Environmental, health and safety assessment of post-combustion CO2 capture processes with phase-change solvents

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Research article

Environmental, health and safety assessment of post-combustion CO_2 capture processes with phase-change solvents

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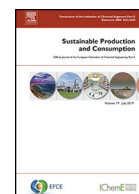
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A B S T R A C T

A class of solvents for chemisorption-based CO_2 capture, phase-change solvents, promises significant energy reductions due to liquid-liquid phase separation and partial solvent recycling before CO_2 desorption. Although energy consumption is a critical aspect of the CO_2 capture process sustainability, a holistic evaluation of health, safety, and environmental impacts is required to confirm the beneficial performance of processes employing phase-change solvents compared to conventional alternatives. This study outlines a method for combining the life cycle and environmental, health and safety hazard assessment. The method is applied for the first time on processes employing two different exemplary phase-change solvents, a reference aqueous solution of methylcyclohexylamine (MCA) and a novel mixture of cyclohexylpropane-1,3-diamine (S1N) and dimethylcyclohexylamine (DMCA). The results show that phase-change solvents have the potential to be a better alternative to conventional amine (i.e., MEA) solvent systems due to the reduced reboiler duty and lower impact on the environment. However, additional care might need to be taken to prevent the potential accumulation of the carcinogenic nitrosamines in the system.

BDA	Butanediamine	MSDS	Material safety data sheet
CCS	Carbon capture and storage	NDELA	N-Nitrosodiethanolamine
CED	Cumulative energy demand	NF	Near-field
DECA	N,N-Diethylcyclohexylamine	OEL	Occupational exposure limit
DMCA	Dimethylcyclohexylamine	PEL	Permissible exposure limit
DPA	Dipropylamine	PoD	Potential of danger
ECA	N-ethylcyclohexylamine	STEL	Short-term exposure
EHS	Environment, health and safety	S1N	Cyclohexylpropane-1,3-diamine
FF	Far-field	TWA	Time-weighted average
GWP	Global warming potential		
HEX	Heat Exchanger		
HSS	Heat stable salts		
IDHL	Immediately dangerous to life or health		
LCA	Life cycle analysis		
MAPA	N-Methyl-1,3-diaminopropane		
MCA	Methylcyclohexylamine		
MEA	Monoethanolamine		
MMEA	Monomethylethanolamine		

1. Introduction

Carbon capture and storage (CCS) is seen as one of the leading mitigation technologies able to facilitate the reduction of CO_2 emissions generated by the power sector. CCS is also the only technology able to mitigate a large part of the CO_2 emissions of industrial plants, when a process or material modifications are not feasible (Budinis et al., 2018). CCS is included in all the future sustainable development scenarios limiting global warming to 2°C (IEA, 2019; Minx, 2014). Even though large-scale CCS implementation seems necessary to meet the current climate change goals, the absence of regulatory frameworks and CO_2 infrastructure, so-

cial acceptance, and, probably, more importantly, lack of financial incentives for industry to invest in CCS hinder its deployment. The high cost of CCS, with the cost of capture being a major contributor, makes CCS investments financially unfeasible without political support (Zapantis et al., 2019).

The most mature among all the existing capture technologies, carbon capture by chemical absorption, is one of the most technically viable carbon capture options for the near-term implementation because of its potential to be retrofitted to existing industrial facilities (Aaron and Tsouris, 2005). However, the high energy penalty of the process and safety hazards associated with the large volumes of solvent in the system (Spigarelli and Kawatra, 2013), hamper the actual implementation of the technology and motivate the identification of different process designs and solvents to make the CCS attractive for industrial-scale application. The primary purpose of the process modifications and new solvent alternatives is to reduce the energy penalty of the capture process (Vega et al., 2020) without negative consequences to people's health and environment (Papadopoulos et al., 2017). Various process design configurations are proposed, including, but not limited to, intercooling (Le Moullec et al., 2014; Xue et al., 2017) or interheating (Dubois and Thomas, 2018; Le Moullec et al., 2014) of an absorber, modification of a split flow (Dubois and Thomas, 2018; Xue et al., 2017), the addition of heat pumps (Dubois and Thomas, 2018; Le Moullec et al., 2014), and alternative stripper designs (Oyenekan and Rochelle, 2015; Pellegrini et al., 2011). Most of the studies report a range between 10-30% of reboiler duty reduction, while the maximum reported reduction reaches 50%, under ideal modeling conditions (Le Moullec et al., 2014). New solvent alternatives could improve the energy requirement of the process even further, along with increasing the safety of the process.

A class of solvents exhibiting liquid-liquid or liquid-solid phase change promises significant energy reductions due to the phenomenon of phase separation triggered by change in temperature or/and reaction with CO_2. The phases formed are CO_2-rich and CO_2-lean phases. The CO_2-lean part can be separated and returned to the absorber, thus, reducing the load of the stripper and decreasing the amount of energy needed for the solvent regeneration. Solvents resulting in liquid-solid phase separation might require the development of the new processes since they may create problems like clogging in the standard absorption/desorption systems (Budzianowski, 2017). At the same time, liquid-liquid phase-change solvents can be easily incorporated into the existing capture systems by the addition of a mechanical separation step (Papadopoulos et al., 2019). That might be the reason why most of the reported phase-change CO_2 capture solutions are solvents demonstrating the liquid-liquid phase separation.

Up to date, various nonaqueous and aqueous solvents exhibiting phase change have been tested for CO_2 capture. Aqueous phase-change solvents typically include amine blends (e.g., DMX solvent (Aleixo et al., 2011), Dipropylamine (DPA)/DMCA (Tan, 2010), Butanediamine (BDA)/DMCA etc. (Shen et al., 2020)) and solutions of salts of amino acids (e.g., sodium glycinate (Chen and Lin, 2018), potassium taurate, and potassium alanate (Sanchez-Fernandez et al., 2014)). Water in nonaqueous solvents is replaced by organic solubilizers (Lai et al., 2019; Zheng et al., 2014) or ionic liquids (Li et al., 2015; Liu et al., 2017) demonstrating advantageous performance in terms of heat capacity, absorption heat and stripping heat (Zhang et al., 2019). However, the practical application of the nonaqueous solvent alternatives might be l imited by the presence of water in the flue gas, which requires costly water management measures. Thus, the CO_2 capture processes with the nonaqueous phase-change solvent have not been adequately assessed, while some aqueous phase-change solvents have reached a technology readiness level of 4-5 (Papadopoulos et al., 2019).

It has also been found that the phase separation can be optimized by introducing inert organic splitting agents (e.g., sulfolane, 1-methyl-2-pyrrolidinone) enhancing the separation behavior, and thus reducing the heat duty (Jiang et al., 2020; Ye et al., 2019). The capture processes deploying phase-change solvent mixtures are reported to decrease the energy use by more than 30% compared to MEA (Zhang et al., 2019). The research on new phase-change solvent alternatives and process designs with substantially reduced energy consumption and costs to ensure the advance of this promising technology and its promotion to a higher level of technology readiness is still ongoing (Papadopoulos et al., 2019).

The beneficial performance of the phase-change solvents in terms of energy reduction has been widely investigated; however, little attention was given to the environmental, health, and safety aspects of these materials and processes (Zhang et al., 2019). Adverse health and environmental impact of amine-based scrubbing systems have been gaining much attention in recent years. Veltman et al. (2010) reported a 10-fold increase in freshwater toxicity impacts, as a result of the emissions coming from the MEA capture system, emphasizing the importance of evaluation of health and environmental aspects of the scrubbing technologies in addition to costs and global warming potential. Karl et al. (2011) expressed a concern about the carcinogenicity of nitrosamines and nitramines formed during the amine solvent degradation under the operation conditions of the capture process. Furthermore, Badr (2016) highlights that change in the process operating conditions can alter the effect of chemicals used or formed in the process. According to Badr (2016), the high stripper temperatures combined with the lower inventories achieved at lower lean loadings lead to lower acute toxicity score and reduced nitrosamine hazard.

Given the lack of a comprehensive safety, health and environmental impact assessment of the existing phase-change solvent-based capture processes (e.g., DMX (Gomez et al., 2011)) and ongoing design of the new efficient phase-change solvent alternatives, the current work aimed to gain some insights on the potential impact of the carbon capture systems associated with the use of this emerging materials. Some of the gained insights can be applied to even nonaqueous liquid-liquid phase-change solvents using the same structure of the process. The focus, however, was on the liquid-liquid aqueous solvent systems with the developed CO_2 absorption processes. To the best of our knowledge, there is no comprehensive environmental, health and safety hazard assessment of phase-change based carbon capture systems. Life cycle assessment (LCA) was applied by Leveque (2018) to a reference system with methyl cyclohexylamine as a phase-change solvent, while Shavalieva et al. (2019) reported preliminary results of the extended assessment including the environmental, health, and safety hazard (EHS) aspects of the same system. Even though phase-change solvent systems are not expected to demonstrate significantly distinct behavior from their conventional counterparts, their operation requires a different process design and operating conditions that might affect their performance in terms of the impact. For this purpose, a framework including LCA and EHS assessment complemented with an exposure analysis was applied in this study. The results of such a comprehensive evaluation with the use of various indicators and scenario based analysis for dealing with inevitable uncertainties at early design stages and low technology readiness level safeguards from the discriminating particular effects over the other and grants insights into possible trade-offs between different aspects of the capture system. While LCA evaluates more longer-term global impact, the EHS and exposure analysis are focused on the impacts occurring locally, also considering short-time effects which are of special importance for social acceptance. Thus, the combined use of LCA and EHS hazard assessment, using a complete index based framework instead of just a few hazard

related properties, along with the use of exposure assessment facilitates sustainability driven multicriteria decision making, which not only is challenging for novel process systems but also, to the best of our knowledge, has not been published for any phase change process system at early design stage. This kind of assessment can be of great importance at early design stages to highlight potential hotspots, trade-offs and win-win cases with respect to the diverse sustainability aspects in a rigorous way. Thus, the results can support the decision-making process and trigger targeted experimentation at pilot and demonstration scale towards optimal conditions for the CO_2 capture system operation (Shavalieva et al., 2019).

2. Method

The assessment framework consisted of LCA, to determine the cradle-to-gate environmental impact of the CO_2 capture process under regular operation, and EHS hazard assessment, to determine the CO_2 capture process hazards that can be relevant in accidental scenarios. The combined LCA and EHS method was supplemented by exposure analysis of working personnel in CO_2 capture plants as a result of leakages and spills.

2.1. LCA

The LCA framework has four well-known distinct phases according to ISO 14040 and 14044: goal and scope definition, inventory analysis, impact assessment, and interpretation of results.

