontinuity or blast wave;
- Toxic Dispersion;
- Environmental Pollution.

This preliminary analysis will allow to focus the subsequent detailed Quantitative Risk Assessment on the real major hazards related to each technology package and phase demo.

4 H&S ANALYSIS RESULTS

4.1 Characteristic of gases

4.1.1 Ammonia

The table below indicates the fire hazard properties of Ammonia.

Table 1. Fire Hazards Properties of Ammonia

Properties		Ammonia
Flash Point [°C]		132
Flammability in Air [%]	Lowest Concentration in air	15
	Highest Concentration in air	33.6
Auto ignition Temperature [°C]		651
Minimum Ignition Energy [mJ]		680

The table below indicates the toxicity hazard properties of Ammonia.

Table 2. Toxicity Properties of Ammonia

Properties	Ammonia
LC_{Lo} [ppm]	5000
IDLH [ppm]	300
TLV-TWA [ppm]	25
TLV-STEL [ppm]	35

Ammonia even at dilute concentrations is highly toxic to aquatic animals, and for this reason it is classified as dangerous for the environment.

The table below indicates the toxicity hazard properties for aquatic life of Ammonia.

Table 3. Toxicity hazard properties for aquatic life of Ammonia

Properties	Ammonia
LC50	0.44 mg/l (Exposure time: 96 h - Species: Cyprinus carpio)
EC50	25.4 mg/l (Exposure time: 48 h - Species: Daphnia magna)
LC50	2.43 mg/l (Exposure time: 96 h - Species: Lepomis macrochirus)

Flammability for gaseous Ammonia only occurs when gas volume concentrations are between 15% and 33.6% by volume in a mixture with air, while auto-ignition only occurs at very high temperatures. Gas clouds may ignite if they meet an ignition source as they disperse. Explosion, on the other hand, requires gas concentrations within the flammability limits in a congested or confined space and the presence of an ignition source.

The primary hazards of Ammonia release are:

- Toxicity. If the concentration of Ammonia is high enough in the air, there is a potential for toxicological hazard for personnel in the immediate area, particularly if the release occurs in confined spaces.
- Release of Ammonia if immediately ignited results in a jet fire, i.e. a turbulent diffusion flame resulting from the combustion of a fuel continuously released with some significant momentum in a particular direction.

- In case of delayed ignition of a high momentum release, the ignition can generate a vapor cloud explosion if the mass of gas and the confinement are sufficient to generate flame acceleration, or a rapid combustion of the gas cloud within flammability limits (Flash Fire).
- Release of liquid Ammonia is dangerous for aquatic life, severe environmental impact.

4.1.1.1 Explosion and Fire Hazards

Ammonia has a characteristic of not only dispersing into the atmosphere due to its lower density than air but also, dissolution in water. In other words, ammonia can easily be absorbed with a large amount of moisture in the event of a leakage, causing the resulting mixture to become heavy and likely to settle on facility. These characteristics must also be considered when evaluating the dispersion risk of ammonia. Table 4 summarizes the different characteristics of Ammonia.

Table 4. Characteristics of ammonia (Aatola et al. 2009; DNV GL 20019; Haynes et al. 2016; Herdzik 2021; Solution 2019; Speight 2011; Valera-Medina et al. 2018)

Fuel Specification	Ammonia
Flash Point	132
Auto-ignition temperature (°C)	630
Low Heating Value (LHV, MJ/kg)	18.6
High Heating Value (HHV, MJ/kg)	22.5
Flammability range (% volume in air, LFL-UFL)	15-28
Density (t/m^3)	0.68
Energy density (GJ/m^3)	11.4
Volume per unit energy (m^3/GJ)	3.14
Toxicity	Highly

As shown in Table 4, the flammability limits of ammonia at standard atmospheric conditions range from 15.0% (lower flammability limit, LFL) to 28.0% (upper flammability limit, UFL). This implies that when 15% to 28% of ammonia mixed with air in the atmosphere can lead to potential fire and explosion hazards depending on the presence or absence of an ignition source. In addition, a phenomenon called BLEVE (Boiling Liquid Evaporating Vapor Explosion) can occur, in which fatal accidents such as fires and explosions are triggered by the storage tank rupture and its associated gas released because the cylinder cannot maintain its structural integrity. It is caused by the rising internal pressure due to the boiling of the saturated liquid inside the storage container when heat is applied from the outside.

4.1.1.2 Health and Safety Hazards

Even though ammonia has a lower fire/explosion potential than other low-flammability fuels, unlike other fuels, it can pose risks such as suffocation and cryogenic burns when exposed to normal atmospheric conditions.

