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Technology overview and environmental considerations for post-combustion carbon capture in Switzerland



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Nomenclature

AMP	Aminomethyl propanol
ASU	Air separation unit
BAT	Best available techniques
BECCS	Bioenergy with carbon capture and storage
BD	Blowdown
BDU	Brownian demister unit
CHP	Combined heat and power
CCS	Carbon capture and storage
CCU	Carbon capture and utilization
CPU	Compression and purification unit
DCC	Direct contact cooler
ELV	Emission limit value
FOEN	Federal Office for the Environment
GHG	Greenhouse gas
HPC	Hot potassium carbonate
LNG	Liquefied natural gas
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MMM	Mixed matrix membranes
MOF	Metal-organic framework
MSW	Municipal solid waste
OAPC	Ordinance on Air Pollution Control
PCC	Post-combustion carbon capture
ppbv	Parts per billion by volume
ppmv	Parts per million by volume
PSA	Pressure swing adsorption
PZ	Piperazine
SCR	Selective catalytic reduction
SNCR	Selective non-catalytic reduction
TRL	Technology Readiness Level
TSA	Temperature swing adsorption
VPSA	Vacuum pressure swing adsorption
WESP	Wet electrostatic precipitator
WPO	Waters Protection Ordinance
WtE	Waste-to-Energy
WWTP	Wastewater treatment plant

Summary

Switzerland aims to reduce its greenhouse gas emissions by 50% by 2030, with a goal of reaching net-zero emissions by 2050. A central element of this strategy is the application of carbon capture technologies, particularly targeting emissions from point sources which, in Switzerland, are mostly waste-to-energy (WtE) and cement plants.

Five technologies – absorption, adsorption, membranes, cryogenics, and oxyfuel – were analyzed in this report for their performance in WtE and cement plants, as well as their environmental impacts. Absorption, particularly with amines and, to a lesser extent, hot potassium carbonate (HPC), is the most mature technology, with a Technology Readiness Level (TRL) of 6 to 9. Adsorption and membranes, both at TRL 5-6, are less suited for the large scales of WtE and cement plants but could play a more relevant role in smaller-scale applications. Oxyfuel combustion is a highly promising concept that allows for easier carbon capture, but requires significant adaptations and cannot be easily retro-fitted, limiting its immediate applicability. Cryogenic technologies, which encompass relatively new concepts, are not expected to play a significant role in the near future.

Although amine absorption shows good economics and is the most mature, it comes with a set of environmental challenges, namely atmospheric emissions and wastewater discharge. Amines and their degradation products are volatile and can escape into the atmosphere through evaporation in the gas phase or by condensation on nuclei (often the result of combustion from incineration processes) in the gas flow, leading to aerosol formation. Some of these degradation products, such as nitrosamines, are known carcinogens, making it crucial to minimize their emissions. Emissions can be limited through: (i) pre-treatment of the flue gas to reduce the potential for degradation and aerosol formation, (ii) making optimal operational choices, and (iii) employing post-treatment techniques after the CO₂ capture process like washing the gas phase and capturing any remaining aerosols. These options also contribute to the discharge of the aforementioned pollutants into the wastewater.

Absorption using hot potassium carbonate solution is an attractive alternative to amines due to its reasonable cost and lack of environmental concerns, as the solvent is non-toxic and non-volatile. However, its slow kinetics poses a challenge. Amine absorption and HPC are expected to be vital for carbon capture in Switzerland, but the absence of clear empirical data complicates predictions about the industry's evolution and regulatory challenges. Therefore, executing demonstration or commercial projects promptly, within regulatory constraints, is essential to gather insights and accelerate development toward achieving net-zero emissions in line with Switzerland's strategy.

Zusammenfassung

Die Schweiz hat sich zum Ziel gesetzt, ihre Treibhausgasemissionen bis 2030 um 50% zu reduzieren und bis 2050 Netto-Null-Emissionen zu erreichen. Ein zentrales Element dieser Strategie ist die Anwendung von Technologien zur CO₂-Abscheidung, insbesondere für Emissionen aus Punktquellen, zu denen in der Schweiz vor allem Kehrichtverbrennungsanlagen (KVA) und Zementwerke gehören.

Fünf Technologien – Absorption, Adsorption, Membranen, Kryotechnik und Oxyfuel – wurden in diesem Bericht hinsichtlich ihrer Leistungsfähigkeit in KVAs und Zementwerken sowie ihrer Umweltauswirkungen untersucht. Die Absorption, insbesondere mit Aminen und in geringerem Masse mit heissem Kaliumkarbonat (Hot Potssium Carbonate – HPC), ist die am weitesten entwickelte Technologie mit einem Technologie-Reifegrad (Technology Readiness Level – TRL) von 6 bis 9. Adsorption und Membranen, beide mit einem TRL von 5 bis 6, sind weniger geeignet für grosse KVAs und Zementanlagen, könnten aber eine wichtigere Rolle in kleineren Anwendungen spielen. Die Oxyfuel-Verbrennung ist ein vielversprechendes Konzept, das eine einfachere Kohlenstoffabscheidung ermöglicht, aber erhebliche Anpassungen der Anlagen erfordert und nicht leicht nachrüstbar ist, was seine unmittelbare Anwendbarkeit einschränkt. Kryotechnologien umfassen relativ neue Konzepte umfassen und werden in naher Zukunft wahrscheinlich keine bedeutende Rolle spielen.

Die Aminabscheidung ist zwar die wirtschaftlichste und am weitesten entwickelte Technologie, bringt aber eine Reihe von Umweltproblemen mit sich, die vor allem mit den Luftemissionen und der Belastung des Abwassers zusammenhängen. Amine und ihre Abbauprodukte sind flüchtig und können durch Verdampfung in der Gasphase oder durch Kondensation an Keimen (oft das Ergebnis von Verbrennungsprozessen) im Gasstrom in die Atmosphäre entweichen, was zur Bildung von Aerosolen führt. Einige dieser Abbauprodukte, wie z.B. Nitrosamine, sind krebserregend, weshalb die Minimierung ihrer Emissionen von entscheidender Bedeutung ist. Die Emissionen können begrenzt werden durch (i) Vorbehandlung des Rauchgases, um die Bildung von Abbauprodukten und Aerosolen zu verringern, (ii) optimierte Betriebsbedingungen, und (iii) Nachbehandlung nach der CO₂-Abscheidung, wie das Waschen der Gasphase oder die Abscheidung verbleibender Aerosole. Diese Prozesse tragen ebenfalls zur Belastung des Abwassers mit den obengenannten Schadstoffen bei.

Die Absorption mit HPC ist aufgrund ihrer angemessenen Kosten und der fehlenden Umweltbedenken eine attraktive Alternative zu Aminen, da das Lösungsmittel ungiftig und nicht flüchtig ist. Allerdings stellt die langsame Reaktionskinetik eine Herausforderung dar. Es wird erwartet, dass sowohl die Amine-Absorption als auch HPC eine zentrale Rolle bei der CO₂-Abscheidung in der Schweiz spielen werden. Die fehlenden empirischen Daten erschweren jedoch Prognosen über die Entwicklung der Branche sowie die regulatorischen Herausforderungen. Daher ist die zeitnahe Umsetzung von Demonstrations- oder kommerziellen Projekten im Einklang mit den regulatorischen Vorgaben essenziell, um Erkenntnisse zu gewinnen und die Entwicklung hin zu Netto-Null-Emissionen gemäss der Schweizer Strategie zu beschleunigen.

Résumé

La Suisse vise à réduire ses émissions de gaz à effet de serre de 50% d'ici à 2030, avec pour objectif de parvenir à des émissions nettes nulles d'ici à 2050. Un élément central de cette stratégie est la mise en place de technologies de captage du carbone, ciblant en particulier les émissions provenant de sources ponctuelles qui, en Suisse, sont principalement des usines de valorisation énergétique des déchets et des cimenteries.