The goal and scope of LCA in this framework was to evaluate the cradle-to-gate impact from capturing one metric tonne of CO_2 by the capture systems that employ phase-change solvents. Thus, the functional unit of the framework was 1 tonne of captured CO_2 from process gas streams (e.g., post-combustion flue gases) under specific process conditions. The system boundary was "cradle-to-gate", including the impacts from solvent, chemical auxiliaries and energy utilities production, the process emissions from the CO_2 capture system and the solvent reclaimer and waste treatment units for processing purge streams from the CO_2 capture process. The LCA framework did not include the energy consumption associated with bringing the CO_2 containing flow (e.g., flue gas) to the CO_2 capture process gate. It is expected that delivering the flue gas to the capture plant is not solvent or process dependent and will be the same for all solvent-based CO_2 capture scenarios. Additionally, the LCA framework did not include the CO_2 compression for storage or utilization purposes defined by the form and mode of transportation of the captured CO_2.

The life cycle impact assessment (LCIA) considered global warming potential (GWP 100a) (Stranddorf et al., 2005), cumulative energy demand (CED) and a single score of the ReCiPe-2008 method based on the hierarchist weighting scheme (ReCiPe) (Goedkoop et al., 2009). These categories were selected because of available short-cut models (FineChem (Wernet et al., 2009)) streamlining cradle-to-gate LCIA calculations for solvent production based on the molecular structure of the solvent. The estimation using the short-cut molecules is required when a solvent molecule does not exist in databases, which is the case for most of the phase-change solvents. Therefore, data is not available regarding impact related to the molecules production,. If there are readily available data associated with solvent production, LCIA can consider additional impact categories. The inventory for all other chemical auxiliaries and energy utilities were based on Ecoinvent v3.4 and other open literature sources. More information on elements of the procedure and data considered in the LCA calculations can be found in the Supplementary material (section S1, Tables S1–S3).

2.2. EHS hazard assessment

EHS hazard assessment addresses potential hazards for health (H), and safety (S) of workers and environment (E) in accidental scenarios of the capture process. The assessment at process level refered only to the CO_2 capture process. Any EHS hazards associated with cradle-to-gate processes for solvent, chemical auxiliaries, energy utilities production, and solvent reclaimer and waste treatment processes for treating process purge streams were outside the scope of this study.

The result of the EHS hazard assessment is presented as separate S, H, and E scores and potential of danger (PoD) per tonne of CO_2 captured by the corresponding process under investigation. It represents the magnitude of EHS effects by a physical unit such as releasable energy content of the system or the volume of air/water required to dilute a dangerous chemical to levels of threshold concentration (Koller et al., 2000). S, H, and E scores and PoDs were calculated based on the maximum values of dangerous properties. The dangerous properties are mobility, fire/explosion, and acute toxicity in the safety category, chronic toxicity in the health, water and air mediated effects, degradation, and accumulation in the environmental category. The maximum PoDs, estimated for every substance present in the process, in S and E depend on the inherent properties and mass of the chemical present in the process. However, in H, only the properties of the substances and their existence in the process play a role since if a carcinogenic chemical exists in the process, precautions should be taken regardless of its mass (Koller et al., 2000).

The EHS hazard assessment framework is based on the works of Sugiyama et al. (2008) and Koller et al. (2000) for the assessment of chemical processes, which was later adapted by Badr et al. (2017) for conventional solvent-based CO_2 capture processes. The EHS framework details and data used in the calculation of S, H, and E scores and PoD values are given in Supplementary material (section S2, Tables S4–S8).

2.3. Exposure analysis

While EHS hazard assessment identifies generic and predominant process hazards for workers and the environment in case of accidental scenarios, special attention needs to be paid to process specific hazards for potentially more frequent (e.g., everyday) exposure of the workers in the plant, for instance, due to leakages and spills. More frequent process-specific hazards may refer, for example, to exposure to potentially carcinogenic solvent degradation products and volatile emissions. They might not necessarily be characterized by significant amounts (e.g., compared to the solvent itself) but may have much stricter threshold values in terms of continuous (or more frequent) exposure of workers. Thus, exposure analysis is required to ensure that the concentration of the chemicals at the plant is under threshold values. The threshold values used in the study were regulatory occupational exposure limits (OELs) and experimental acute toxicity levels (Badr, 2016). Recommended or mandatory OELs used were (a) the time-weighted average (TWA) specifying a limit for 8-h workday repeated exposure without adverse effects, (b) short-term exposure (STEL) giving a threshold for 15 min exposure that should not be exceeded at any time during the working day or (c) the permissible exposure limit (PEL), which has been established in many countries for airborne exposure to gases, vapors and particulates (ILO, 2020). OEL values represent maximal exposure concentrations of chemicals during the working day below which there are no adverse health effects for the workers (JSON, 2017). The experimental acute toxicity levels, often expressed as LD_{50} (oral, dermal) or LC_{50} (inhalation) values, refer to adverse effects as a result of oral/dermal exposure or exposure by inhalation, accord-

ingly, to a single or multiple dose of a substance within a specific time frame. Based on LD_{50} and LC_{50} values specifying the dose of a chemical leading to the death of 50% tested animals, the National Institute for Occupational Safety and Health (NIOSH, 2019) calculates the immediately dangerous to life or health (IDLH) values. IDLH values specify air concentrations of chemicals, to which workers should not be exposed any time without proper protection. For specific chemicals, OELs, IDHLs, and experimental acute toxicity limits can be found in databases (e.g., provided by European Chemicals Agency (European Chemicals Agency, 2018)) and material safety data sheets (MSDS).

Two main cases were evaluated in this study: exposure to solvent via leakages (long-term) and spills (short-term) and accumulation of nitrosamines above safety levels of 13.7–14 mM (Badr, 2016; Fine, 2015) in the system. The estimation of exposure to the solvent was based on the equations provided by Nicas (2016) and Keil and Nicas (2003). The equations estimated the concentration of chemicals in the air assuming constant amount and evaporation rate in case of a leakage and decreasing emission rate in case of a spill. Thus, it was considered that in case of a leakage, especially in tiny amounts difficult to detect, a worker might be exposed to a chemical during longer periods, and the air concentration was compared to the regulatory TWA limit. In case of a spill, dangerous to health air concentrations for a chemical were assumed to be reached during the first seconds after the spill and compared to IDHLs or inhalation LC_{50} limits for humans. The air concentration of a chemical after 15 min of the spill was compared to STEL or TWA. For the exposure to nitrosamines, the study of Fine (2015) was used to estimate the potential steady-state concentration of nitrosamines accumulated in the system and to compare it to the respective thresholds established by Fine (2015) and Badr (2016) to avoid dangerous levels of nitrosamines in the treated flue gas and the working environment, respectively. The different way of addressing the nitrosamines exposure was required due to the unknown concentration profile of nitrosamines in the system.

Details for the data and modeling assumptions used in the exposure analysis are given in the Supplementary material (section S3, Tables S9–S14).

2.4. Uncertain aspects influencing the results of LCA and EHS

Various aspects have a significant effect on the results of the LCA and EHS and should be taken into account when performing the assessment. The main aspects to consider are the quality of the flue gas, oxidative and thermal degradation of solvent molecules, and emissions of solvent and other harmful compounds formed during the process. All these aspects are also common for the conventional capture solvents; however, different process design and capture conditions of the phase-change systems are expected to affect the magnitude of the effects. Due to the limited experimental data on phase-change solvents and their behavior under the process conditions, scenarios and assumptions to evaluate the influence of different parameters were used.

2.4.1. Quality of the flue gas

Potential problems of the capture plants are greatly influenced by the quality of the flue gas fed to the CO_2 capture process. Flue gas quality has a significant influence on solvent degradation, formation of nitrosamines and aerosols, foaming and corrosion. These complications are mainly associated with oxygen content and flue gas impurities such as NO_x, SO_x, and particles. Oxygen facilitates the degradation of the solvent and possibly the formation of nitrosamines. The evolution of ammonia, a volatile product of oxidative degradation, is reported to be linear with oxygen up to 17% (vol) and increased at higher O_2 concentrations

(Goff and Rochelle, 2004). It has been reported that SO_x levels higher than 10 ppmv at the inlet of the MEA-based CO_2 absorber can create process problems, including foaming, corrosion, fouling, plugging, and solvent loss. SO_x and particles increase emissions due to elevated aerosol formation. Therefore, commercial MEA processes set a maximum of 10 ppmv of SO_2 as a feed specification to keep solvent consumption and make-up costs at reasonable values (Lee et al., 2009). NO_x-species in the flue gas will lead to the formation of nitrosamines and nitramines and must be expected from any amine (Fostås et al., 2011).

All the process problems influence the results of LCA and EHS assessment and, thus, are discussed in more detail in the following paragraphs. However, process complications like foaming, corrosion, fouling, and plugging were omitted from the evaluation due to difficulty in quantifying the extent of these kinds of complications.

2.4.2. Oxidative and thermal degradation

Oxidative and thermal degradation leads to the loss of the solvent and can pose a hazard to human health and the environment due to the formation of harmful degradation products. While both types of degradation happen in the CO_2 capture system, oxidative is responsible for most of the solvent loss. Thermal degradation is expected to be minor in the phase-change solvents systems operating at stripper temperatures below 110°C (Zhang, 2013).

Phase-change solvents are relatively new solutions for CO_2 capture with no or limited data of their industrial use. For that reason, estimation of solvent degradation was done in relation to the degradation of MEA. Industrial-scale data available for the MEA-based CO_2 capture, together with the experimental lab studies found in literature both for MEA (Thong et al., 2012) and the alternatives, were used to calculate proportionality factors and estimate the degradation of phase-change solutions at industrial scale. In case there are no lab experiments conducted on the phase-change solvents, structurally similar compounds were used for approximations. The impact of these uncertainties is expressed in terms of best- and worst-case degradation rate scenarios for the phase-change solvents. Solvent degradation products were assumed based on the lab experiments or degradation behavior of the structurally similar compounds.

Solvent degradation is expected to have a considerable impact on H and E scores of EHS and all the LCA categories. LCA impact is affected by the loss of the solvent that needs to be continuously compensated to ensure steady-state operation of the capture process. The presence of harmful chemicals that can be released to the working area of the capture plant or the atmosphere puts human health and the environment at risk.

2.4.3. Solvent reclaiming

Lean solvent purging and reclaiming plays a significant role in avoiding the accumulation of solvent degradation products, including nitrosamines, in the solvent recirculation streams. Fine (2015) claims that the steady-state nitrosamine concentration can be regulated by thermal decomposition combined with the base treatment. The concentration of the nitrosamines and other degradation products is reduced in the reclaimer, typically located after the stripper in the single-phase solvent systems. It should be noted that due to the different design of the capture system utilizing phase-change solvents, a different placement of the purge stream or an installation of an additional reclaimer may be necessary to prevent the accumulation of nitrosamines in the system. However, thermal reclaiming may not be as efficient if the parent amines, for example, tertiary amines or amino acids, are non-volatile (Fine, 2015). Alternately, in a more novel design, nitrosamines and other harmful compounds could be treated by UV light and ozone (Dong et al., 2019).