Ammonia is a toxic gas and basic compound that can cause asphyxiation. The severity of its effects on humans depends on the route of exposure, dose and duration of exposure. However, exposure to high concentrations of ammonia in the air can cause immediate burns to the eyes, nose, throat, and respiratory tract, and may cause corrosive injuries including skin burns, blindness, lung damage, or even death. Because of this effect, much more careful management in terms of toxicity than other fuels are required.

In general, the concentration of ammonia in the blood is less than 50 μmol/L, which is generated from waste products obtained from protein and is metabolised by the liver to urea or glutamine and excreted in

the urine. Most of the ammonia inhaled, not the ammonia generated by the human body, is in the form of gas or vapour, which immediately interacts with moisture in the skin, eyes, mouth, respiratory tract, and especially the mucous membranes to form ammonium hydroxide. Ammonium hydroxide causes tissue necrosis through cell membrane destruction to destroy cells, and as cellular proteins are decomposed, water is extracted, causing an inflammatory response, causing further damage. Concentrations of ammonia above 100 µmol/L may cause disturbance of consciousness, and from 200 µmol/L, coma or convulsions may occur. When ammonia gas is inhaled, the airways are blocked, breathing becomes difficult, and laryngitis or bronchitis occurs. Exposure to ammonia can be treated by immediately flushing the skin and eyes with plenty of water (Public Health England, 2015).

Table 5 summarizes the different levels of ammonia exposure time and concentrations and their corresponding effects on humans. AEGL (Acute Exposure Guideline Levels) indicate acute exposure threshold levels to ammonia, and measures risks ranging from stage 1 to stage 3, where stage 3 is fatal. Accordingly, if a human is exposed for about 30 minutes at an ammonia concentration of 1,600 ppm, it may cause life-threatening effects). In addition, at a concentration of 5,000 ppm or more, a risk of respiratory arrest may be induced regardless of the exposure time, and at a concentration of 10,000 ppm or more, a burn may occur immediately upon contact with the skin (Council & Levels, 2009).

Table 5. Risk classification based on the exposure time and concentration level

Risk	Exposure Time			Effect
	10 min	30 min	60 min	
AEGL-1	30 ppm	30 ppm	30 ppm	Discomfort, irritation, or asymptomatic numb effect
AEGL-2	220 ppm	220 ppm	160 ppm	Irreversible or other serious and long-lasting adverse health effects or impaired ability to escape
AEGL-3	1,600 ppm	1,600 ppm	1,100 ppm	Life-threatening health effects or death

4.1.1.3 Corrosive Hazards

Ammonia is highly corrosive and can cause chemical corrosion resulting in structural damage.

The main materials corroded include copper, brass and zinc alloys forming green/blue corrosion. Therefore, in order to reduce the risk of corrosion when using ammonia fuel, it is necessary to avoid the use of these materials in the manufacture of storage tanks, engines and various fuel systems.

In terms of structural damage, ammonia can cause Stress Corrosion Cracking (SCC), a phenomenon that can occur in metals exposed to a combination of stress and corrosive environments. This produces cracks by destabilising the protective oxide layer without causing general corrosion under certain circumstances. In the process of failure, general external signs such as surface corrosion or reduction in thickness are not seen. In other words, when a structure or part is damaged due to SCC, the damage occurs suddenly without any warning signal, resulting in a large structural and economic loss due to an accident that cannot be prepared in advance.

Therefore, if not handled properly, SCC can occur, which can lead to vessel rupture and pose a serious threat. This is due to two factors: the stress condition applied to the part or structure and the corrosive atmosphere condition, so each damage condition can be identified, and its occurrence can be suppressed during prevention. In terms of stress, cracks can be caused by both internal and external factors. The internal factor refers to the residual stress formed during product processing, or the residual thermal stress generated during the welding/heat treatment process. The external factor refers to stresses that occur during periodic use, such as operating pressure or external load.

Typically, anhydrous ammonia can cause stress corrosion cracking in containments and systems made of carbon-manganese steel or nickel steel. Therefore, in this prototype to which the ammonia system is applied, the use of those materials is strictly prohibited, and the welding area requires stress relief heat treatment after work.

To minimize the risk of stress corrosion cracking in containment structures and in process systems made of sensitive materials such as carbon-manganese and nickel steel, the following measures must be taken:

- Carbon-manganese steel with yield stress above the standard value is subjected to stress relief heat treatment after welding.
- The tensile and yield properties of the electrode must be greater than those of the tank or piping material at the smallest actual value.
- Do not use nickel steel with a nickel content exceeding 5% or carbon-manganese steel with a yield stress higher than the standard value without heat treatment.
- Nickel steel exceeding 5% nickel content can be used if the transport temperature does not exceed -20℃.
- It is recommended to keep the dissolved oxygen content of less than 2.5ppm by mass.
- Mercury, cadmium, copper, zinc or alloys of these substances are not normally used in fuel tanks and related pipelines, valves, fittings and other equipment in direct contact with ammonia liquid or vapor.
- It is not recommended to use components made of rubber or plastic materials that may deteriorate when exposed to ammonia.