Cinq technologies – l'absorption, l'adsorption, les membranes, la cryogénie et l'oxycombustion – ont été analysées dans ce rapport selon leur performance dans les usines de valorisation énergétique des déchets et les cimenteries, ainsi que selon leur impact environnemental. L'absorption, en particulier avec les amines et, dans une moindre mesure, le carbonate de potassium à haute température (Hot Potassium Carbonate – HPC), est la technologie la plus mature, avec des niveaux de maturité technologique (Technology Readiness Level – TRL) de 6 à 9. L'adsorption et les membranes, toutes deux au TRL 5-6, sont moins adaptées aux grands volumes des usines de valorisation énergétique des déchets et des cimenteries, mais pourraient jouer un rôle plus important dans les applications à plus petite échelle. L'oxycombustion est un concept très prometteur qui facilite le captage du carbone, mais elle nécessite des adaptations importantes et ne peut pas être facilement intégrée à des installations existantes, ce qui limite son applicabilité immédiate. Les technologies cryogéniques, qui englobent des concepts relativement nouveaux, ne devraient pas jouer un rôle important dans un avenir proche.

Bien que l'absorption par amines soit économiquement intéressante et l'option la plus mature, elle s'accompagne d'une série de défis environnementaux, principalement liés aux émissions atmosphériques au niveau de la cheminée et de la charge des eaux usées. Les amines et leurs produits de dégradation sont volatils et peuvent s'échapper dans l'atmosphère par évaporation ou par condensation sur des particules présentes dans le flux gazeux (souvent le résultat de la combustion dans les processus d'incinération), ce qui entraîne la formation d'aérosols. Certains de ces produits de dégradation, tels que les nitrosamines, sont des cancérigènes connus, d'où la nécessité de minimiser leurs émissions. Les émissions peuvent être limitées par : (i) le prétraitement des gaz de combustion pour réduire le potentiel de dégradation et la formation d'aérosols, (ii) des choix opérationnels optimisés, et (iii) l'utilisation de techniques de traitement des gaz après le processus de captage du CO₂, tels que le lavage de la phase gazeuse et le captage des aérosols restants. Ces processus contribuent également à la pollution des eaux usées par les polluants mentionnés auparavant. L'absorption à l'aide d'une solution de carbonate de potassium à haute température (HPC) est une alternative intéressante aux amines en raison de son coût raisonnable et de l'absence d'enjeux environnementaux, le solvant n'étant ni toxique ni volatil. Cependant, sa cinétique lente pose problème. L'absorption par amines et le HPC devrait être essentielle pour le captage du carbone en Suisse, mais l'absence de données empiriques claires complique les prévisions concernant l'évolution de cette industrie, tout comme les défis législatifs qui l'accompagnent. Par conséquent, il est essentiel de réaliser rapidement des projets de démonstration ou commerciaux au sein du cadre réglementaire, afin de recueillir des informations et d'accélérer le développement pour parvenir à des émissions nettes nulles, conformément à la stratégie de la Suisse.

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1. Introduction

1.1. Industrial emitters in Switzerland

To achieve the ambitious goals set out in the Paris Agreement, Switzerland aims to reduce its greenhouse gas (GHG) emissions by 50% compared to 1990 levels by 2030, and to net-zero by 2050 [1,2]. This requires significant decarbonization efforts across all sectors, primarily through a combination of measures focusing on energy efficiency, renewable energy sources, and technological innovation, as outlined in the long-term climate strategy by the Federal Council [3]. However, 12 million tons of GHG emissions can be attributed to hard-to-abate sectors, where reduction of emissions is difficult if not impossible. Of these, 5 million tons can be mitigated through point source carbon capture, coupled either with permanent disposal of the captured CO_2 (carbon capture and storage, CCS), or with CO_2 utilization (carbon capture and utilization, CCU), while the remaining 7 million will need to be balanced by negative emission technologies such as bioenergy with CCS (BECCS), or direct air capture [4]. BECCS generates negative emissions by capturing CO_2 from biogenic sources such as biomass at point sources, while direct air capture aims to extract CO_2 directly from the atmosphere. The latter utilizes technologies that are rather different from those used for point source capture and is therefore out of the scope of this report.

Among the hard-to-abate point source emitters, around two-thirds can be considered large industrial emitters, whose CO₂ emissions are predominantly due to the process of combustion [5,6]. They may be categorized into Waste-to-Energy (WtE) plants, cement production, and chemicals production, and are shown on a geographical map of Switzerland in Figure 1.1. As part of their overall net-zero strategy, Switzerland has committed to reducing its industrial CO₂ emissions by 90% by 2050. The main strategy considered for these industrial sectors [7] is to capture the CO₂ before it enters the atmosphere through post-combustion capture (PCC), which in this report entails traditional PCC technologies as well as oxyfuel combustion. As more than 87% of CO₂ emissions of the large industrial emitters came from WtE plants (29 facilities emitting 4.6Mt/a), and cement plants (6 facilities emitting 2.3Mt/a) in 2022, the report will mainly discuss the application of carbon capture technologies at the scale and for flue gases that are typical for such installations. Additionally, the Swiss waste sector is planning to incorporate PCC to the first installations by 2030 [8,9]. Since WtE plants incinerate municipal solid waste (MSW) that is 50% biogenic, and cement plants may also use biomass as fuel, PCC integration will generate negative emissions. Note that among the facilities, there is a spread in

the scale of the CO₂ emissions (smallest is \sim 80kt/a, largest is \sim 300kt/a), which has potential consequences on the expected technology to be implemented.



Figure 1.1: CO₂ point sources in Switzerland with emissions larger than 80kt/a, divided into three main categories, the size of the point indicates the relative amount of emissions [5,6]. WtE plants and often cement plants include emissions from biogenic origin, which are counted as negative emissions once they are captured and stored. Point sources with emissions smaller than 80kt/a (e.g., chemicals, steel, lime) are not shown in the figure and are responsible for around 2Mt/a of CO₂ entering the atmosphere.

Smaller sectors with point sources for which PCC is relevant consist of biomass combined heat and power (CHP), the production of steel, lime, pharmaceuticals, and chemicals. Although their flue gas compositions may differ from those of WtE or cement plants and therefore, they require slightly different plant designs or requirements from those described in this report, the concepts for PCC described still apply. Furthermore, there are many point sources operating at even smaller scales, such as industrial boilers or small wood-fired plants, that can have very different flue gas properties relative to WtE or cement. Although some aspects described in this report may be relevant to them, a detailed analysis of the application of carbon capture to these smaller point sources is out of scope. Similarly, notable emissions arise from sources that do not capture the CO₂ post-combustion such as biogas installations and pre-combustion processes like wood pyrolysis and gasification; there are thus also outside the scope of this report.

1.2. Overview of capture technologies

Several technologies have been developed for carbon capture from industrial point source emitters. Figure 1.2 shows the hierarchy of the relevant techniques applicable to WtE and cement plants. There are two carbon capture concepts relevant to this report, referred to as follows:

- 1. **Retrofittable post-combustion**: this involves capturing the CO₂ from the flue gas exiting the plant, which may be done using a variety of techniques as will be discussed later in this section; these techniques allow for retrofitting of existing installations.
- 2. **Oxyfuel combustion**: here, oxygen is separated from air in an air separation unit (ASU), and pure oxygen is used for combustion, which generates flue gas with high CO₂ and almost no nitrogen content, allowing for easy capture; this technology requires not only an ASU but also reworking or even possibly rebuilding of the existing plant.



Figure 1.2: Breakdown of the methods and techniques for carbon capture including an assessment of the TRL for the cement industry or WtE, based on interviews with industry, scientific literature, [10–13] and other relevant sources [14]. Below the diagram, examples are given of commonly studied materials for each technology.

Note that in this report, the term "post-combustion capture" is used as an umbrella term that encompasses both oxyfuel processes and what is conventionally considered PCC – now coined "retrofittable post-combustion". Concepts not applicable to cement or WtE or those with TRL lower than what would allow for full scaling within the next 5 years are not within the scope of this report. Examples are e.g., pre-combustion or metal oxide looping [10,11]. As for retrofittable post-combustion, four main techniques are available: (i) absorption, (ii) adsorption, (iii) membranes, and (iv) cryogenics. These can be further sub-categorized for specific configurations, materials, or solvents, each having a TRL associated with it, which makes it impossible to assign a unique TRL to each of the main techniques. However, specific sub-categories are considered most mature, which is what the TRL numbers reported in the diagram of the figure refer to. A general technical description of the technologies, as well as an overview of the latest developments, is given in the next sections.