Purging and reclaiming, highly influenced by the rate of solvent degradation, decrease the amount of harmful substances in the system, thus, reduce the hazards associated with human health and the environment. However, energy and chemicals required for the reclaiming process, treatment of the reclaimer waste and compensation of the additional loss of the solvent during the reclaiming, increase the LCA and potentially EHS impact of the system.

2.4.4. Emissions

2.4.4.1. Nitrosamines. Nitrosamines are known carcinogens, and even at low air concentrations of 2.39-7.55 mg/m^3 (Badr, 2016), they are harmful to human health. The cancerogenic compounds are formed when amine reacts with NO_x entering the system with the flue gas. In the experiments performed by Fostås et al. (Fostås et al., 2011), the formation rate of nitrosamine N-Nitrosodiethanolamine (NDELA) increased along with the increase of NO_x and oxygen concentration. Furthermore, the authors observed the nitrosation of MEA even at low levels of NO_x (5 ppm). A recent study by Shi et al. (2017) found that nitrosamines can be detected even in the absence of NO_x, making it even more challenging to control their formation. Nitrosamines are formed both in the absorber and stripper as well in the atmosphere when the solvent molecules escape the system with the treated flue gas.

Water and acid wash are used to control nitrosamines leaving with the gas phase. Still, according to Fine (2015), the majority of nitrosamines formed during the capture process are relatively non-volatile and, thus, might stay in the liquid phase. Unstable nitrosamines staying in the liquid phase are reported to be partly destroyed at elevated temperatures of the stripper (Fine, 2015). However, due to the liquid-liquid phase separation phenomenon, a part of the solvent flow is returned to the absorber without being exposed to the higher temperatures of the stripper and reclaimer, which might lead to increased nitrosamine build-up rates in the phase-change solvent-based systems. Moreover, temperatures used for regeneration of many thermomorphic phase-change solvents are lower compared to the conventional solutions, meaning that the decomposition rates of nitrosamines can be slower (Fine, 2015). The accumulation of nitrosamines in the system increases the risk of the personnel being exposed to these harmful substances in case of leakages, spills, or emissions from the process equipment.

Cleaning the flue gas from NO_x, measurement of nitrosamine concentrations, and, if required, additional nitrosamine elimination measures (e.g., extra washing, UV light treatment, ozonation (Dong et al., 2019)) might be necessary to guarantee the safety of the workers at the capture plant. The additional safety measures may require extra energy and material flows contributing to both LCA and EHS impacts of the system.

2.4.4.2. Aerosols and losses of the solvent due to volatility. It has been reported that aerosol formation can increase emissions from CO_2 capture plants up to two orders of magnitude (Khakharia et al., 2013). The amount of aerosols is directly affected by the flue gas quality, especially SO_x and soot particle content (Fulk, 2016; Khakharia et al., 2013). Khakharia et al. (2013) indicate that increasing fine soot concertation from 10^4 to 10^6 particles per cm^3 raised MEA emissions from 2 to 4 times compared to the base value emission rate (no soot or SO_x). The same study states that H_2SO_4 mist in the flue gas with a particle number concentration in the order of 10^8 particles per cm^3 can increase the MEA emissions up to 25 times compared to the base level. Solvent emissions also occur due to the volatility of the solvent molecules contributing to the loss of the solvent. A washing unit at the top of the absorber and additional cooling at the top of the stripper is required to recover the solvent and avoid the release of the harmful substances to the environment. Significant residence times in washing columns can also induce the removal rate of the formed aerosols

Table 1
Composition of the flue gases.

	Lime plant (vol%)	Power plant (vol%)
CO_2	12.3	3.6
O_2	5.8	12.9
NO_x	400 (mg/Nm^3)	10 (mg/Nm^3)
SO_x	350 (mg/Nm^3)	-
CO	-	5.5 (mg/Nm^3)
H_2O	12.5	8.4
N_2+Ar	69.4	75.1
Dust	30 (mg/Nm^3)	Present as fine soot

(Fulk and Rochelle, 2013). However, this might not be enough, and extra equipment, e.g., Brownian demister unit (Khakharia et al., 2014b), could be required to control the aerosol formation.

Solvent volatility and aerosol formation in the phase-change solvent systems are expected to be responsible for the loss of the solvent and elevated risk of the harmful compounds being carried with the treated flue gas to the working environment and atmosphere. These aspects directly affect LCA impacts and increase risks to human health and the environment. Due to high uncertainties associated with the phenomena of aerosol formation, assumptions on the amount of emissions needed to be made, and emission control measures to be introduced. All the assumptions with regards to the aspects discussed above and auxiliary process units required to ensure the safety of the process are case-specific. The assumptions and systems boundaries used for this study are described in the Case study section below.
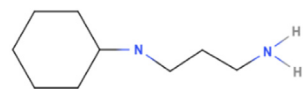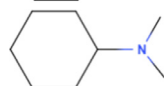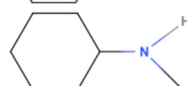
3. Case study

3.1. CO_2 emitting plants

Environmental, health and safety assessment was performed to analyze the life cycle impact and potential hazards associated with the operation of CO_2 capture units that employ phase-change solvents, designed for two industrial sites: a quick lime plant, producing 150 tonnes of lime per day, and a 400 MW natural gas combined cycle power plant. The composition of the flue gases, reflecting full capacity operation for the lime plant and average base load operation for the power plant, is given in Table 1.

3.2. Phase-change solvents for CO_2 capture

The following phase-change alternatives were considered for this study: a novel solvent, a mixture of cyclohexylpropane-1,3-diamine (S1N), and dimethylcyclohexylamine (DMCA) (Papadopoulos et al., 2020) and the known phase-change solvent methylcyclohexylamine (MCA), previously studied by Zhang (2013). Structures of the solvent molecules can be seen in Table 2. The

Table 2
Structures of the solvent molecules (Papadopoulos et al., 2020).

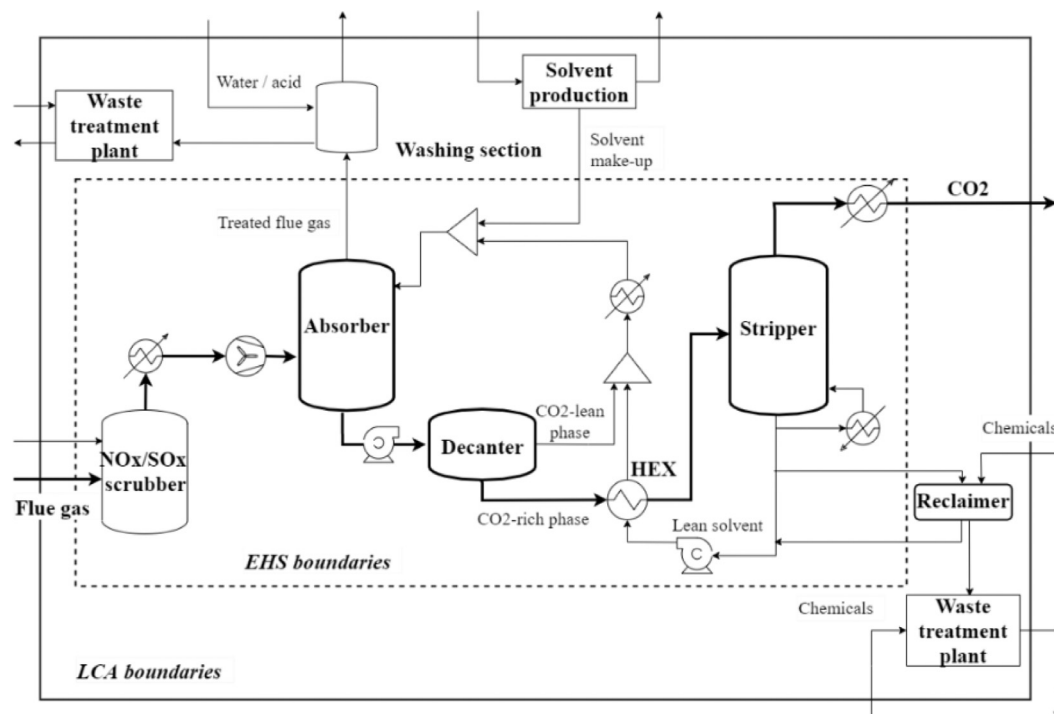| Molecule name	Structure
cyclohexylpropane-1,3-diamine (S1N)	
dimethyl cyclohexylamine (DMCA)	
methylcyclohexylamine (MCA)	

Fig. 1. Process structure and scope for LCA and EHS assessment. The process is shown for the S1N+DMCA solvent. The process for MCA differs by the position of the decanter which is located after HEX (See Fig. S1 in Supplementary material)

novel mixture had been identified through computer-aided molecular design (Papadopoulos et al., 2020b). Equilibrium data were derived experimentally for both solvents and used in the models estimating material and energy flows of the capture systems (Jeon et al., 2014; Tzirakis et al., 2019; Papadopoulos et al., 2020). More details on the selection of the novel solvent can be found in the work of Papadopoulos et al. (2020b).

3.3. Process flowsheets for CO_2 capture with phase-change solvents

The two phase-change solvents correspond to the two types of phase-change process diagrams, depending on the placement of the liquid-liquid phase-separator (Papadopoulos et al., 2019). S1N is an absorption activator containing both primary and secondary amine groups, which in combination with a regeneration promoter like DMCA, can achieve desirable capture and solvent regeneration properties (Papadopoulos et al., 2020). During the phase separation, hydrophilic S1N tends to accumulate in the aqueous CO_2-rich phase, while hydrophobic DMCA is concentrated in the organic CO_2-lean phase. The CO_2-rich flow contains significant amounts of water, whereas the CO_2-lean phase, recycled back to the absorber, carries a small amount of water. By comparison, the CO_2-lean flow of the MCA system mostly consists of water. Both MCA and S1N/DMCA are thermomorphic solvents.