4.1.2 Hydrogen

Hydrogen (H2) is a nontoxic flammable gas.
The table below indicates the fire hazard properties of Hydrogen.

Table 6. Fire Hazard Properties of Hydrogen

Properties		Hydrogen
Flash Point [°C]		Not Available
Flammability in Air [%]	Lowest Concentration in air	4
	Highest Concentration in air	76
Auto ignition Temperature [°C]		566
Minimum Ignition Energy [mJ]		0.02 (as per Group IIC – ATEX)

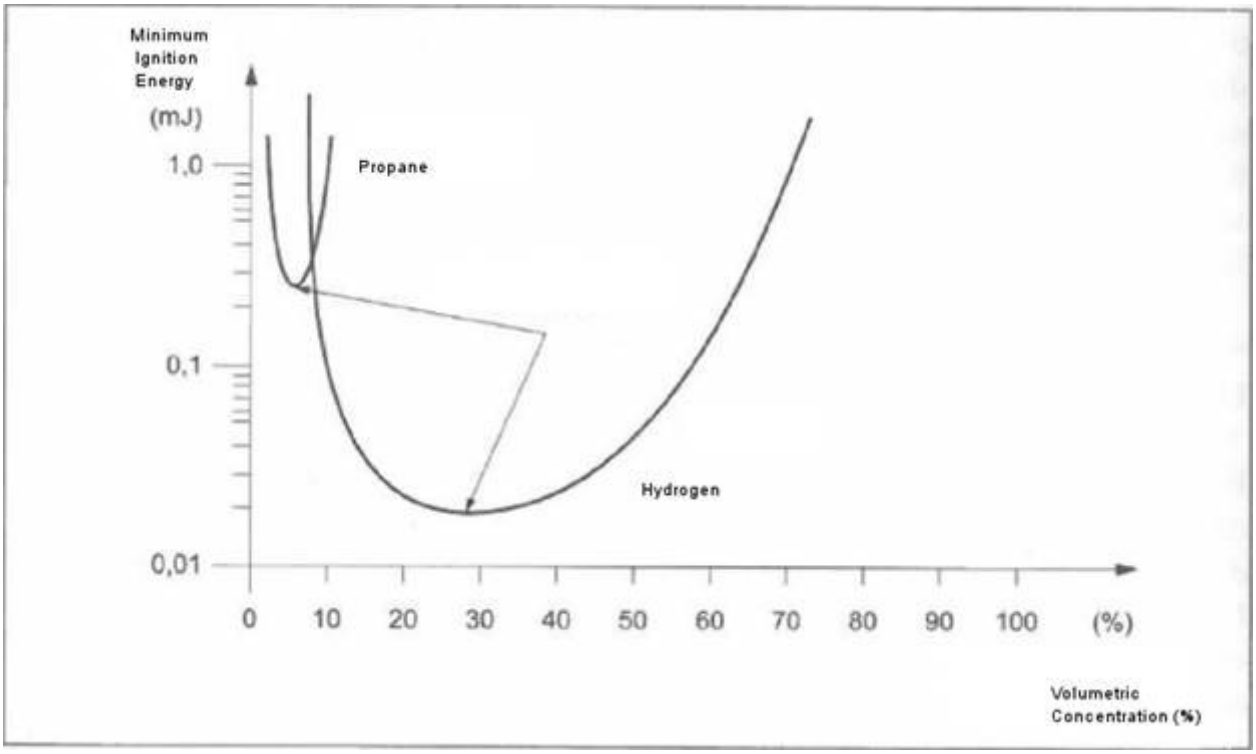


Figure 1. Hydrogen Ignition Energy

Regarding environmental aspects, no ecological damage caused by this gas.

Flammability for Hydrogen occurs when gas volume concentrations are between 4% and 75% by volume in a mixture with air. Auto-ignition only occurs at very high temperatures, but minimum ignition energy is very low. Gas clouds may ignite if they meet an ignition source as they disperse. Explosion, on the other hand, requires gas concentrations within the flammability limits in a congested or confined space and the presence of an ignition source.
The primary hazards of Hydrogen release are:

- Release of Hydrogen if immediately ignited results in a jet fire, i.e. a turbulent diffusion flame resulting from the combustion of a fuel continuously released with some significant momentum and buoyancy in a particular direction.
- In case of delayed ignition of a high momentum release, the ignition can generate a vapor cloud explosion if the mass of gas and the confinement are sufficient to generate flame acceleration, or a rapid combustion of the gas cloud within flammability limits (Flash Fire).
- Asphyxiation. If the concentration of hydrogen is high in the air, there is a potential for asphyxiation hazard for personnel in the immediate area, particularly if the release occurs in confined spaces.