There is consensus that absorption processes are the furthest developed for their use in PCC. In fact, CO₂ absorption processes are operational today at large scale, albeit not specifically in the WtE or cement sector. Also, many large-scale demonstration projects for various flue gases and configurations have shown that this technology can be implemented commercially (TRL 8-9) [15]. Table 1.1 lists examples of commercial carbon capture projects within the European WtE sector and cement sector under construction or in advanced development [14], i.e., this list excludes research, pilot, or demonstration projects. Among the projects where the selected technology is known, all utilize absorption-based methods. Of Switzerland's 29 WtE plants, KVA Linth is included in the table as it is the most advanced in developing CCS integration, with the goal to operate a PCC facility by 2030. Additionally, 17 other WtE plants are in the "planning phase", indicating an intention to renew their facilities with CCS integration in mind, of which 3 facilities have CCS integration timelines targeting 2035 [16].

Sector	Facility	Location	Stage	Technology
WtE	Hafslund Oslo Celsio	Oslo, NO	IC	Amine absorption (CANSOLV®)
WtE	Amager Bakke	Copenhagen, DK	AD	Amine absorption (MEA, CESAR-1)
WtE	KVA Linth	Niederurnen, CH	AD	Amine absorption (<i>N.R.</i>) or HPC
WtE	Protos	Cheshire, GB	AD	Absorption (N.R.)
WtE	Kvitebjørn Varme	Tromsø, NO	AD	N.R.
WtE	Pard Adfer	Deeside, GB	AD	N.R.
Cement	Schwenk Latvija	Broceni, LV	AD	HPC (Capsol EoP™)
Cement	Heidelberg Materials	Brevik, NO	IC	Amine absorption (<i>N.R.</i>)
Cement	Heidelberg Materials	Slite, SE	AD	Amine absorption (<i>N.R.</i>)
Cement	LafargeHolcim	Martres-Tolosane, FR	AD	N.R.

Table 1.1: Overview of commercial carbon capture projects in WtE sector or the cement sector considered to be in construction (IC) or advanced development (AD) according to the CCS institute; N.R. = not reported [17]

Bioenergy with carbon capture and storage (BECCS) is also gaining traction and being implemented in Europe, with notable projects such as BECCS Stockholm by Exergi Stockholm that plans to use HPC [18], and the large-scale BECCS project by Drax in the UK that aims to capture 8 million tons of CO₂ every year. As some of the WtE plants in Switzerland, e.g., KVA Hagenholz in Zurich and KVA Basel, are part of an integrated system including wood-fired plants, it is expected that BECCS will also be integrated into the biomass facilities in the near future [19]. Adsorption and membranes are common technologies applied in industry as well, and some pilot and demonstration projects testing their application for PCC have been built and operated or are under development (TRL 6-7). Nevertheless, these technologies must still be proven at the scale and/or for flue gas compositions relevant for WtE and cement production. Cryogenics refers to various plant designs that utilize the sublimation of CO₂ at low temperatures to separate it from flue gases. At this point, the available literature on this is limited, and as far as the authors know, these technologies are at pilot scale (TRL 5-6) or lower. Recently a research project was finalized that advanced oxyfuel technology for the cement industry to TRL 6 [20]. Furthermore, several large-scale demonstration projects applying oxyfuel technology are in development, and a commercial oxyfuel cement plant was recently commissioned in China [17], thus potentially bringing TRL up to 7-8.

1.3. Objective and structure of the report

Implementing carbon capture in Switzerland presents several significant challenges. Firstly, the varying conditions – such as location, flue gas composition, and energy availability result in different technological demands. The technologies themselves are mostly still under development or being scaled up for application on different types of installations. As a result, selecting the most suitable technology for each specific emitter is complex. Moreover, the technologies raise environmental concerns that need to be addressed when transitioning from theory to practice. It is essential for the operators of carbon capture installation to understand these issues, their underlying causes (e.g., NO_x in the flue gas resulting in toxic byproducts during amine absorption), and to provide mitigation strategies. Additionally, it is the responsibility of the authorities to establish clear guidelines to ensure that suitable measures to protect the environment are incorporated during the design of capture installations. At present, there are no existing installations, not only in Switzerland but anywhere in the world, where the best available techniques (BAT) could be thoroughly assessed and used as a basis for these guidelines. However, scientific literature and pilot studies provide valuable information on what is technically feasible, and thus on what the guidelines might include.

This report aims to provide an overview and assessment of the most promising post-combustion carbon capture technologies for large point source emitters in Switzerland, with a specific focus on WtE and cement plants. The current state-of-the-art and challenges of leading as well as emerging technologies will be laid out, with a focus on their environmental impacts and considerations, along with an overview of the relevant regulatory landscape. The primary goal is to assist regulatory authorities and the interested public in understanding the current state of PCC technology development and the key environmental impacts that need to be addressed for the successful full-scale implementation in Switzerland to achieve net-zero emissions. This information will help prepare the regulatory authorities to provide guidance and support to companies that want to implement these technologies.

The structure of the report is as follows: Chapter 1 provides an overview of the currently available technologies with TRL 6-9 that are applicable to the first emitters with plans for PCC. Chapter 2 then describes the required equipment and resources needed for each of the technologies, highlighting crucial issues for each (positive and negative), and providing an outlook on the latest research developments. In Chapter 3, the potential environmental impacts of each technology, including the underlying causes, as well as the mitigation strategies against these environmental impacts are outlined. Chapter 4 presents a comparative analysis of the technologies, considering performance, cost, energy type and consumption based on the available scientific literature. Finally, the findings are discussed and concluded in Chapter 5.

2. CO₂ capture technologies and latest developments

This chapter offers a general technical description of the five technologies selected for this report. It highlights the key advantages and disadvantages as well as the materials utilized, and it provides an overview of the current development status and challenges for each technology. While the separation technologies discussed here are not new and are already employed in various industrial applications, their use in PCC introduces specific challenges and accordingly corresponds to design specifications.

	WtE plants	Cement plants
Flue gas flow rate [kt/a]	1096	1418
Temperature [°C]	40	150
Composition		
CO ₂ [vol%]	12	20
O ₂ [vol%]	5	8.5
N ₂ [vol%]	77	61.5
H ₂ O [vol%]	6	10
NO _x [ppmv]	<50	<200
SO _x [ppmv]	<80	<400
Particulates [mg/m ³]	<10	<10

Table 2.1: Overview of typical flue gases properties at the stack for WtE and cement plants in Switzerland, < indicates a legislative limit [5,6,21–23].

The separation to be performed is that of CO₂ from flue gas, which arises mainly from combustion processes. Different types of fuel can be burned, ranging from purely biogenic (biomass), to partially biogenic (MSW), to purely fossil. Although flue gas compositions of different combustion processes can vary, typical values for WtE plants and cement plants are summarized in Table 2.1. In WtE plants, the CO₂ emissions result solely from MSW combustion, while cement plants incinerate a large variation of waste fuels with varying compositions and phases, such as used tires, sewage sludge, and chemical waste [24]. Cement production (and other industrial processes such as lime production) also

have process-specific emissions, resulting in higher CO₂ partial pressure in the flue gas, which makes its capture slightly easier than from WtE plant flue gases. The impurities found in flue gas, such as NO_x, SO_x, and dust vary significantly depending on the fuel type and the specific combustion parameters. The less ideal a fuel is, the more incomplete the combustion process is, resulting in lower CO₂ concentration and higher emissions of pollutants. A careful selection of flue gas purification techniques is necessary to remove these pollutants, which ultimately determines the final emissions and the remaining flue gas impurities relevant for PCC. An alternative approach is oxyfuel combustion, in which fuel is burned in pure oxygen instead of air. This produces a flue gas with significantly higher CO₂ concentrations (over 75%) and minimal nitrogen, simplifying the capture process but introducing additional challenges, as discussed in Section 2.5.

Flue gas purification/scrubbing is essential to meet regulatory emission limits, and currently a variety of purification methods are used across Switzerland. For example, about half of the WtE installations use a combination of wet scrubbing (SO_x and dust) and selective catalytic reduction (NO_x), whereas others use a combination of other technologies [21]. These differences in impurity levels can significantly affect the design, operational stability, and environmental impact of the capture processes in a negative way. Additionally, certain capture technologies are more susceptible to the negative impacts of these impurities, which in turn may offer advantages to other technologies. This will be highlighted in this chapter and examined in greater technical detail in Chapter 3.