In the process that uses S1N+DMCA, the phase-separator is placed before the intermediate heat exchanger because the liquid-liquid phase-split appears at 40°C (Fig. 1). In the process using MCA, the phase-separator is placed after the intermediate heat exchanger because the phase-split appears at 90°C. The material flows were adjusted to incorporate aspects that are important for the LCA and EHS hazard assessment of the system that were not tested experimentally, such as loss of the solvent due to degradation, aerosol formation, and solvent reclaiming. Additionally, material flows associated with pretreatment of the flue gas, washing of the treated flue gas, and wastewater treatment were added. The modeling approach and assumptions for complementing these flowsheets with these aspects are presented in the following paragraphs. Critical operating parameters of the processes are summarized in Table 3. More details on the process flowsheet used for the impact assessment can be found in the Supplementary material (section S4, Tables S15-S22).

3.3.1. Degradation aspects of MCA solvent

MCA is a secondary amine subjected to degradation under CO_2 capture conditions. Zhang (2013) reports higher MCA loss compared to monoethanolamine (MEA) when exposed to oxygen and high temperatures. Based on the results of Zhang (2013), degradation rate 1.2-3 and 2 times higher than that of MEA was used in the calculation for oxidative and thermal degradation, respectively.

Table 3
Critical operating parameters, from (Kazepidis et al., 2020).

	S1N+DMCA lime plant	S1N+DMCA power plant	MCA lime plant	MCA power plant
Solvent per CO_2 captured, kg/tonne CO_2	11000	10000	8000	14000**
$\frac{G_{mol}*}{L}$, mol/l	6.7	23.5	7.93	16.1
Solvent regeneration temperature,°C	90	85	106	101
Reboiler duty, MJ/tonne CO_2	2340	2083	2346	2091

*inlet flue gas flow to circulating liquid flow rate; ** MCA flow is larger than the S1N/DMCA flow for the power plant case. That is because the flowsheets were optimized based on economic assessment, and the estimated cost per kg of solvent for the S1N/DMCA system is higher than that of MCA.

It should be noted that the exact ratio, as well as the nature of all the degradation products and their quantities, are unknown because the experiment of Zhang (2013) was carried out in an open batch system. Only degradation products remaining in the liquid phase and total loss of amines were quantified.

Experiments carried out by Lepaumier et al. (2011) and Vevelstad (2013) on a secondary amine, monomethylethanolamine (MMEA), showed that 15–33% of heat-stable salts (HSS) could be formed during oxidative degradation, while the rest are volatile compounds. Thus, it was assumed that during oxidative degradation, MCA also generates mostly volatile components, ammonia being the main of them. According to Zhang (2013), the major non-volatile product of oxidative degradation is cyclohexanone oxime. Degradation scenarios and assumptions used in the assessment are gathered in Table 4. Only products reported as the major degradation products were used for the evaluation. It is recorded that the evolution of ammonia has a linear correlation to the concentration of oxygen. Therefore, an elevated amount of oxygen might escalate the MCA degradation rate; thus, an additional case was considered in the case of the power plant flue gas, which carries twice as much oxygen as the lime plant. For this scenario, the oxidative degradation rates stated in Table 4 were increased by a factor of 2. This additional scenario was used to analyze the influence of the elevated degradation due to excess of oxygen on LCA results. However, it was not included in computing the average LCA impact.

Thermal degradation transforms MCA to other amines like cyclohexylamine, DMCA, and N-methyldicyclohexylamine, which can act as additional CO_2 capture molecules. However, the formation of other amines as a result of thermal degradation was considered to be very small; therefore, only the loss of MCA was calculated without taking into account the impact of the generated amines. According to Zhang (2013), thermal degradation of MCA is about two times higher than of MEA at 120°C; taking into account the process temperature of 100°C used for the MCA system, a thermal degradation ratio of 2 was assumed for the MCA/MEA as the worst case. MEA thermal degradation loss was believed to be low at 100°C and was taken as 0.003 kg/tonne CO_2 (Davis and Rochelle, 2009).

3.3.2. Degradation aspects of the S1N+DMCA solvent

S1N is a diamine with secondary and primary amino groups. Its structure is similar to a combination of cyclic MCA and linear N-Methyl-1,3-diaminopropane (MAPA). No experimental data were found for degradation of S1N under CO_2 capture conditions; thus, MCA and MAPA data were used in this analysis.

Voice et al. (2013) report ten times faster degradation rates of MAPA in the presence of oxygen, compared to MEA, leading to the formation of ammonia and aldehyde; however, according to Voice et al. (2013) ammonia represents only a minor part of the amine loss. Vevelstad (2013) confirms high degradation rates of MAPA but reports only three times higher degradation rate than for MEA. Formation of volatile allylamine and non-volatile N-methyl-N,N'-trimethyleneurea (1-Methyltetrahydro-2(1H)-pyrimidinone) and an amide as potential degradation compounds are suggested, amide being the main product in the liquid phase (Vevelstad, 2013). Thus, if S1N is assumed to predominantly follow the MAPA degradation mechanism, ammonia, allylamine, aldehyde, urea and amide might be formed during the oxidative degradation products. If S1N is assumed to predominantly follow the MCA oxidative degradation path Zhang (2013), an oxime (e.g., cyclohexanone oxime) or a ketone (e.g., cyclohexanone) and other amines could be produced. The MAPA degradation mechanism was taken for the oxidative degradation of S1N, where the primary amino group reacts with oxygen more easily, since the secondary group in the molecule is more sterically hindered. Amounts of degradation products are not known, therefore the same kinds of scenarios as for the MCA were used, but with

the assumption that the majority of degradation products are not volatile. For calculation, only allylamine as the major volatile compound, and amide, as the major non-volatile compound, were considered. Propyl formamide was assumed as an amide that could potentially be formed.

The thermal degradation of MAPA is found to be slightly lower than for MEA at 135°C (Eide-Haugmo, 2011). The thermal degradation of MCA is reported to be higher than the degradation of MEA at 120°C (Zhang, 2013). During its thermal degradation, S1N, as a lipophilic amine similar to MAPA and MCA, could also follow either MAPA or MCA degradation mechanism. In case S1N follows the MAPA mechanism, ureas, pyrimidinones, or dimers could be formed (Voice et al., 2013). If the MCA degradation path is followed, the thermal degradation of S1N might result in the generation of other amines (Zhang, 2013). The latter was considered to estimate the thermal degradation of S1N. However, due to the lower regeneration temperature of 90°C and greater steric hindrance of the secondary amino group, the thermal degradation rate was assumed to be similar to the rate of MEA.

DMCA is a tertiary sterically hindered amine; therefore, it is considered to be very stable both to thermal and oxidative degradations. The degradation scenarios of the DMCA were composed following the information provided by Zhang (2013). In his experiments, the degradation rate of DMCA was lower than of MEA, and the degradation products remaining in the liquid phase were other amines like MCA and N-ethylcyclohexylamine (ECA) for oxidative degradation, and MCA and N,N-Diethylcyclohexylamine (DECA) for thermal degradation. The volatile degradation products were not analyzed. Hence, ammonia was assumed to be the volatile product of the oxidative degradation

Table 5 presents the scenarios and possible products for S1N and DMCA oxidative degradation. Only one scenario was assumed for DMCA. The influence of increased oxygen level to the oxidative degradation rate of S1N and DMCA molecules is uncertain. The correlation of oxygen content to ammonia production observed in the case of MCA probably cannot be used here since the molecules have a different structure, and ammonia might not be the main volatile degradation product of their degradation. Therefore, no other scenario of increased oxidative degradation rates because of higher oxygen content in the flue gas was analyzed for the S1N+DMCA solvent. The thermal degradation rate was considered to be low for both S1N and DMCA. Thus, the degradation rate for both of the molecules was taken as 0.8 of the MEA degradation rate.

From the potential oxidative degradation products, the presence of allylamine can pose a severe risk to the safety and health of the personnel and the environment. Allylamine is a highly flammable compound, toxic to humans and aquatic life. The lowest reported concentration resulting in a toxic effect (TCl_0) in humans is 5 ppm over 5 minutes, while being a strong irritant already at 2.5 ppm. Allylamine violently reacts with oxidizing materials and acids and may create an explosive mixture with air (National Center for, 2020, n.d.).

3.3.3. Auxiliary process units

Among various reclaiming techniques, thermal reclaiming is the most commonly used and was also used herein. The amount of purge of the lean solvent stream going to the reclaimer was calculated assuming steady-state non-volatile degradation products concentration of 1.5 wt. % in the circulating flow. The amount of steam and caustic soda required for the reclaiming process and a 5 % solvent loss in the reclaimer were assumed (Sexton et al., 2016).

For the lime plant, a flue gas pretreatment unit was considered as an additional equipment for emissions control because of the high content of NO_x and SO_x (i.e., more than 5 ppm). NO_x and SO_x cleaning was assumed to be done simultaneously by 5

wt. % sodium hydroxide (NaOH) and 1 wt. % sodium hypochlorite (NaOCl) solution in a wet contact scrubber (Hultén et al., 2017; Kuropka, 2011). The scrubber was believed to reduce the NO_x and SO_x concentrations to levels below 5 ppm. No flue gas cleaning of the power plant was assumed because of the low content of NO_x and SO_x in the flue gas.

Both of the flue gases contain small particles; therefore, there is a high probability of increased emissions of the solvent due to aerosol formation. It was assumed that the aerosol formation would increase the emissions by one order of magnitude. Still, the majority of these increased emissions were considered to be avoided due to a NO_x/SO_x wet scrubber and the wash columns with installed demisters treating the off-gas leaving the absorber. Only material flows associated with the wash columns were directly included in the assessment.

Water and acid wash columns were modeled in Aspen Plus ® based on Khakharia et al. (2014a). Chilled water was used to wash the solvent leaving the absorber due to aerosol formation and solvent volatility. Water wash is also believed to increase the size of aerosol droplets, which makes it more difficult to escape the demisters (Fulk and Rochelle, 2013).

Acid wash was required for the systems where ammonia is expected to be generated due to oxidative degradation. It was assumed that NH_3 was mostly produced in the MCA-based system, while for the S1N+DMCA-based system, ammonia generation was believed to be small. In the latter case, an additional water wash instead of the acid wash was added to remove the volatile emissions of allylamine, which is well soluble in water (1000000 mg/L at 20°C (National Center for, 2020, n.d.)).

Wastewater flows from the flue gas pretreatment, the reclaimer and the treated flue gas washing part were also taken into account, the LCA impact of the treatment was calculated based on generic life cycle inventories of waste treatment models (Köhler et al., 2007).

None of the solvent molecules could be found in LCA databases; therefore, the impact of the production process of the solvent molecules was estimated by the short-cut FineChem models (Wernet et al., 2009). Additionally, the impact values calculated using the rigorous solvent production models generated in Aspen Plus ® (Gustafsson and Rosin, 2019) were used. That helped to estimate the influence of the uncertainty of the values on the overall impact of the system.