4.1.3 Nitrogen

Nitrogen is a nontoxic and non-flammable gas.
At ambient temperature is non-reactive, it is odourless, colourless and tasteless gas.

Table 7. Properties of Nitrogen

Properties	Nitrogen
Boiling Point [°C]	- 195

The primary hazard of Nitrogen release is:
Asphyxiation. If the concentration of Nitrogen cause Oxygen to fall below 18%, there is a potential for Asphyxiation hazard for personnel in the immediate area, particularly if the release occurs in confined spaces.

The relevant safety regulations of using ammonia will be introduced with due consideration of its potential hazards in terms of its toxicity, corrosive and flammability/explosion.

5 HAZID

The HAZID Review is a structured and systematic brainstorming developed through the application of specific guidewords. The Purpose of the Analysis is to effectively manage project risks through the identification of hazards and environmental issues and capture potential mitigating and/or preventive actions to be incorporated into the design to further improve and enhance the overall safety level.
The HAZID is relevant to the inherent external and internal hazards for the project, and it is focused mainly on components and processes, materials, external events, project philosophies and operational concepts.
The analysis will be aimed at the normal operational of the facility.
The HAZID developed for ANDREAH project is reported below.

Category	HAZID Guideword	Top Event (Hazard Release)	Consequence (Hazard Effect)	Existing Control Measures	Recommendation	
					Action	Responsible
Natural	Climate Extremes	The prototype will be installed outdoor. Potential extreme wind condition	Potential for failure and leak of ammonia/hydrogen. Refer to leakage keyword		Consider wind speed during the design	project
		Potential for flooding	Potential damage to equipment		Consider the potential flooding during drainage design	project
	Lightning	The prototype will be installed outdoor, potential for lightning	Lightning strike. Fatality		Forsee installation of lighting protection as per IEC 62305	project
	Ground movement	Seismic event, subsidence, failure in ground bearing capacity	Potential failure of foundation leading to misalignment of the asset, connection failure and leak of ammonia/hydrogen. Refer to leakage keyword			
Man Made	Terrorist activity	Unauthorized access to facility	Direct attack on installation leading to loss of containment.			

			Refer to leakage keyword			
Effects of the Facility on the Surroundings	Visual	Technology will be installed outdoor, installation will be in industrial site, thus not configuring an adverse effect for the surroundings				
	Socio-Economic					
	Land/sea Take					
	Protected Areas					
	Sensitive habitats					
	Threatened Species					
	Sites or species of special interest					
Infrastructure	Produce Emergency Response Plan	Fire from hydrogen	Potential impact on personnel, asset and environment		Suitable fire fighting device to be identified for installation	Project
		Release of ammonia in the atmosphere	Potential impact on personnel		Suitable remediation strategies shall be identified for ammonia incidental events	Project
Environmental emissions and discharges	Continuous Plant Discharges to Air	Venting of retentate gas after treating in washing bottles	Potential traces of unconverted ammonia release to atmosphere	PH analyser in washing bottles	Provide safe location for venting point	
	Continuous Plant Discharges to Water	No issued identified since the technology does not include continuous discharges to water				
	Continuous Plant Discharges to Land	No issued identified since the technology does not include continuous discharges to land				
	Emergency/upset Discharges	Overpressure scenarios	Potential for discharging overpressure through blow-down connection		Provide safe location for blow-down discharge point	Project
Control Methods / Philosophy	Control Philosophy	Specific scenarios shall be identified once the control strategy will be detailed				
	Manning/Operations Philosophy	the prototype shall be remotely operated. Potential scenarios will be reviewed once the control strategy will be detailed				