2.1. Absorption

Absorption separation is a process that uses a solvent to selectively remove one or more components from a gas mixture, by exploiting the differences in solubility of the gaseous components to achieve separation.

2.1.1. Process description

Figure 2.1 shows a basic flow diagram of an absorption process. Generally, a pre-treatment step is required before the flue gas enters the PCC process in order to cool the gas to the desired temperature and to remove impurities. As WtE and cement flue gases need to adhere to strict emission standards, most of the pre-treatment is already handled by the existing flue gas purification units, and additionally required pre-treatment consists of measures to address the aerosol emissions (discussed in Section 3.1.2) as well as flue gas cooling (quenching) to reach the absorption temperature. The cooled flue gas enters the bottom of the first column (absorber), where it is contacted with a CO₂ lean solvent, which flows down the packing or trays. CO₂ is absorbed in the solvent at a low temperature (and/or high pressure), and at the top, the CO₂ lean gas is sent to post-treatment to prevent emissions of harmful pollutants to the environment and then released to the atmosphere. The liquid collected at

the bottom, rich in CO_2 , may then be heated up by the hot CO_2 -lean solution in the cross-heat exchanger before being fed to the top of the stripper or desorber column, where CO_2 is desorbed at a higher temperature (and/or low pressure). The released gaseous CO_2 is collected at the top, and after a purification step (e.g., condensation of contaminants) the gas is compressed. At the bottom of the stripper, the liquid stream is sent to a reboiler, which provides heat to the system by evaporating part of the liquid and returning it to the stripper. The remaining CO_2 -lean and cooled solution is pumped back to the absorber and reused. Such an absorption-based capture process relies heavily on the properties of the solvent used, as these influence its overall efficiency, cost, and environmental impact.



Figure 2.1: Basic flow scheme of absorption separation using temperature to drive the process. Liquid streams indicated in blue, while gaseous streams indicated in gray.

2.1.2. Solvent systems for CO₂ capture

A large variety of solvents have been developed, each with their specific advantages and disadvantages. The key properties are (i) CO₂ uptake capacity, (ii) absorption/desorption kinetics, (iii) energy requirements for regeneration, (iv) stability, i.e., in terms of chemical degradation and/or of physical evaporation, and (v) corrosiveness. The three main solvent groups are amines, inorganic salts, and ammonia. Among them, the most common solvents with high TRL are summarized in Table 2.2 with a qualitative relative assessment of some of their key properties using a color code. Table 2.2: Qualitative relative assessment of key properties of well-studied solvents: monoethanolamine (MEA), piperazine (PZ), amino-methyl-propanol (AMP), HPC (hot potassium carbonate), CAP (chilled ammonia process) [25,26]. Color-coded from best to worst: Dark green, light green, yellow, orange, red.

Mole	cule <i>i</i>	$\begin{array}{c} Capacity \\ [mol_{CO_2}/mol_i] \end{array}$	Kinetics [mol _{CO2} /s Pam ²]	Energy [MJ/mol _{CO2}]	Stability [-]	Costs [CHF/kg _i]
	MEA					
Amines	PZ					
	AMP					
Salt	HPC					
NH ₃	CAP					

2.1.2.1. Aqueous amines

The most developed solvents for absorption are aqueous amine solutions, known for their relatively high CO_2 uptake and fast kinetics, allowing for a relatively small absorption column [27–29]. The downside of amines is that they tend to be unstable, which decreases the efficacy of the solvent over time while potentially generating harmful emissions. These degradation processes are accelerated by the presence of NO_x and SO_x , and is a phenomenon that must be dealt with, as will be discussed in detail in Chapter 3.

Monoethanolamine (MEA), piperazine (PZ), and aminomethyl propanol (AMP) are among the most prominent examples of amines studied for CO₂ capture in scientific literature, each with their specific advantages and disadvantages. MEA is an effective and most widely applied solvent for carbon capture due to its fast reaction rate with CO₂, low cost and mature technology. Still, it poses challenges such as high energy requirements for regeneration, corrosiveness, chemical stability, and potential environmental hazards. Piperazine has very high absorption rates and better thermal stability compared to MEA and has been proposed as the new benchmark amine [30]. However, it is a relatively expensive amine and more toxic than MEA. It also presents challenges with precipitation and slurry formation, which causes operational issues [31]. AMP provides superior CO₂ absorption capacity and lower energy requirements compared to MEA and PZ. However, it offers fewer advantages in terms of kinetics, stability, and overall unit costs.

Moreover, AMP (and other amines), when used in mixes of amines, can create synergistic effects that enhance the overall absorption performance. In this regard, solvent blends are developed to obtain a solvent that is better than the sum of its parts. An example of such a blend that is studied in the literature is the CESAR-1 solvent [32], a mixture of AMP and PZ. This solvent exhibits very favorable characteristics in terms of capacity, kinetics, energy requirements and stability, and although its components are relatively costly, the overall process costs are lower than in the case of individual amines like MEA, PZ, or AMP [33]. Many proprietary blends have also been and continue to be developed to optimize the overall solvent behavior, specifically the aforementioned properties. However, the specific composition of these blends is unknown, which poses challenges in predicting the potential hazards associated with them (see Section 3.1.1).

2.1.2.2. Inorganic salt solutions

Inorganic salt solutions are another group of solvents that provide greater stability and lower corrosion compared to amines. Potassium carbonate is an excellent and promising example for such an inorganic salt solution for CO₂ capture not least because of its high availability and low costs. Due to the low toxicity and high stability in terms of chemical degradation and/or of physical evaporation, there is significantly less concern of solvent loss and of emissions of toxic compounds into the atmosphere. Notably, degradation issues caused by reactions with NO_x, common in amines, are also not of concern. However, their biggest disadvantage is that they present much slower reaction kinetics than amines, requiring larger columns thus resulting in higher capital expenditures.

Reaction kinetics can be enhanced by operating the absorption process at high temperatures as is generally done with potassium carbonate in the hot potassium carbonate (HPC) process. This process has already been widely used in the removal of CO₂ from other gas streams, such as natural gas in natural gas sweetening [34]. The HPC process relies on a pressure swing between absorption and regeneration, unlike amines that rely on temperature swing. As a result, the heat requirements are much lower compared to amine-based absorption; in fact, the main energy requirements come in the form of electricity from the flue gas compression, as it needs to be compressed before entering the pressurized absorption column. By adjusting the operating conditions, it is also possible to run the HPC process using electricity only, making it an appealing option for applications where heat availability is limited, e.g., cement plants [35].

Despite operating at temperatures above 100°C, the reaction rates of HPC are still slower compared to amines. To address this, catalysts, often called promoters, can be used instead or additionally to further enhance the kinetics [36]. These are categorized into three main groups: organic, inorganic and enzymatic. Organic promoters include amines such as MEA and PZ, which are among the most widely studied. While amines can greatly enhance kinetics, they bring about the same challenges that are seen in amine-based absorption, namely higher energy consumption, corrosion and degradation in MEA, and precipitation in PZ. Other well-studied promoters include boric acid, arsenious acid (inorganic), and carbonic anhydrase (enzymatic).

2.1.2.3. Aqueous ammonia

Aqueous ammonia is another well-studied solvent exhibiting high CO₂ loading capacity, low energy demand, relatively low solvent costs, and reasonable kinetics. It also offers high stability and low corrosiveness, addressing one of the main drawbacks of amine-based solvents. However, the high

volatility of NH₃ is the most critical issue. To mitigate this and control the NH₃ slip, multiple aqueous ammonia-based CO₂ capture processes have been developed, usually involving complex plant designs that incorporate some kind of water wash step and/or temperature control [37,38].