4. Results and discussion

4.1. LCA

LCA results are presented in Fig. 2. The net CO_2 savings range from 0.33 to 0.47 kg-CO_2 per kg-CO_2 captured (taking into account 90% capture) for the various investigated cases, the higher performance is observed for the MCA lime plant. The results in Fig. 2 show that the main contributor to the overall environmental impact for all the systems in all three life cycle impact metrics is steam for solvent regeneration, followed by electricity required to deliver seawater for cooling purposes. However, the effects of the remaining contributors vary depending on the system and impact category. For both solvent systems, the higher impact is observed for the power plant case. The main difference is coming from the impact of the electricity for the blower and for cooling (sea) water delivery, which can be explained by the lower concentration of CO_2 in the flue gas and the higher amount of solvent required to capture 1 tonne of CO_2, respectively. It must be stressed that the Greek mix was used as an electricity mix because because the two CO_2 emitting plants under investigation are located in Greece. The Greek electricity mix has generally higher life cycle impacts compared to a greener electricity mix, as the Swedish electricity

mix, for example (e.g., 0.27 vs. 0.036 kg CO_2-eq per kWh, respectively). A smaller difference in favor of the lime plant is observed for the wastewater treatment impacts, which are lower because of less washing required for the lime plant. On the other hand, there is no impact associated with the NO_x and SO_x cleaning of the flue gas of the power plant. That is due to lower NO_x and SO_x concentrations in the respective flue gas, but this lower impact is too small to counteract the impacts of electricity for the blower and seawater pumping.

The overall performance of S1N+DMCA is similar to MCA for the case of the power plant in all the investigated life cycle metrics. The profile of these metrics is mainly different in two categories: the impact of solvent make-up is higher for S1N+DMCA, while the impact of electricity for cooling water delivery to the capture plant is lower. Due to the estimated higher degradation rate of the S1N+DMCA solvent, the impact coming from the solvent make-up is more significant for S1N+DMCA than for MCA. The higher degradation rate also leads to an increased load on the reclaimer unit, preventing the accumulation of the degradation compounds in the CO_2 capture process; thus, the impact of reclaiming is also higher for S1N+DMCA in all the cases. Other impacts affected by the degradation and reclaiming of the solvent are those of the wastewater treatment process, neutralizing the waste of the reclaimer. However, the impacts of treating wastewater flows from washing sections, and to a lower extent from the NO_x/SO_x scrubber, are also included in this category. That explains the higher impact coming from the wastewater treatment of the MCA power plant because of the larger solvent flow in the system and more volatile emissions of the solvent and degradation products, and, thus, washing demands. The largest solvent flow (per tonne CO_2) of the MCA-based system also explains the higher impact coming from the electricity for cooling water delivery to the plant compared to the S1N+DMCA system.

On the other hand, the overall performance of S1N+DMCA is inferior to MCA for the case of the lime plant in all the investigated life cycle metrics. The reason is the higher make-up solvent impact of the S1N+DMCA process, as explained above, but in this case, the impacts of electricity for cooling water delivery are similar. The cooling requirements of the lime plant-based capture systems are almost identical. Another difference is that in this case, the wastewater impact of the MCA system is practically negligible. The reason is the lower degradation and emissions rate of MCA that results in lower waste flows requiring the treatment.

The contribution of the solvent production was estimated by the short-cut models of the FineChem tool and rigorous solvent production models using Aspen Plus ®. As can be seen in Fig. 2, the difference in impact (patterned area in Fig. 2) coming from the make-up of the solvent when estimated by these two approaches is not significant. It can be concluded that FineChem provided valid predictions. All background data for the LCA calculations are given in the Supplementary material (Tables S2–S3).

Among all factors influencing the environmental impact of the carbon capture plant, the degradation of the solvent is subject to the highest uncertainty. The effect of the various degradation scenarios presented in Tables 4 and 5 regarding the LCA results is shown in Fig. 3. The largest uncertainty is observed for S1N+DMCA cases, represented by the wider spans between the best and worst cases. No experimental data exist on the degradation behavior of the S1N molecule, which could exhibit 3 to 10 times higher degradation than MEA. Depending on which degradation scenario is applied, the results of LCA can change considerably. For instance, the CED impact differs between the best and the worst case of S1N+DMCA from 15% to 30% for the 33/67% and 15/85% scenarios, respectively.

Generally, the increase of volatile degradation products from 15 to 33% and consequently the decrease of degradation products that
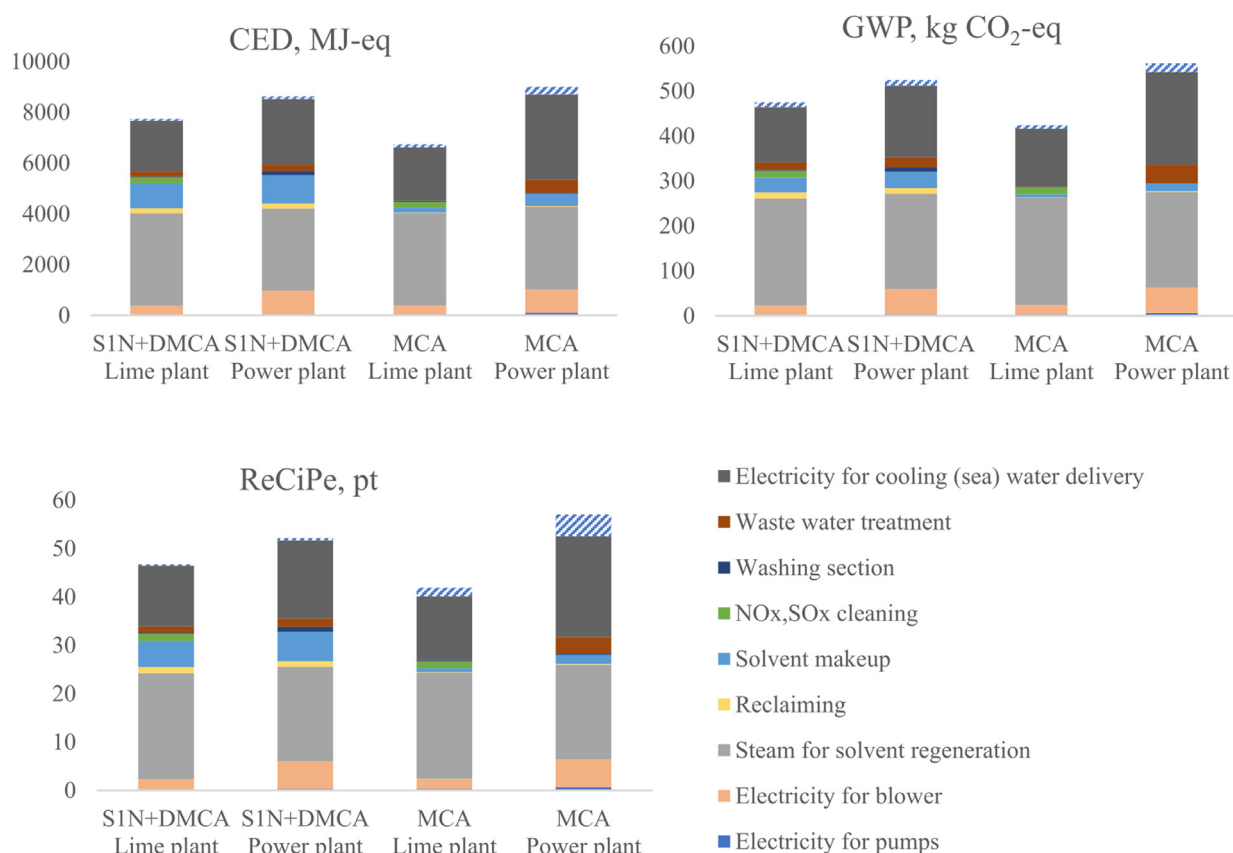
Fig. 2. Contributors to the LCA impact per tonne CO_2 captured based on average values between four main degradation scenarios. Patterned area indicates the increase in LCA impact if the impact of solvent production is calculated based on rigorous process modeling (Gustafsson and Rosin, 2019)

Table 4
MCA main oxidative degradation scenarios and assumptions.

Case	MEA degradation volatile compounds kg/t CO_2 (Thong et al., 2012)	MCA/MEA degradation ratio	MCA degradation compounds, %		Major degradation products (Zhang, 2013)
			volatile	non-volatile	
Low oxidative degradation (best case)	0.320	1.2	85	15	Ammonia, cyclohexanone oxime
			67	33	
High oxidative degradation (worst case)	0.572	3	85	15	Ammonia, cyclohexanone oxime
			67	33	

Table 5
S1N and DMCA main oxidative degradation scenarios and assumptions.

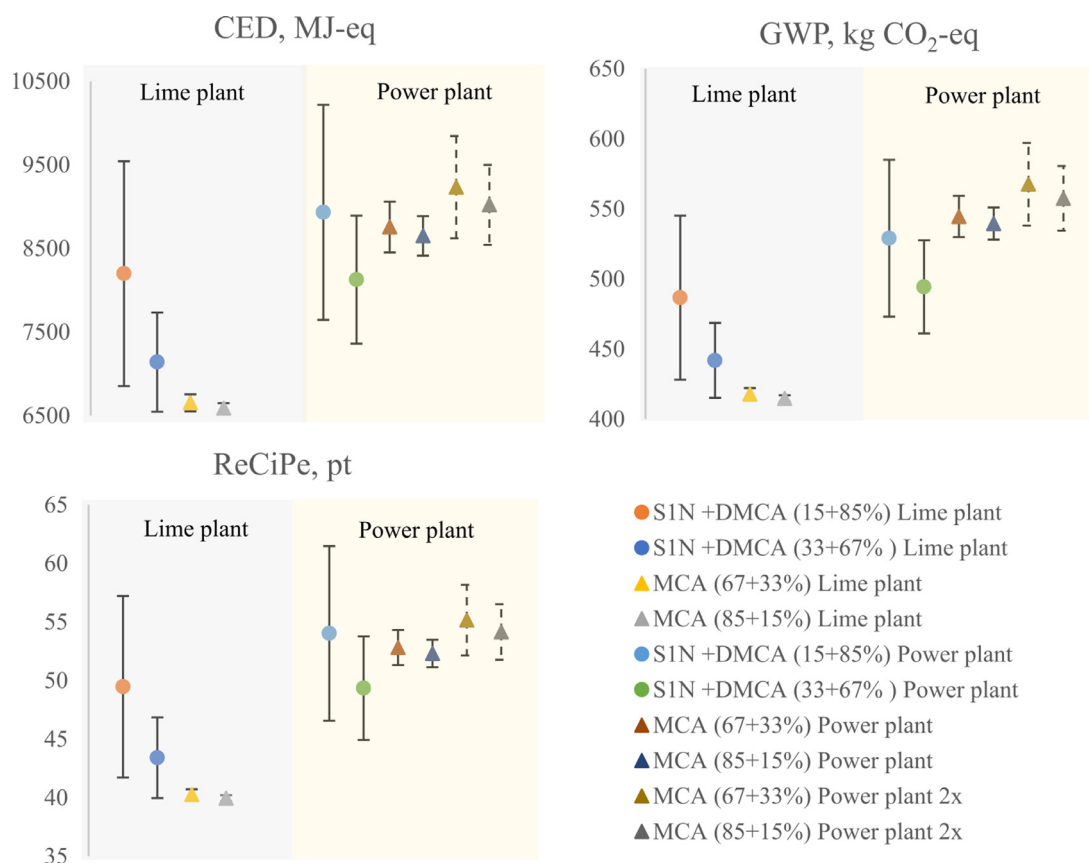| Case	MEA degradation volatile compounds kg/t CO_2 (Thong et al., 2012)	Solvent/MEA degradation ratio	Solvent degradation compounds, %		Major degradation products
			volatile	non-volatile	
		S1N			
Low oxidative degradation (best case)	0.320	3	15	85	Allylamine, Propyl formamide
			33	67	
High oxidative degradation (worst case)	0.572	10	15	85	Allylamine, Propyl formamide
			33	67	
		DMCA			
Oxidative degradation		0.6	67	33	Ammonia, Other amines