	Maintenance Philosophy	Lack of maintenance/ impossibility to perform proper maintenance	Deterioration of the prototype potentially leading to asset damage and leakages		Maintenance strategy shall be evaluated and cross checked with ergonomic requirements	Project
	Emergency Response	Impossibility to control a emergency scenario	Potential for escalation internal to the prototype or external to nearby equipment		Define a shut-down and isolation strategy and provide necessary devices (shut-down valves, fire/leakage detection etc.)	Project
Fire and Explosion Hazards	Stored Flammables	Leakage of hydrogen or ammonia	Potential for fire/explosion escalation		Ref. to "Produce Emergency Response Plan" Provide adequate F&G system with relevant actions	Project
	Sources of Ignition	Hot surfaces and electric components	Potential for ignition of flammable atmosphere (if any)		ATEX certification to be evaluated considering also the potential installation of the proposed technology inside external ATEX zones	Project
	Fire Protection and Response	External fire	Potential fire escalation		Ref. to "Produce Emergency Response Plan" and "Emergency Response" Consider Fire cases for sizing PSV rupture disks on ammonia e hydrogen holdup	Project
	Lifting by crane	Dropped object	Potential for fire/explosion and toxic gas (ammonia) dispersion		Perform material handling study	project
	Forklift operation	Impact with process equipment	Potential for fire/explosion and toxic gas (ammonia) dispersion		Provide policy for worklift training and certification	project
	Operator protection	Operator exposure to adverse condition	Potential injuries		Provide PPE	
Process Hazards	Inventory/ Loss of Containment	Random rupture (e.g. flange, fittings, connection etc.)	Potential for fire/explosion and toxic gas (ammonia) dispersion		Ref. to "Produce Emergency Response Plan" and "Emergency Response"	Project
	Over Pressure	Vacuum pump working against a blocked outlet	External leakage potentially leading to fire/explosion event		Consider providing suitable high pressure protection devices (high	Project

		Overtemperature leading to overpressure	External leakage potentially leading to fire/explosion event		pressure automatic block, PSV, etc.)	
	Overtemperature	Overtemperature leading to failure of flanges and fittings	External leakage potentially leading to fire/explosion event		Consider providing suitable high temperature protection devices (high temperature automatic block)	Project
	Mechanical Failure	Error during prototype installation (misalignment during section stacking or defecting welding etc.)	External leakage potentially leading to fire event			
Utility Systems	Firewater System	External fire			Provide firewater for cooling purposes as per relevant NFPA standard	project
	Inert Gas	Lack of Nitrogen supply	Impossibility to perform purging and inertization leading to delay in operation. No significant issues identified		Provide Nitrogen injection points, venting connection at high point to guaranteed effective purging	Project
	Instrument air	Lack of instrument air	Impossibility to control the system potentially leading to unsafe operations		Verify safe position of actuated valves	Project
	Power supply	Lack of power supply	Impossibility to control the system leading to shut-down		Provided diesel generator or UPS for critical system	
Health Hazards	Direct Contact / Disease Hazards	Ammonia is corrosive	Potential for skin			
	Asphyxiation hazards	Leakage from nitrogen connection	No consequence since the prototype will be installed outdoor			
	Toxic	Ammonia	Potential hazardous effect for operators		Verify MSDS of proposed materials and enforce safety requirements if any	Project
	Physical	Personnel contact with hot surfaces	Health effect for operators (skin burn)		Provide thermal insulation, PPE and safety signs in compliance with applicable safety regulation	Project
		Personnel contact with moving and rotating parts (vacuum pump)	Health effect for operators (injuries)		Provide mechanical barriers, PPE and safety signs in compliance with applicable safety regulation	Project

		Personnel contact with equipment under voltage	Health effect for operators (electrocution)		Provide electrical insulation, PPE and safety signs in compliance with applicable safety regulation	Project
	Working at height	potential for slip, trip and fall	Potential for fatality		Provide adequate fall protection (harnesses and similar)	
	vehicle impact	Potential for leakages	Potential for loss of containment		Provide driving policy to ensure zero alcohol tolerance and driving licence mandatory	
Contracting Strategy	External Standards	Lacking product certification	Delay in technology utilization and commercialization		Evaluated certification required for technology use and commercialization	Project
Competency	Training Requirements	Usage of new technology	Potential for misoperation leading to asset damage and health effect for operators		Define training requirements for the installation, usage and maintenance of the proposed technology	Project

6 SAFETY STARTEGY FOR ANDREAH PROJECT

Safety of system and installation are always key considerations. A good knowledge of ANDREAH Project, ammonia behavior and a conception in accordance with European codes, standards and best practices allows to maintain a high safety performance.

The overall safety strategy for the ANDREAH Project is detailed below.

6.1 General

All people involved in ANDREAH Project should be fully informed of the hazards that may result from a leakage of ammonia either as gas or liquid, and the consequences of improper handling of the equipment. Operators should be trained in the use of the equipment by a competent supervisor, who should satisfy himself that the operator understands not only how to correctly use a properly functioning equipment, but also how to deal with an emergency. A 'spare man' should not be used to replace a normal operator who does not report for duty unless he has been adequately trained.

The management should follow up frequently to ensure that safe practices are followed, the protective equipment is worn, when necessary, safety showers, drinking fountains and eye wash bottles, and personal protective equipment are available in good condition for use during emergency and operators are trained in the use of respiratory protective devices and other protective equipment.