Among them, the most common method is the chilled ammonia process (CAP). It is the only ammoniabased process that utilizes low temperatures to overcome the NH₃ evaporation issue. In CAP, the absorber is operated at well below ambient temperature, which requires large chilling duties, thus incurring additional energy (electricity) penalties [39]. However, despite operating at chilled temperature, NH₃ slip is still significant such that an additional NH₃ recovery plant is required after the absorber, essentially introducing another absorption process [40,41]. Nevertheless, the heat duties of the CAP are known to be significantly lower than amine-based processes, offering an advantage that may overcome the operational complexity. While NH₃ is a toxic substance, it is commonly available around installations equipped with selective catalytic reduction (SCR) for the treatment of NO_x in the flue gas, reducing the need for maintaining a separate inventory of the solvent.

2.1.3. Current research and challenges

Solvent optimization is ongoing, focusing on not only mixing different amine solvents as mentioned earlier, but also mixing different solvent classes, e.g., mixing potassium carbonate with amines, ammonia, or other additives [42–44], in an attempt to obtain a solvent that is both stable while at the same time exhibiting fast kinetics. A key challenge here is to find the design and the operating conditions that work well for such complex solvent systems. Besides that, entirely new classes of solvents are being investigated, of which prime examples are ionic liquids (salts that are liquid at room temperature) or enzyme solutions, but these are still at low TRL. On the one hand, enzyme solutions exhibit good CO₂ uptake, are non-volatile, and are non-toxic [45]; on the other hand, the solubility of enzymes is low, posing challenges in undesired precipitation. Ionic liquids [46] also show favorable characteristics for CO₂ absorption, but these compounds are currently only produced at a laboratory scale, and technical challenges exist like significant increase in viscosity.

Many pilot and demonstration projects have been performed for CO₂ capture from flue gas utilizing absorption (for a list, the reader is directed elsewhere [47]), most of them use amines. Many of these projects successfully demonstrated absorption at industrial scale and under industrial conditions, but they have also revealed new challenges related to industry-wide implementation. Specifically, the environmental aspects of amine absorption and the related mitigation strategies required have received significant attention. Some pilot projects have also encountered challenges of foaming in the absorber and stripper columns, which is caused by solvent contamination from impurities and degradation products that form stable foam [48,49]. Foaming is an issue that is mainly associated with amine solvents such as MEA, but can also occur in inorganic salt solutions, especially when used in

combination with amine promotors. It can lead to reduced CO₂ absorption capacity and mass transfer, as well as high pressure drops and solvent carry-over to downstream processes. Several methods have been explored to control foaming, including the addition of antifoaming agents, filtration with activated carbon, and careful control of operating parameters, such as pressure and temperature [50].

Apart from optimizing the solvent itself, countless efforts are being made to minimize the energy requirements of absorption-based CO_2 capture via process intensification. This can be done by (i) optimizing the plant and the operating conditions [51], such as equipment size, pressure, temperature, solvent concentration, or (ii) developing more advanced configurations that include split flow variations, multi-pressure columns, intercooling and heating units [52,53]. While these modifications can introduce complexity and increase plant costs, they offer improved capture performance. Ultimately, a careful balance must be struck between these factors.

2.2. Adsorption

Adsorption separation is a process used to separate specific components from a mixture based on their differing abilities to adhere to the surface of a solid material or to penetrate the micropores (the adsorbent), through chemical or physical interaction. Currently, it is widely used in industries such as gas purification (e.g., removing impurities from natural gas) and water treatment (e.g., removing organic contaminants) [54].

2.2.1. Process description

Adsorption processes operate in a semi-continuous fashion where a first column with adsorbent is used to clean the gas, while a second column is regenerated by means of an increase in temperature or decrease in pressure while flushing it with gas. Once the adsorbent in the first column is saturated and the second column regenerated, they swap roles, and the cycle repeats. In these applications, the non-adsorbing components are those to be purified, i.e., only the non-adsorbing components are the product, and the adsorbing components are waste. The special feature of CO_2 adsorption is that the CO_2 is the component to be adsorbed and at the same time a product to be purified. This fact has led to the development (in the laboratory and through modeling [55,56]) of a wide variety of fixed bed configurations with two or many more columns and steps. These adsorption cycles may utilize a swing in temperature (TSA) or a swing in pressure (PSA) to drive the process, which results in the requirement of different energy types, i.e., heat or electricity. For flue gas separations, vacuum pressure swing adsorption (VPSA), i.e., a swing in pressure between ambient pressure and vacuum, is considered superior to utilizing a swing in pressure that requires compression, while TSA is considered superior to VPSA for high capture efficiencies from flue gases [56]. Figure 2.2 shows a schematic of a relatively simple VPSA system for CO_2/N_2 separation consisting of 4 steps [57]:

- Adsorption: The feed gas (dried flue gas) is fed to the vessel at ambient pressure and the CO₂ adsorbs to the bed, the top end is open and cleaned CO₂-lean flue gas flows out.
- Blowdown (BD) 1: The bed is depressurized through the top end to an intermediate pressure to remove as much N₂ as possible that is still present in the vessel while retaining the CO₂ adsorbed to the bed.
- Blowdown (BD) 2: The column is evacuated from the bottom end to the low-operating pressure with the top end closed, such that the CO₂ desorbs and is captured with high purity.
- 4. **Pressurization:** The vessel is repressurized with cleaned flue gas to ambient pressure from the top end

CO₂ lean gas to post-treatment



Figure 2.2: Basic flow scheme of absorption separation using temperature to drive the process. Liquid streams indicated in blue, while gaseous streams indicated in gray.

Numerous, more complex configurations are developed and studied to enhance the performance of the adsorption process. These include, among others, multi-bed systems with more columns that operate in parallel or series, and additional steps such as pressure equalization and purge cycles in order to increase capture rate, recovery and/or purity [58]. Other reactor concepts like fluidized beds or moving beds have also been proposed [59], although their application is less common. A specific moving bed system worth mentioning here, namely a rotating moving bed system, has recently been tested at demonstration scale for capturing CO₂ from cement flue gas [60].

2.2.2. Adsorbents

The most studied adsorbents for CO₂ capture are adsorbents that utilize different physical interactions (van der Waals forces) between the components to be separated and the adsorbent. These are porous materials with a high available surface area for adsorption and include activated carbon, zeolites, silica gel, and metal-organic frameworks (MOF). The physical properties of these materials, e.g., porosity or chemical composition, can be altered such that they exhibit favorable characteristics for the

separation to be performed [61–63]. Some key characteristics of adsorbents are [64]: (i) the CO₂ adsorption capacity, (ii) the selectivity (e.g., the ratio of CO_2/N_2 molecules adsorbing), (iii) the adsorption/desorption kinetics, (iv) the energy requirement for an adsorption-desorption cycle, and (v) stability against inactivation. Two well-studied adsorbents for CO_2 capture are 13X zeolite [65] and the MOF UTSA-16 [66]; these two materials are the subject of the performance analysis presented in Chapter 4. Another MOF worth mentioning, which is now being commercialized, is CALF-20 [60,67]; unfortunately, little public information is available in terms of economic performance

2.2.3. Current research and challenges

Considerable research effort is dedicated to developing tailor-made porous media, which offer properties beneficial specifically to CO₂/N₂selectivity. In particular, MOFs are of great interest because of their large adsorption capacities and high selectivity, which makes them highly suitable for CO₂ capture (of which UTSA-16 and CALF-20 are prime candidates). Moreover, chemical adsorption using adsorbents that are activated with amines have gained a lot of interest [68-70]. The amines introduce a chemical interaction with CO₂, which greatly improves CO₂ capacity and energy requirement of the adsorbent. A variety of methods



Figure 2.3: Amine functionalized porous silica, through three methodologies, taken from [69]

exist to produce these types of materials, as illustrated in Figure 2.3, which shows amine-activated silica produced in three ways, namely (i) impregnation of amines into the support's pores which results in relatively weak, non-covalent interactions with the support surface, (ii) amines bound to the support surface through covalent bonds and (iii) in situ polymerization of amine-containing monomers to create polyamines inside the pores, which have both covalent and non-covalent interactions with the surface. A downside is that these amines are chemically unstable, which causes a decrease in their capacity over time, making their implementation infeasible at this point. The degradation, similar to liquid amines, is accelerated by flue gas impurities such as SO_x and NO_x. Furthermore, this may lead to unwanted emissions of amines or of degradation products that would have to be dealt with.