Fig. 3. LCA impact (per tonne of CO$_2$ captured) of the carbon capture plant for different degradation scenarios. The dots show the average value between the lowest (best case) and the highest (worst case) degradation rates. For the same system, the case to the left has a higher amount of non-volatile, and the case to the right has higher volatile degradation products. Power plant 2x represents two times the MCA degradation increase scenario because of the elevated amount of oxygen in the flue gas.

remain in the solvent flow from 85% to 67% weaken the average impact value of the S1N+DMCA system by 9–12% depending on the LCA category. The decrease of impact is mostly influenced by the reduction of degradation products accumulating in the recirculating solvent, which, in turn, lowers the amount of purge stream sent to the reclaimer and reduces the required solvent make-up and amount of the reclaimer waste to be treated.

On the contrary, the difference between LCA impacts of the MCA system for the various degradation scenarios is not as high. The uncertainty spans between best and worst-case degradation rates scenarios and between distribution of degradation products to volatile and non-volatile are quite similar. The experimental studies showed that MCA degrades 1.2-3 times more than MEA (Zhang, 2013). The highest difference is observed for the Power plant flue gas (Power plant 2x), where the impact between the best and worst values for the same case of percentage of volatile products varies by around 10%. For scenarios with different partitioning between volatile/non-volatile degradation products, the change in impact values is no more than 2%. However, the case with the higher amount of non-volatile degradation products still performs worse. The results presented in Fig. 3 suggest that, in terms of LCA impact in the three considered categories, accurate degradation rates might be more important than the correct distribution between volatile/non-volatile degradation products.

4.2. EHS

There are various chemicals present in the carbon capture systems that can be hazardous for working personnel and the environment. Hazard-related properties of the chemicals used in the

assessment can be found in the Supplementary material, Tables S6–S8. Fig. 4 illustrates the contribution of every compound existing in the system to the potentials of danger in the EHS categories. Two aspects determine the EHS impact of the chemical: inherent properties of the chemical to cause harm to human health and the environment and mass of the compound in the process, which scales the inherent hazardous potential. It can be seen that in almost all the subcategories, the solvent present in the process in large amounts has a considerable contribution to the potential of danger. Chronic toxicity is an exception as it belongs to the Health category and is not dependent on the mass flow of a substance in the process.

The safety performance of S1N+DMCA is better than that of MCA due to the reduced mobility of the S1N+DMCA solvent. The contribution of MCA is higher in all the Safety subcategories, namely mobility, flammability/explosiveness, and acute toxicity, due to its low boiling and flash points. The most critical concern in terms of safety hazard is observed for the MCA-based power plant capture due to the higher quantity of the solvent per tonne CO$_2$ captured needed in the process. Similar to MCA, low boiling and flash points of DMCA, together with its amounts, make the contribution of DMCA most significant in the S1N+DMCA system. Furthermore, the mobility of MCA and DMCA is also the reason they have the greatest contributions in the acute toxicity. Even though acute toxicity is not directly correlated with boiling and flash point of the molecules, it is strongly affected by the mobility of a substance since damage occurs only after the transmission via air (Koller et al., 2000). The second largest contributor in acute toxicity after the solvents themselves are nitrosamines. The highest value of nitrosamine-based acute toxicity is observed in the MCA-
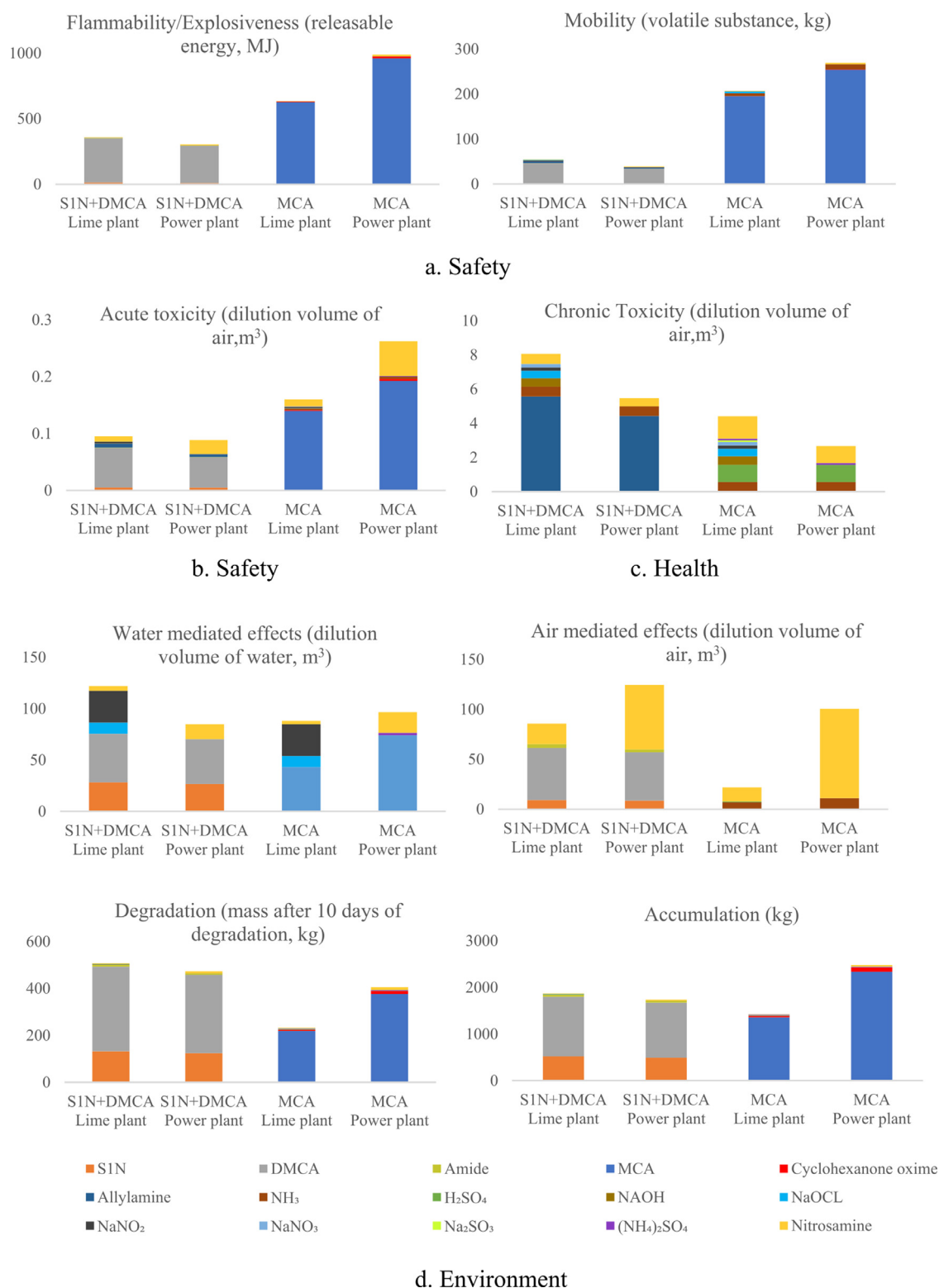
Fig. 4. Potential of danger per tonne CO_2 captured (Health category uses a fixed mass of 1 kg). The worst-case scenario is taken for nitrosamines at NO_x=5 ppm. CO_2, H_2O, O_2, and N_2 molecules are considered as non-hazardous and omitted. Note: average values between four main scenarios are presented, and only chemicals with contribution more than 2% are shown.

based capture unit of the power plant, due to the largest solvent flow per tonne CO_2 in the process recycle stream. Despite that the MCA steady-state concentration of nitrosamines is similar to that of the S1N+DMCA case, the solvent flow is smaller in the latter system. As a result, the nitrosamines contribute less to toxicity in

the S1N+DMCA capture unit of the power plant. The lime plant capture units are similar in both steady-state nitrosamine concentrations and the amount of solvent flow in the process. Overall, the S1N+DMCA capture systems have lower safety metrics than the MCA ones mainly because of higher boiling and flash points

but also because of smaller amounts of S1N and DMCA per tonne of CO_2 captured compared to MCA.

The health effects are defined by the dose of the chemical a worker is exposed to during a specified period of time, which depends on the process equipment, the working conditions, and additional safety measures installed to prevent damage to workers. As soon as a dangerous chemical is identified in the process, precautions should be taken regardless of the mass of the chemical. In this respect, the health category was calculated, considering a standard mass of 1 kg for all the substances (Koller et al., 2000). Thus, the impact of the chemicals present in the capture systems is defined by the potential of each chemical to cause harm in case of exposure. According to Fig. 4c, allylamine, a possible product of S1N degradation, can be the most serious concern in the S1N+DMCA solvent case, followed by nitrosamines and ammonia (NH_3). For the MCA systems, nitrosamines, sulfuric acid (H_2SO_4) used for ammonia washing, and ammonia generated during the degradation of MCA, are the main contributors in chronic toxicity. In the case of the lime plant, there is also a noticeable contribution coming from NaOH and NaOCl used for the flue gas pretreatment. The overall danger that results from the use of these chemicals is higher for the MCA capture unit operating at a higher desorption temperature (highest temperature of the process); hence the chemicals exhibit higher mobility.