6.2 Leak detection System

To minimize the effects of ammonia release on products, detection systems need a capability for alarm and detection much below LEL levels (15 percent — 150,000 ppm [150,000 mg/lit]). For prevention of contamination, the instrument should be sensitive and reliable in the 50 – 100 ppm (50 – 100 mg/lit) range. The instrument also should be reliable in refrigerated areas where moisture condensation and freezing situations are possible. Location and spacing of detectors in refrigerated areas or machine rooms will require adoption of the manufacturer's guidelines. The best advice is to put detectors in the vicinity of potential leaks. This would be mostly near the chillers in the refrigerated areas. In machine rooms a more widespread distribution would be needed due to numerous leak sources. An old machine room may have typical normal levels in the 25 – 50 ppm (25 – 50 mg/lit) range due to older equipment leakage. This background level would affect the setting of alarm levels and could possibly affect detector sensitivity. Maintenance of the detection system will require frequent calibration, at least monthly. Actual operating experience might indicate a need for more frequent calibration. Calibration of the equipment should only be done by those trained for the operation and following detailed instructions.

6.3 Safety precautions for Handling Leak Detection Systems

Under normal circumstances, ammonia is a colorless gas and is lighter than air. It is easily recognizable by its extremely pungent odor. Ammonia is easily liquefiable under pressure. At atmospheric pressure saturation temperature of ammonia is about -33°C. It absorbs heat while evaporating.

Foot protection: Rubber ankle or knee boots will give complete foot protection against liquid ammonia. Trousers should be worn outside boots.

Body and skin protection: The degree of body protection required must necessarily for practical reasons, be related to the potential hazards of the job. Liquid ammonia will cause severe burning of the skin. Ammonia gas when in contact with damp areas of the body form ammonium hydroxide which is a strong alkali very corrosive to the skin and it can give quite severe burning.

For optimum protection of the body a number of simple precautions can be taken. Rubber, PVC, or some other type of protective gloves should be worn with the cuff tucked under the sleeve.

'Terylene' boiler suits should be worn in preference to cotton suits. The collar should be kept buttoned, and the suit should be free from rents and holes. If the danger of liquid splashes is great, lightweight PVC suits should be worn. In the event of a major spillage of liquid ammonia, complete body protection is essential before entering the contaminated zone. 'Normal air' make a two-piece rubber lined textile suit for this purpose which can easily and quickly be put on over the wearer's normal clothes.

6.4 Protective Measures Against Corrosion

To mitigate ammonia corrosion, several strategies can be employed, including controlling ammonia concentration through ventilation and containment, using corrosion-resistant materials, and implementing protective coatings. Additionally, proper maintenance and inspection practices are crucial for identifying and addressing potential issues early.

- ✓ **Controlling Ammonia Concentration**:

Ventilation: Adequate ventilation systems, both local exhaust and general ventilation, are essential to prevent the buildup of ammonia vapors and maintain concentrations below hazardous levels.
Containment: Enclosing chemical processes involving corrosive substances and implementing secondary containment systems for leaks and spills can minimize exposure.
Leak Detection and Monitoring: Installing ammonia detection and monitoring systems allows for early detection of leaks and prompt response.

- ✓ **Material Selection and Design**:

Corrosion-Resistant Materials: Choosing materials with inherent resistance to ammonia corrosion, such as certain alloys (e.g., cupro-nickel, austenitic stainless steels) and non-metallic materials, can significantly reduce the risk of corrosion.
Alloy Upgrading: Modifying the surface composition of materials by adding specific alloying elements (e.g., chromium, nickel, molybdenum) can enhance resistance to ammonia corrosion.
Proper Post-Weld Heat Treatment (PWHT):
PWHT can help prevent stress corrosion cracking, especially in steel equipment.

- ✓ **Protective Measures**:

Protective Coatings: Applying protective coatings, such as epoxy coatings with antibacterial agents, can create a barrier against corrosion.
Inhibitors: Adding small amounts of water to anhydrous ammonia can help inhibit stress corrosion cracking in steel.

- ✓ **Maintenance and Inspection**:

Regular Inspections: Routine inspections, including NDT techniques like eddy current testing or ultrasonic testing, can help identify areas of corrosion and stress corrosion cracking before they become critical.
Preventive Maintenance: Implementing a preventive maintenance program that addresses potential corrosion issues can help extend the lifespan of equipment and prevent failure.

6.5 Personnel Protection Equipment

Personal protection equipment should not be regarded as substitute for good safe working conditions with properly designed equipment. In certain cases, however, particularly in an emergency, it is the only means of protecting the worker. Also, because of the severe effect of ammonia on the person, partial bodily protection is recommended during certain routine operations to guard against mishap. The degree of bodily protection taken will depend on the magnitude of the hazard.