An issue with physical adsorbents is the preferential adsorption of water over CO_2 ; as raw flue gas contains significant amounts of water vapor, this is a key challenge. This problem may be tackled by a pre-treatment that completely dries the gas before entering the adsorption system, or by the introduction of a so-called guard layer, which adds a lot of complexity to the system. Worth mentioning is that most amine-activated adsorbents exhibit preferential adsorption of CO_2 over water and thus do not have the issue with water that physical adsorbents have [71]. In fact, in the presence of moisture, many of these materials exhibit higher CO_2 uptake because of more favorable surface chemistry, which is another reason amine functionalized adsorbents are among the most promising materials.

2.3. Membranes

2.3.1. Process description

Membrane separation is a technique used to separate components of a mixture through a semi-permeable membrane. This process relies on the membrane's physical and/or chemical properties to selectively allow certain molecules or ions to pass through while retaining others. It is widely used in various industries outside gas separation, including water treatment, food processing, and purification of pharmaceuticals [72]. Membrane processes utilize a pressure difference as the driving force for separation: the flue gas (the feed) is fed along one side of the membrane at high partial pressure; the CO₂ selectively passes through the membrane and is collected at the other side at low partial pressure (the permeate); The CO₂-depleted gas is collected at the end of the membrane (the retentate). The passing





of molecules through the membrane follows the solution-diffusion mechanism, i.e., CO_2 molecules absorb at the high-pressure side of the membrane and then diffuse through the membrane to the lowpressure side, where the molecules then desorb. Thus, for CO_2 capture from flue gas, one aims for a material with high solubility and diffusivity for CO_2 and low solubility and diffusivity for N_2 and other molecules. To illustrate, Figure 2.4 schematically shows a so-called hollow fiber module, that is proposed for gas separations due to the high available surface area per module, which is advantageous in the case of large volume gases [73] to be treated. In this module, the hollow fibers act as the membrane, the inside of the fiber is the feed/retentate side, while the outside of the fibers is the permeate side. Other configurations for membranes exist, e.g., tubular modules, spiral wound modules, and plate modules, each with specific advantages and disadvantages. It should be noted that for high purity (>90%), designs with two or three stages are required for the optimum operation [74].

2.3.2. Membrane materials

The two key characteristics determining the separation performance of a membrane are [75]: (i) their permeability for the target gas, i.e., how easy the target gas is pushed through, and (ii) their selectivity, i.e., their permeability relative to the other gases in the mixture. Polymeric membranes were among the first class of materials identified for carbon capture and are also the furthest developed; these are also subject to the performance analysis presented in Chapter 4. Polymeric materials are well known for their gas separation properties, their ease of production, and their relatively low cost. Some polymeric materials considered suitable for separating CO₂ from flue gases are polyimides, substituted poly-acetylenes, and polyethylene oxide-based polymers, for details on these materials the reader is referred elsewhere [76]. Another important class of materials is porous inorganic membranes, which are similar materials to those utilized in adsorption, i.e., zeolites, silicas, and MOFs. These materials are able to achieve high selectivities and have high chemical and thermal resistance. However, they are more difficult to manufacture into membrane structures than polymeric materials.

2.3.3. Current research and challenges

Mixed matrix membranes (MMM) are materials that combine the flexibility, processability, and costeffectiveness of polymers with the superior mechanical, thermal, and separation properties of the inorganic materials [77]. Materials such as zeolites, silica, metal-organic frameworks, or molecular sieves are relatively simply integrated into a polymer matrix and then processed into a membrane structure, although challenges in achieving homogeneity still exist [78]. The hybrid nature of MMMs allows for tailored properties that can address specific separation challenges more effectively than traditional mono-material membranes.

Another line of research is transport facilitated membranes, i.e., membranes that are designed to improve the transport of certain molecules, such as CO_2 , through the membrane. In addition, specific carrier groups inside the membrane, which bind reversibly with target molecules, can significantly improve the selectivity and permeability compared to conventional membranes. An example of such materials is polymeric membranes, which have amine groups attached to the polymer backbones; the amine groups (the carriers) facilitate the transport of CO_2 through the membrane. The gas separation

properties of these membranes are far superior to normal polymeric membranes, but stability is still a challenge [79], as the amine groups tend to react with flue gas impurities like SO_x or NO_x.

2.4. Cryogenics

Cryogenic technologies refer to the separation of CO₂ from flue gases based on differences in sublimation or condensation temperatures of the gas components. Very low temperatures are required to perform such separations, e.g., at ambient pressure pure CO₂ de-sublimes at -78.5 °C. For flue gases, this temperature is even lower. It is claimed that cryogenic methods are able to achieve higher CO₂ recovery (99.99%) and purity (99.99%) than other separation technologies [80] although challenges exist to make the technology work, like blockages from the freezing of water. Many of the proposed technologies utilize liquefied natural gas (LNG) evaporation as a cold source [81], limiting their applicability to locations where LNG re-gasification operations). A cryogenic technology based on external cooling loops, only requiring electricity, has recently been tested at a pilot scale [82]. The reported results are promising, but details are limited, and an independent analysis of this process has yet to be found in the scientific literature.

2.5. Oxyfuel

Oxyfuel combustion for the purpose of PCC, commonly known as oxyfuel, involves burning fuel using pure oxygen instead of ambient air (which contains about 21% oxygen and 78% nitrogen), as shown in the flow scheme in Figure 2.5 below. The required oxygen is obtained by separating it from the air in an onsite ASU, generally by cryogenic distillation, which requires substantial amounts of electricity. It is then sent to the combustion chamber, where the fuel of the process, such as energy production or cement manufacturing, is burned to create flue gas that consists primarily of CO₂, water, and impurities. Pilot studies have shown that the concentration of CO₂ on a dry basis can reach over 90% and depending on the fuel type and combustion process, the water content in the flue gas can reach up to 30%. As combustion in a pure oxygen environment generates extremely high temperatures leading to thermal inefficiency and formation of unwanted byproducts, a part of the flue gas is usually recycled and mixed with the oxygen stream to act as a diluent and regulate the combustion temperature. The key characteristic of oxyfuel combustion is the absence of nitrogen, which (i) reduces the emission of nitrogen-based pollutants, such as NO_x , (ii) reduces the flue gas volume by up to 75%, and (iii) most importantly, simplifies the separation of CO_2 capture from the flue gas. The remaining flue gas is sent to a compression and purification unit (CPU), where the water vapor is condensed, and impurities such as SO_x, residual O₂, and particulate matter are separated. The purified CO₂ can then be compressed, while the water is vented to the atmosphere.



Figure 2.5: The generic steps of the oxyfuel combustion process, where the flue gas is possibly recycled [83]

Due to the changes in gas composition and the recycling of flue gas, significant adaptations are required for this technology to be implemented, and it cannot be retrofitted to existing facilities without significant modifications. One of the main challenges is the difficulty in isolating the flue gas recycle and preventing air from leaking in from the atmosphere which has detrimental effects on the effectiveness of the capture process. This applies particularly to WtE and cement plants, where in the former case, lump solid waste has to be fed to the system, while in the latter case, the large solid clinker has to be withdrawn from the system, all the while preventing air leakage. WtE plants typically store the waste in enclosed areas maintained at a slight negative pressure to control odor and emissions, further complicating efforts to prevent air leakage. Furthermore, the changes in gas composition and flow rate alter the heat transfer, which may affect the process' performance (e.g., cement production or energy production). The increase in oxygen content creates higher flame temperatures, which results in higher thermal stresses in the refractory linings and requires redesigning in some cases. For cement production, the CO_2 concentration influences the reversible calcination reaction. Hence, the high CO_2 concentration in the recirculated flue gas requires higher temperatures to achieve an appropriate degree of calcination.

Oxyfuel has been investigated in the context of cement manufacturing [83], with multiple pilot projects being undertaken and a first commercial oxyfuel plant being commissioned. A more detailed process scheme when oxyfuel is applied in cement production is provided in the appendix in Figure 6.1. In a recent project, a group with Holcim commissioned by the Swiss Federal Office of Energy has studied a new implementation of the oxyfuel process, the so-called 2^{nd} generation oxyfuel combustion, whereby the flue gas recirculation is omitted and instead, excess oxygen at over-stoichiometric conditions was fed. This modification has been reported to reduce the costs of the process and increase the CO₂ partial pressure in the flue gas, facilitating the CO₂ separation, but requires more oxygen and thus higher associated electricity duties.