The smallest environmental hazard concern is observed for the MCA-based capture system of the lime plant. At the same time, there is no clear trend in the Environment category regarding the most considerable environmental hazard concern. The presence of both MCA and DMCA is intense in the Environment subcategories. While DMCA has substantial contribution in all of them, MCA does not appear in the air mediated effects because of its much lower chronic toxicity (PEL = 235 mg/m^3) to humans compared to DMCA (PEL = 5 mg/m^3) and S1N (PEL = 10 mg/m^3). MCA is also less persistent in the environment (16 days) than DMCA (28 days) and S1N (25 days). That means that MCA exhibit higher biodegradability in the environment compared to S1N+DMCA. The mass of the solvents defines the magnitude of water mediated effects and accumulation impacts since their aquatic toxicity and accumulation properties (ability to accumulate in the food chain) responsible for the impact in these two subcategories are similar.

Apart from the solvent molecules, several other chemical substances present in the capture system have a considerable contribution to the potentials of danger in different environmental categories. A significant contribution in air mediated effects is observed for nitrosamines due to their carcinogenicity to humans even at small amounts. The greatest contribution is seen for the power plant-based capture units. The higher levels of steady-state concentrations of nitrosamines in the power plant-based capture units is observed due to the lower stripper temperatures and increased inlet flue gas flow to circulating liquid flow ratio compared to the lime plant-based capture. For this reason, nitrosamines were also separately studied in the exposure analysis of the framework; more details can be found in Section 4.3 and chapter S3 in the Supplementary material.

It should be stressed that the potential of danger in air mediated effects, unlike the chronic toxicity, takes into consideration also the mass of the chemicals; for this reason, the result contributions of the substances are different from those in chronic toxicity. Considerable contribution in water mediated effects might come from NaOCl and $NaNO_2$ because of their high toxicity to aquatic life. These chemicals can exist in the pretreatment unit of the lime plant flue gas.

Overall, S1N+DMCA is better than MCA for CO_2 capture systems (both at lime and power plant) with respect to plant safety, however, worse with regard to health hazards. As far as the environ-
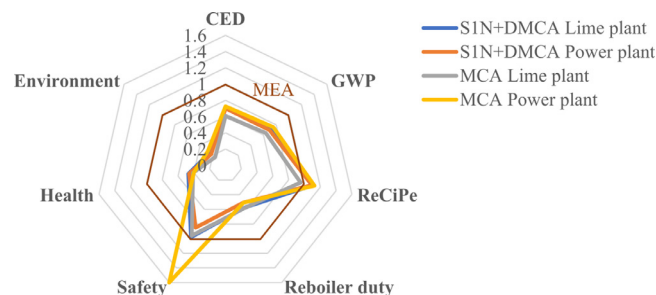

Fig. 5. Multicriteria comparison of different solvent systems for CO_2 capture normalized to the impact of the conventional MEA (30wt%)- based carbon capture system at solvent regeneration temperature 120°C. The impact data for the MEA system given per tonne of CO_2 captured: Reboiler duty – 4.1 GJ, S – 15369.6, H – 2.0, E – 4433.2, CED – 10000 MJ$_{-eq}$, GWP – 600 kg CO_{2-eq}, ReCiPe – 38.6 pt (Papadokonstantakis et al., 2015). The ReCiPe is calculated based on the EI99 value (Dieterich, 2017).

mental hazards are concerned, there are mixed trends, depending mainly on the amount of solvent used per tonne of CO_2 capture.

Fig. 5 shows the results of multicriteria assessment for the MCA and S1N+DMCA CO_2 capture systems where the impact of the studied carbon capture systems is normalized to the impact of the MEA based system (Papadokonstantakis et al., 2015). It can be seen that the reboiler duty, the LCA, and the health and environmental hazard metrics are better for the phase-change alternatives, compared to MEA. It must be emphasized that the impact in terms of health hazards for the phase-change solvents is based on a preliminary assessment and should be studied further in experimental solvent degradation studies. Since the H value is not dependent on mass but rather influenced by the presence of various chemicals in the system, the number of different substances (i.e., degradation products) of a well-studied MEA system is higher due to the known mechanisms behind the MEA degradation. Phase-change solutions are still a relatively new class of solvents with limited experimental data.

4.3. Exposure analysis

When leakage or spills occur, the concentration of the solvent in the breathing air might pose a danger to the health of the workers. The analysis aims to evaluate if a leakage and solvent spills of different volumes could potentially pose a hazard to the personnel working in the carbon capture plant and what is a safe distance for workers after 15 min of a spill accident. Exposure limits for critical compounds are given in the Supplementary material (Tables S9-S10).

4.3.1. MCA

Fig. 6 and Table S11 in the Supplementary material present the range of the MCA concentrations in the working environment corresponding to two leakage and spill compositions at stripper temperature conditions: pure solvent and MCA/water mixture.

It was found that in case of a leakage (Fig. 6a) or spill (Fig. 6 a–c) there is no danger for the workers after 15 min in the near-field (NF) (1 m from the center of the spill) and in the far-field (FF) (10 m from the spill) areas. All the values in NF and FF are much lower than the TWA (time-weighted average, 8-h concentration limit for repeatedly workers exposure) of MCA (235 mg/m^3). In case of leakage (Fig. 6a), only NF was considered as the most probable, assuming that the size of the leakage is minimal and hard to be noticed by workers. The leakage might occur at places obstructed for immediate access; however, workers might be in close proximity of the leakage.

For the initial phase of the evaporation of the spill, a peak of solvent concentration occurs after a few seconds after the accident.
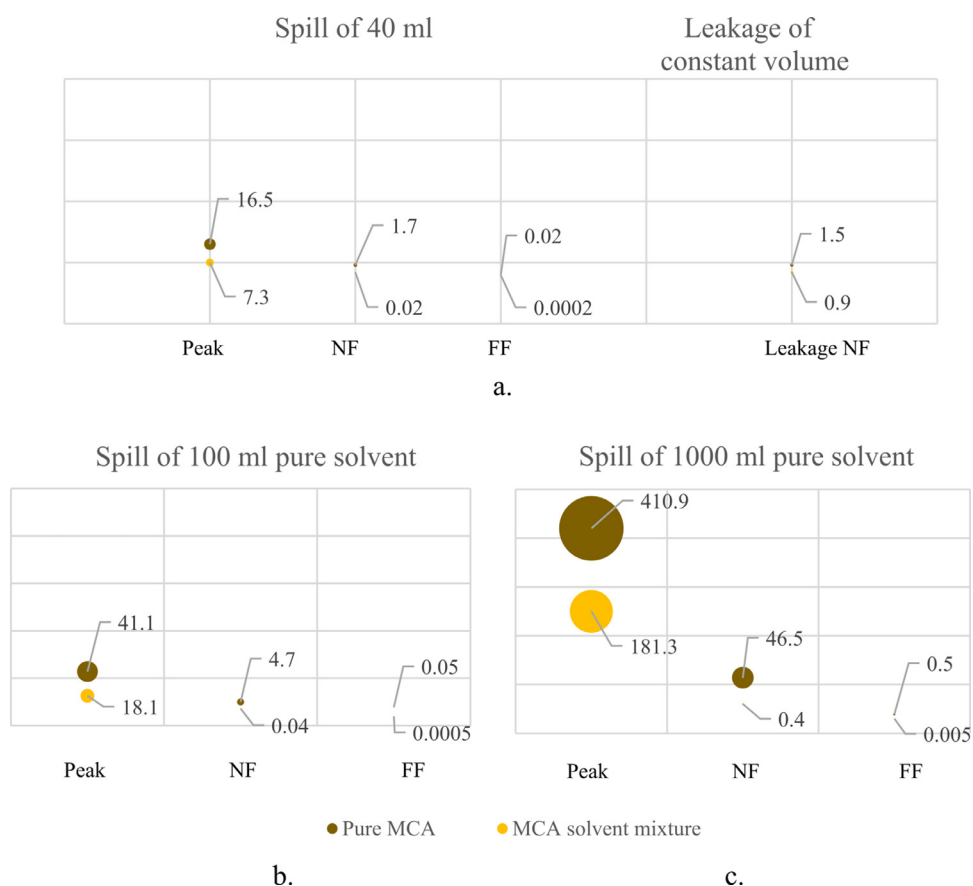
Fig. 6. Air concentration of MCA (mg/m^3) in case of leakage and spills of different volumes if the spill is pure MCA(upper value) or MCA solvent mixture (lower value). Peak is the concentration during the first seconds of the spill, NF- concentration in the near field (1 m from the center of the spill), FF - concentration in the far field (10 m from the center of the spill). The TWA value for MCA is 235 mg/m^3 (for comparison with the value in NF/FF field); IDLH is 827.8 mg/m^3 (for comparison with the peak concentration).

It might be dangerous for a person to be located directly next to the spill. Therefore, a peak concentration during the first seconds of the spill close to the center of the spill should be computed and compared to immediately dangerous to life or health (IDLH) values likely to cause death or irreversible health effects. There is no published IDLH value for MCA; therefore, a number for the most structurally similar compound from a list of substances with available IDLH values was used, namely secondary amine diisopropylamine (IDLH = 827.8 mg/m^3). According to the results, only large spills of pure MCA (spill volumes more than 1000 ml, Fig. 6c) could potentially pose an immediate danger to the plant workers.

4.3.2. S1N +DMCA

Similar to the MCA case, two cases were considered at stripper temperature conditions: spill or leakage of the pure S1N and DMCA chemicals and the mixed stream S1N+DMCA+water. The results of the exposure analysis are summarized in Fig. 7 and are also presented in more detail in Table S12 in the Supplementary material.

The calculated air concentrations of the solvents in NF and FF caused by the spill or leakage were compared to TWA, 5 mg/m^3 for DMCA, and PEL (permissible exposure limit), 10 mg/m^3, for S1N. It can be seen that leakages of pure solvents or solvent mixture do not result in air concentrations of concern neither for DMCA nor S1N. However, spills of pure DMCA and S1N can be dangerous at close distances to the spill if the spill volume is 100 ml or more (Fig. 7d, f). Spills of solvent mixture can also result in NF air concentrations of concern for DMCA for spills with volumes larger than 100 ml (Fig. 7j).

Similar to the MCA case, the concentration during the first seconds of the spills (peak concentration) should be compared to IDLH. There is no published IDLH value for S1N; therefore, the same amine as for the MCA was used as a benchmark (IDLH = 827.8 mg/m^3). According to MSDS, the acute exposure limit for DMCA is 35 mg/m^3 (LC$_{50}$), the DMCA air concentrations during the first seconds of the spill were compared to this value. The results (Fig. 7f, g) show that spills of pure DMCA and the solvent mixture leaving the stripper might pose an immediate danger to the health of the workers (i.e., due to the resulting air concentrations of DMCA) when the spill volume is larger than 100 ml. S1N does not pose an immediate danger to the health of the workers. However, due to the absence of exposure information, extra care should be taken in case of a spill, especially when the pure solvent is spilled.