Eye protection: Goggles should be worn by all personnel entering liquid ammonia storage areas where leaks may occur from pump glands, valves, etc.

Respiratory protection: Exposure to ammonia may occur in tanks during routine cleaning, when the nearby area is contaminated due to leakage / spillage / failure of equipment.
A number of different types of respirators are available; these are described below. Respiratory equipment must be regularly maintained, inspected and cleaned.

d) Chemical Cartridge type respirators

These respirators (such as the 'Puretha') are suitable for protecting the wearer from inhaling disagreeable, but relatively harmless, concentrations of ammonia vapor. They should not be used where there is likely to be a shortage of oxygen in the atmosphere. These respirators will give limited protection where toxic concentrations are encountered, but in such circumstances, they should be used as a means of escape only. With this type of respirator only the face and eyes are protected from contact with liquid ammonia and vapor.

d) Air Fed-Face Masks

These masks can be supplied in two types, either a close-fitting mask with the air supplied through a control valve on the mask or a hood here a much greater volume of air is supplied than required, the excess leaks away at the edges. The former is used for maintenance or process operations of one-time nature for duration; the latter is useful for routine operations which is for short duration but occurs frequently.

The masks may be supplied with air from the factory compressed / breathing air system, a portable compressor, or a bottled supply. In the first two cases care must be taken to ensure that the air is free from

oil, mist and dirt. This may be done by means of traps and filters. When a portable compressor is used, the danger of oil mist can be eliminated by using a non - lubricated compressor. A filter should still be fitted, however, to remove small dirt particles.
There are a number of disadvantages with the air-fed mask of either type.

The working radius is reduced to the length of hose, the hose itself can be an encumbrance, and the means of escape (while still being supplied with air) is limited to the direction of the source of air supply.

Air-fed masks should not be used unless conditions permit safe escape in case of failure of the compressed air supply.

d) Self-contained Breathing Apparatus

This type of apparatus allows the wearer to carry a supply of bottled air with him and thus ensures his complete mobility. Two types are available giving a 30-minute and 2-hour supply, weighing 20 lbs and 40 lbs respectively. This type of equipment is the only suitable equipment to rescue work.

A breathing mask, marketed by 'Normal air' of Yeovil, Somerset, has recently become available which is supplied with air under normal conditions from an external source by means of hose.
In addition, a 30-minute supply of bottled air comes into operation automatically if the main air supply fails. The advantage of this equipment is that the wearer is assured of continuous supply of air and has complete mobility if emergency escape is necessary.

When using this type of mask, it is important to ensure that the pressure of the main air supply never falls below that of the bottled supply reducing valve exit pressure; otherwise, the bottle will empty referentially.

d) Filter Type Respirators

This type of respirator does not offer protection against gases and is unsuitable for use when working with ammonia.

Head protection: Hard hats should be worn even if it is considered that there is no danger from falling objects since they will offer protection from liquid splashes.

When ammonia is leaking from a piece of equipment or a pipe, the working people shall use breathing air (respiratory equipment) masks and other people move away from the leaky area.
The leaky area / zone should be thoroughly ventilated as soon as possible. In view of the fact that ammonia is lighter than air, ventilation by upward draught will be most effective.

If any work has to be carried out in rooms / equipment contaminated with ammonia, for lessening the hazards, respiratory equipment and protective clothing must be used.

In addition, it is important that persons working in rooms contaminated with toxic gases are observed by a buddy standing outside with suitable safety equipment to rescue such persons in emergencies.

Over and above, the personnel working in hazardous area shall use the respiratory equipment and protective clothing covering the whole body.

Such protective clothing comprises:

- A long sleeved working jacket.
- Long trousers and underwear (If possible, made from cotton, since cotton is more resistant to alkalis than wool).
- Rubber boots.
- Rubber gloves.

- Protective helmet with rim.

The sleeves should be worn outside the rubber gloves and the trousers outside the boots. An ointment or Oil can also protect certain areas of skin.

If necessary, the above-mentioned protective clothing can be replaced by a tight anti-gas suit covering the whole body.

6.6 First Aid

It is of primary importance to take the injured / ammonia affected of the endangered area as quickly as possible. In case of serious injuries to the eyes, a medical practitioner must be summoned at once. In the meantime, as much ammonia as possible must be eliminated, e.g. by dosing with plenty of water, discarding contaminated clothing including underwear. The patient should then be made to lie down and wrapped in blankets to keep him warm.