In the WtE sector, only early lab-scale research has been conducted so far [84]. However, the first demonstration plants for oxyfuel combustion in WtE are planned in Norway, with the aim of installing the first full-scale WtE plant using oxyfuel combustion in the near-term future [85]. Similarly, a first oxyfuel installation is planned in Switzerland's sole lime production facility [86].

3. Environmental considerations for carbon capture

While designed to mitigate CO₂ emissions, most carbon capture technologies may introduce new environmental burdens (over and above those associated with energy consumption). This chapter will explore the environmental risks associated with each technology and outline their potential mitigation measures. Where available, relevant pilot study results will be provided to give an insight into what is feasible in practice. For some technologies, such as amine-based absorption, environmental risks have been identified but not quantified (see Section 3.1). For others, like amine-functionalized adsorption, the risks are less understood, though despite knowledge gaps, potential concerns exist (see Section 3.3.1). In some cases, like membrane separation using simple polymeric materials, i.e., not functionalized, the environmental risks are minimal (see Section 3.3.2).

3.1. Amine-based absorption

Although amine-based absorption technologies' main drawbacks are the large amounts of emissions from the amines, the different species that are created and their interactions have been extensively studied. This is a highly complex matter due to the intricate chemical reactions involved and the interactions with impurities in the flue gas. Amines degrade under high temperatures and oxidative conditions, producing a myriad of byproducts whose formation depends on the specific amine and process conditions. The following section aims at highlighting the key considerations.

3.1.1. Species in amine-based absorption

Amines are nitrogen-containing organic compounds derived from ammonia; they are classified by the number of carbon-containing groups attached to the nitrogen atom (see Figure 3.1 for examples of chemical structures) as follows:

- 1. Primary amines: One carbon-containing group, e.g., MEA
- 2. Secondary amines: Two carbon-containing groups, e.g., PZ
- 3. Tertiary amines: Three carbon-containing groups, e.g., methyldiethanolamine (MDEA)



Figure 3.1: (a) the primary amine MEA, (b) the secondary amine PZ, and (c) the tertiary amine MDEA

Each amine type has distinct chemical properties and reactivity based on the number and nature of the substituent groups attached to the nitrogen atom. Smaller amines (e.g., MEA and AMP) are more prone to evaporation than larger ones (e.g., PZ and PZ derivative), which is an environmental and health concern if these are released into the atmosphere. In fact, many (commercial) amines have high vapor pressures that result in concentrations of up to 100 ppmv in the gas phase within the absorber [87], thus requiring the implementation of mitigation concepts. Although larger amines are less prone to evaporation, they increase solvent viscosity, exhibit lower kinetics, and are often more complex to produce. Ultimately, the selection of a suitable amine involves weighing these advantages and disadvantages, or mixing different amines to optimize overall performance, as discussed in Section 2.1.2.1. Apart from amine evaporation, several chemical processes take place during operation, transforming amines into other compounds, which are important to understand for both environmental considerations (formation of toxic compounds) and operational aspects (decreasing solvent efficacy). The main chemical processes considered in this report are (i) oxidative and thermal degradation, (ii) heat-stable salt formation, and (iii) nitrosamine and nitramine formation. Furthermore, a section is devoted to the toxicity and volatility features of nitrosamines.

3.1.1.1. Oxidative and thermal degradation

Amine degradation is a complex issue with significant implications for the operation of and the emissions from the absorber [27]. While a detailed description of the degradation processes is beyond the scope of this report, a summary is provided here. Generally, the main amine degradation pathways can be categorized as either oxidative or thermal.

Oxidative degradation has the potential to break the C-N bonds in amines, yielding small, volatile molecules. For illustration, an oxidation reaction for a generic secondary amine is shown in Figure 3.2. The cleavage of the C-N bond in a secondary amine yields a carbonyl (aldehyde if R¹–H, ketone, otherwise) and a primary amine, both of which may have a high vapor pressure. Note that through this mechanism, a primary, secondary and tertiary amine has ammonia as a first-order degradation product, second-order degradation product, and third-order degradation product, respectively. The carbonyls can follow several reaction pathways with either the parent amines or with thermal degradation products; these reaction pathways tend to form heavy molecules with low vapor pressure.

Overall, the following three degradation products with high vapor pressure are expected (i) ammonia, (ii) amines, and (iii) carbonyls, all of which are of concern for atmospheric emissions.



Figure 3.2: Oxidative cleavage of the C-N bond in a generic secondary amine, yielding a carbonyl and a primary amine

Thermal degradation reactions mostly take place at the top of the stripper, which operates at higher temperatures and has high CO₂ loading. The potential reaction differs among amines, and it is impossible to provide a generalized reaction scheme. However, thermal degradation often results in heavier molecules like dimers, oligomers, urea, etc., although some light products have been observed in experiments [88]. Typical lighter products observed through thermal degradation are ammonia and alkylated parent amines, similar to oxidative degradation. The heavier products are less concerning for atmospheric emissions, but they will have to be purged from the system as they decrease CO₂ uptake while increasing the solvent viscosity.

3.1.1.2. Heat-stable salt formation

In the context of amine-based absorption, heat-stable salts (HSS) are ionic or covalent combinations of an amine and an acid (note that the amine is not degraded but merely bound). Acid-forming impurities in the flue gas like SO_x or NO_x are the main sources of ionic HSSs, while organic acids from oxidation of amines (aldehydes have the potential to further oxidize to carboxylic acids) are the main sources of covalently bonded HSS [89]. These HSS contain inactive amines, are corrosive, and thus have to be removed from the solvent loop. Note that avoidance of NO_x and SO_x entering the capture plant can prevent the formation of ionic HSS and consequently reduce the amine purge and thus the solvent makeup, which increases overall process stability.

3.1.1.3. Nitrosamine and nitramine formation

 NO_x , a prominent impurity in flue gases, dissolves readily in amine solutions, where it is transformed into a variety of species such as, NO_2^- , N_2O_3 , etc. Many of these species have nitrosating and/or nitrating properties, i.e., the ability to form nitrosamines or nitramines in the presence of amines (see Figure 3.3). The exact chemistry is rather extensive and complex, and for the details, the reader is referred to the appropriate scientific literature [90,91]; only a summary is provided here.

Only secondary amines form nitrosamines, while both secondary and, to a lesser extent, primary amines can form nitramines [90]. Nevertheless, primary amines and tertiary amines may form secondary amines through thermal and/or oxidative degradation; hence, all amines have the potential to

form nitrosamines and nitramines. The exact rate of formation and the types formed depend on the specific amines present in the solvent and on the operating conditions. As a consequence, it is difficult to make a specific statement about this. Still, as the dissolved NO_x concentration is low, also the nitrosamine and nitramine concentrations are low (ppmv range or less); nevertheless, due to their highly toxic nature, which is especially the case for nitrosamines, their formation is important to consider. Nitrosamines and nitramines themselves are not stable and break down at high temperatures in the stripper into various oxidation products and N₂O. The rate of decomposition depends on multiple factors and a steady state concentration is reached in the solvent loop after a period of operation. The volatile nitrosamines, nitramines, and degradation products are carried over in the gaseous streams of the absorber and the stripper columns, where further purification will be required via washing or condensation (see Section 3.1.2), while the less volatile species remain in the liquid phase, where they will need to be purged through the wastewater in the thermal reclaimer to avoid accumulation.