4.4. Nitrosamines

The liquid concentration of nitrosamines in the capture system should not exceed 13.7 - 14 mM (Badr, 2016; Fine, 2015) to ensure that nitrosamines do not pose harm to human health. The details of the methodology for the steady-state concentration of nitrosamines for all degradation scenarios can be found in the Supplementary material. Table 6 presents the average results of all the investigated cases.

The steady-state concentration of nitrosamines was highly influenced by the amount of the reclaimer purge (i.e., which is in turn affected by the estimated degradation rate of the solvent), by the NO$_x$ concentration in the feed flue gas, by the ratio of inlet
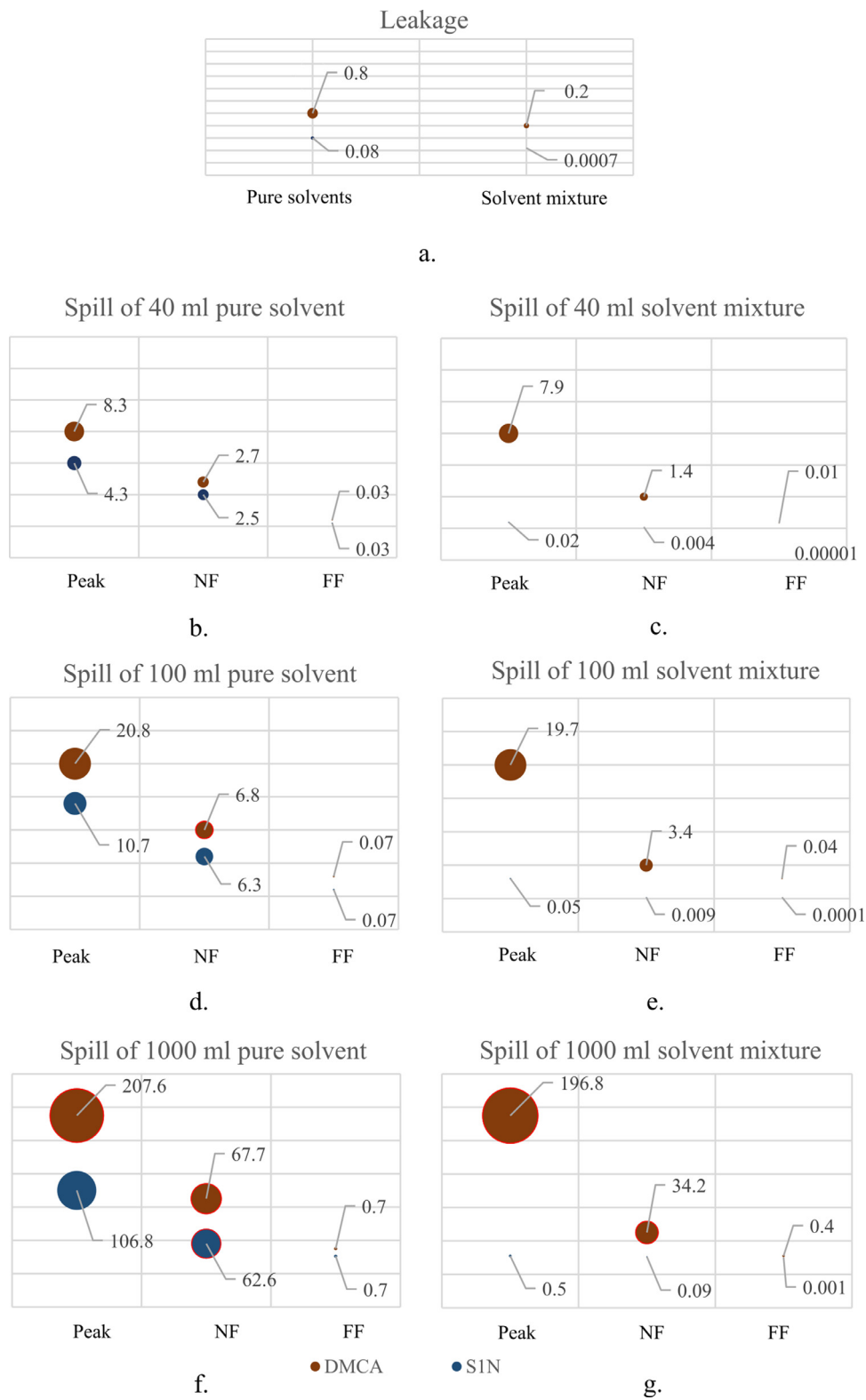
Fig. 7. Air concentration of DMCA (upper value) and S1N (lower value) (mg/m^3) in case of leakage and spills of different volumes. Peak is the concentration during the first seconds of the spill, NF- concentration in the near field (1 m from the center of the spill), FF - concentration in the far field (10 m from the center of the spill). Bubbles marked with red outline indicate values exceeding or close to the safe limits: the TWA value for DMCA is 5 mg/m^3, PEL value for S1N is 10.2 mg/m^3 (for comparison with the value in NF/FF field), IDLH for S1N is 827.8 mg/m^3, acute toxicity value for DMCA is 35 mg/m^3 (for comparison with the peak concentration).

Table 6
Potential steady-state concentration of nitrosamines (mM).

NO_x level, ppm	S1N+DMCA Lime plant	S1N+DMCA Power plant	MCA Lime plant	MCA Power plant
1	0.76	8.26	0.59	2.23
5	3.81	13.77*	2.96	11.12
10	7.62	27.54*	5.93	22.25*

*numbers in bold indicate cases when the safe limits are exceeded

flue gas flow rate to circulating liquid flow rate ($\frac{G_{mol}}{L}$) and by the temperature of the stripper. The larger the amount of flow going into reclaimer and the higher the temperature of the stripper, the lower was the steady-state concentrations of nitrosamines accumulating in the system. The increased inlet NOx levels and the gas-to-liquid ratio value of the system promoted the accumulation of nitrosamines. The different assumptions used for the calculations (see the Supplementary material, section S3) also had a considerable impact on the results. However, the principal trends could still be identified.

The values in Table 6 show that nitrosamines could reach the threshold values for the power plant case already at NO_x concentrations of 5 ppm for the S1N + DMCA and 10 ppm for the MCA case. The lower NO_x limit for the power plant can be explained by higher gas-to-liquid ratio and slightly lower stripper temperatures for the carbon capture unit of the power plant. The lower stripper temperatures decreasing the decomposition rate of the unstable nitrosamines (k_{Des} of Eq. (2.9) in Supplementary material) might promote the accumulation of the nitrosamines in the system. Furthermore, the results above were calculated under the assumption that nitrosamines follow the CO_2-rich phase and are partially destroyed in the stripper and removed by the reclaimer unit. In case a substantial part of nitrosamines follows the lean phase, the accumulation rate might be even higher. Thus, further experimentation is necessary to quantify the accumulation of nitrosamines for the investigated and other phase-change amines.

5. Conclusions

Phase-change solvents have the potential to be a better alternative to the conventional amine solvent systems due to the reduced reboiler duty and possibly lower impact on the environment. In the present study, this potential was tested under a life cycle impact, and hazard assessment framework for phase-change CO_2 capture systems using available process data, inherent solvent properties, and theoretically estimated degradation rates and products complemented by scenario analysis for relevant uncertain parameters.

The results of the LCA assessment showed that the energy required for solvent regeneration and the cooling of the process flows are still the main contributors to the impact of the capture process that uses phase-change solvents. In the studied cases, the steam demand in the stripper and the electricity required to deliver the cooling media were responsible for most of the life cycle impact. The results of the LCA showed that the use of greener electricity and industrial waste heat (i.e., at 90–100°C) could decrease the LCA impact of the phase-change capture plant by 70–90%. In particular, changing the electricity mix, used for pumps, blower and cooling media delivery to the Swedish electricity mix, can reduce the overall impact of the system by more than 30%. Utilizing waste heat for solvent regeneration, with the assumption that it bears no life cycle impacts and does not compete with other processes using that heat, the impact can be further reduced by more than 40%. If all the auxiliary process units change to the greener electricity mix and utilize waste heat, the impact theoretically could be reduced by 90%. Then, the remaining im-

pact will be dominated by the degradation behavior of the solvent molecules. Experimental tests evaluating the degradation behavior of the solvents as well as measures to reduce the degradation rates, are of great importance. Comparison with the LCA results of the conventional systems with MEA indicated an improved performance of phase-change solvent systems, mainly due to decreased energy requirement for solvent regeneration, by, on average, 45%.

EHS assessment demonstrated that less mobile solvent molecules (i.e.,solvents with a higher boiling point) are beneficial from the safety and human health perspective. Environmental hazards mainly depend on the amounts rather than the type of solvent used per tonne of CO_2 capture as well as the presence of additional harmful chemicals (e.g., chemicals used or formed during flue gas pretreatment) required for the process. S1N+DMCA as a less mobile and less flammable solvent is better in terms of plant safety. As far as the environmental hazards are concerned, there are mixed trends, depending mainly on the amount of solvent used per tonne of CO_2 capture. Hazards to health are determined by the inherent toxicity properties of the chemicals used and formed during the carbon capture. Substances exhibiting cancerogenic or adverse toxic properties are potentially present for the investigated phase-change solvents and should be experimentally identified and controlled.

According to the exposure analysis, the NO_x level in the incoming flue gas should not exceed 5 ppm. However, this limit is also influenced by the type of the solvent molecule, operating conditions of the particular capture system and should be assessed individually in every case. Phase-change separation phenomena with the recycling part of the solvent flow bypassing the regeneration process, together with the decreased temperature of the regeneration, might promote the accumulation of the cancerogenic nitrosamines in the system. In this work it was assumed that all nitrosamines follow the the CO_2 rich phase, which generally contains a higher organic load compared to the CO_2 lean phase. However, the allocation of nitrosamines formation is challenging to analyse theoretically and further experimentation is required. Comparison with the MEA-based system showed significantly improved performance of the phase-change systems in terms of health and environment. However, the impact, especially to human health, is affected by chemicals used or formed in the system. Phase-change solvents are still a relatively new class of solutions with minimal data on the behavior of the molecules under the process conditions. Thus, a more accurate comparison will only be possible after phase-change solvents are experimentally evaluated with respect to their degradation under CO_2 capture conditions. Nevertheless, the sustainability assessment proposed in this study reveals the benefits of the investigated phase-change solvents from a multicriteria sustainability perspective. It highlights the points of concern to be investigated for safely advancing the technology readiness level to demonstration and full-scale plants.

Declaration of Competing Interest

None.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.spc.2020.07.015.

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