A gas mask can be regarded as a limited respiratory equipment, provided there is sufficient oxygen in the breathing air cylinder, the gas mask fits tightly, and the special ammonia filter has been screwed into the gas mask. The personnel may enter the contaminated e rooms for a limited period of time if the ammonia content in the room is below 2%. The filter manufacturer's data will give precise information on the time limit, the maximum permissible ammonia concentration and the life of a new gas mask filter whose container seal has not yet been broken.

Positive pressure air masks offer better protection than filter canister masks as a regulated external source of air (from an instrument air or service air point) is connected to the face mask.
Monitoring of air pressure is needed.

A sufficient number of gas masks should be available at all points where ammonia might possibly leak and enable operating personnel to evacuate the leaky area quickly.

If, for any reason, a gas mask is not available, the next best protection will be by holding a wet rag over nose and mouth.
In emergencies, a dry handkerchief or a sleeve will offer some protection. In all such cases, it is important to choose a route of escape against the wind.

The breathing apparatus is used whenever the ammonia concentration exceeds the limit value mentioned above or if it is not known or if it is likely to. increase or if the oxygen content is too low, or if the life of the gas mask filter is likely not to be adequate. Breathing apparatus of the type connected by means of a hose to an air intake located in a non-contaminated area will frequently have too high a line resistance and will mechanically impede both the work and the radius of action. Any person using such breathing apparatus should, prior to use, ensure that sufficient air is contained in the bottle, the valve is set correctly, the hose connection is properly fixed and the mask fits properly.

Eyes affected by ammonia must immediately be washed with plenty of clean water. This can be followed by an eye bath in diluted acetic acid (0.5%) or boric acid (3%), after which the eyes should again be washed with clean water.

If ammonia has been breathed in, inhalation of steam or vinegar vapor is recommended.
Artificial respiration is forbidden.

If possible, the breathing air should be enriched with oxygen. If Ammonia bearing water has been swallowed the patient may be given milk to drink provided, he is fully conscious.

6.7 Emergency Response Plan

Having a well-defined Emergency Response Plan, including procedures for containment, evacuation, and first aid, is crucial for minimizing the impact of accidental releases.

7 CURRENT PROGRESS AND NEXT STEPS

The Risk Analysis developed in this report have been focused on “major” accidents potentially arising from the operation of the technologies that will be implemented in the ANDREAH phase demo, i.e. on those occurrences such as a major emission, fire, or explosion resulting from uncontrolled developments in the course of the operation of any installation, leading to serious danger to human health or the environment. Proposal for improvements have been issued, in order to reduce the risks related to the application of ANDREAH technology in the selected phase demo, as well as in any other sites where similar technologies will be replicated.

During the next phase of the project, it is recommended to conduct a HAZOP (HAZard and OPerability), a Quantitative Risk Assessment (QRA), and a Gas Dispersion Study to enable a thorough and integrated Health and Safety evaluation of the facility.

8 CONCLUSIONS

The Health and Safety assessment carried out within the ANDREAH project has identified the main hazards associated with the use of ammonia, hydrogen and nitrogen in the proposed Catalytic Membrane Reactor technology, highlighting the key risks related to toxicity, flammability, explosion, corrosion and loss of containment. Through the application of a structured HSE philosophy, a preliminary risk analysis and a HAZID assessment, a comprehensive set of preventive and mitigation measures has been defined to support the safe design, installation, operation and maintenance of the demonstration system. The recommendations provided in this report establish the basis for integrating safety-by-design principles into the technology development process and for ensuring compliance with relevant health, safety and environmental requirements. As the project progresses towards demonstration and scale-up phases, further analyses, including HAZOP, Quantitative Risk Assessment and gas dispersion studies, will enable the refinement of the safety strategy and support the safe industrial deployment and future replication of the ANDREAH solution.

9 ABBREVIATIONS

ALARP	As Low as Reasonably Practicable
ATEX	Atmospheres Explosives
CAPEX	Capital Expenditure
CMR	Catalytic Membrane Reactor
CMSM	Carbon Molecular Sieve Membrane
CRM	Critical Row Materials
FC	Fuel Cell
HAZID	Hazard Identification
HAZOP	Hazard and Operability
HSA	Health and Safety Assessment
HSE	Health, Safety and Environment
ISBL	Inside Battery Limit
IDHL	Immediately Dangerous to Life and Health
LC	Lethal Concentration
LCA	Life Cycle Assessment
LCC	Life Cycle Cost
LFL	Lower Flammable Limit
LoC	Level of Concern
MR	Membrane Reactor
OCF	Open Cell Foams
OPEX	Operational Expenditure
OSHA	Occupational Safety and Health Administration
RA	Risk Assessment
SoA	State of Art
UFL	Upper Flammable Limit