Figure 3.3: (a) a generic secondary amine, (b) the corresponding nitrosamine, (c) the corresponding nitramine

Nitrosamines are a class of chemical compounds that are notable for their toxicity and carcinogenic properties. Some nitrosamines have been extensively studied and are known to have the ability to induce tumors in various organs, such as the liver, bladder, and stomach. Nitrosamines themselves are not highly reactive in the body, but when they are metabolized in the liver, they are converted into reactive intermediates, which can form so-called DNA adducts. These adducts, a segment of DNA bound to a chemical, can lead to erroneous DNA replication and transcription, resulting in genetic mutations that can trigger cancer development. The specific arrangement and type of substituents attached to the nitrosamine molecule can greatly influence its carcinogenic potential. Thus, not all nitrosamines are equally toxic, and it is generally considered that the potential for adduct formation is high for nitrosamines having small alkyl groups. For instance, N-nitroso dimethylamine (NDMA) is highly carcinogenic, while other nitrosamines with bulkier substituents like N-nitroso piperidine (NPIP) are less potent, although still carcinogenic. Table 3.1 lists a set of known nitrosamines and their toxicity in terms of TD50 (the chronic dose given to rats that will lead to 50% of the population developing cancer), as well as their vapor pressure and boiling points. Indeed, the three nitrosamines with the small alkyl groups, NDMA, NMEA, and NDEA, have the highest carcinogenic potential. Unfortunately, these tend to be the nitrosamines with the highest vapor pressure and thus with the highest probability of being emitted into the atmosphere

Compound name	Abbreviation	VP [kPa]	BP [°C]	TD50 [mg/kg/day]	MW [g/mol]
N-nitrosodimethylamine	NDMA	0.4	152	0.0959	74
N-nitrosomethylethylamine	NMEA	0.15	154	0.0503	88
N-nitrosodiethylamine	NDEA	0.11	179	0.0265	102
N-nitrosopiperidine	NPIP	0.012	225	1.43	114
N-nitrosodipropylamine	NDPA	0.011	206	0.186	130
N-nitrosodibutylamine	NDBA	0.006	237	0.691	158
N-nitrosopyrrolidine	NPYR	0.005	214	0.799	100
N-nitrosomorpholine	NMOR	0.005	224	0.1	116
N-nitrosopiperazine	NPZ	0.002	265	8.78	115

Table 3.1: Several known nitrosamines that can form during amine-based absorption processes [92–94]. VP is vapor pressure, BP is boiling point, TD50 is the median toxic dose, and MW is the molecular weight.

Because of their significant health risks, regulatory agencies have established strict limits on nitrosamine levels in consumer products, particularly in food, pharmaceuticals, and tobacco. However, no specific regulatory constraints exist for emissions of nitrosamines from flue gases of industrial emitters in most countries (including Switzerland, see Section 3.5), as the emission level has never been one to raise concern. In a few countries, exposure limits for nitrosamines have been established based on the toxicity data of NDMA. Norway has set the limit at 0.3 ng/m³ [95], at an excess life-time cancer risk of 1 in 100'000 or lower, while the UK has set theirs at 0.2 ng/m³ [96]. These limits are derived by taking dose-response measurements from exposure to mostly rats and relating a threshold for humans by applying certain risk factors; for the detailed calculations and methodologies used, the reader is referred to the cited report [94].

3.1.2. Relevant material flows

Several material flows have to be considered in order to assess potential harmful effects on the environment or human health. Figure 3.4 shows a more detailed process flow diagram of an amine-based CO₂ capture process including a pre-treatment section and a post-treatment section. The pre-treatment in this context refers to any additional treatment that is needed on top of existing flue gas purification steps of the facilities, as detailed below. Four material flows that are relevant for environmental and health considerations have been identified and are depicted in the diagram. They are: (I) the CO₂ lean gas released into the atmosphere, (II) the purified CO₂ ready for compression, transport, and storage, (III) the amine purge, and (IV) the wastewater stream.



Figure 3.4: Process flow diagram for amine-based absorption capture including a flue gas pre-treatment and a post-treatment section

3.1.2.1. Atmospheric emissions (I)

Broadly speaking, there are three strategies to reduce the release of unwanted species into the atmosphere: pre-treating the flue gas before it enters the absorber, adjusting the operating conditions to minimize contaminant formation and solvent loss, and post-treating the flue gas after it leaves the absorber. Since no single approach is entirely effective on its own, a combination of these methods is typically employed. Each strategy is described in more detail in the following section.

Pre-treatment

Typical pre-treatment steps to purify the raw flue gas before the absorption process, specifically to remove NO_x, SO_x and particulate matter, are already part of the flue gas treatment of the existing facility to comply with Swiss regulations (see Section 3.5). NO_x removal is necessary for PCC to avoid the formation of nitrosamines in the solvent loop and is carried out via selective catalytic reduction (SCR) or other systems like selective non-catalytic reduction (SNCR). Flue gas desulfurization is generally applied in the form of wet or dry scrubbing with an alkaline material or solution to absorb gaseous SO_x (mainly SO₂), aerosols (sulfuric acid mist), and particulate matter (dust and soot). Electrostatic precipitation units, such as a dry electrostatic precipitator are also commonly used in WtE plants to remove aerosols and particulate matter.

Although these measures can effectively treat the flue gas to reach stringent environmental targets, additional considerations are necessary when integrating with an amine-based absorption plant. Specifically, extra care has to be taken when dealing with aerosol emissions, as it has been reported that most of the amine emissions from the absorber are attributed to aerosol formation [97]. Flue gas prescrubbing, although effective at reducing SO₂ in the flue gas, is known to generate sulfuric acid mist – aerosol precursors that are not effectively removed by conventional measures such as water spraying or demisters. Two of the most common measures to address this are:

- A wet electrostatic precipitator (WESP) can reduce sulfuric acid mist and dust by up to 95%. However, it is inefficient for small particle sizes from 0.1-1µm, and it has also been reported to cause the formation of even smaller nanoscale sulfuric acid mist in the presence of SO₂, which acts as nuclei in the absorber, negating any positive effects [98]. Thus, care should be taken when a WESP is utilized, e.g., ensuring almost all of the SO₂ in the gas is removed beforehand, adjusting the voltage, or combining with other technologies.
- A Brownian demister unit (BDU) is another effective measure to remove small aerosols (down to < 0.01 µm). Although commonly applied end-of-pipe, it has also been shown to be effective when placed before the absorber [99]. They may be used in combination with WESPs to mitigate the nanoscale aerosol formation. However, BDUs can also lead to high pressure drops, increasing energy consumption of the plant [100].

Other measures that have been studied include fabric filters, steam injection into the flue gas, and reheat burners [100,101]. Ultimately, the optimal mitigation strategy will depend on the facility's existing flue gas purification system and emissions, warranting a case-by-case analysis and pilot testing. Apart from reducing impurities, the flue gas temperature has to be further cooled down to the absorption temperature, which is typically lower than the stack temperature, generally between 30-40°C (but can be as low as 10°C in the case of the CAP). Thus, an additional flue gas cooling unit is generally required, e.g., a direct contact cooler (DCC). This consequently further removes impurities through condensation. Some configurations may combine the cooling step with the wet scrubbing process by designing the latter to reach the required temperature. It should be noted that even with ideal pretreatment, the evaporation of low-boiling-point species from the solvent into the gas is not entirely prevented, making a post-treatment section always necessary to wash the gas before it is released.

Operating conditions

There are significant chemical differences between various solvent systems, and the use of a stable, non-volatile amine solvent can have a substantial impact on reducing the evaporation of low-boiling species. Operating the system under conditions that minimize the formation of low-boiling degradation products is crucial. In practice, this means maintaining moderate temperatures in the stripper, as excessive heat can accelerate amine degradation. High CO₂ concentrations can also promote degradation processes e.g., via formation of cyclic urea or carbamate polymerization, thus the CO₂ loading also may have to be limited during absorption, e.g., by increasing the liquid-to-gas ratio. For both measures there is a tradeoff with process efficiency, high desorption temperatures accelerate the desorption, and high CO₂ concentration are an efficient use of the solvents' capacity. Additionally, regular purging of the solvent loop is required to avoid accumulating degradation products in the solvent, along with a corresponding amine makeup stream.

Post-treatment

As a post-treatment step, a washing section is installed at the gas outlet, with several possible configurations (discussed below). In this wash section, volatile components are absorbed, while water in the gas is also condensed and returned to the solvent loop to help maintain the water balance. This ensures the removal of contaminants from the gas phase, as well as the proper regulation of water content within the system. It should be mentioned that a water wash of at least two steps is effective in reducing gaseous emissions but is not very effective against aerosol emissions. Since one of the primary degradation molecules happens to be NH₃, the emissions of which are regulated, an acid wash step might be necessary.

A variety of wash section designs can be implemented, whereby the simplest design consists of a single water wash stage positioned on top of the absorber within the same column. However, in most

cases, a design with two wash steps is more optimal, as this configuration acts as a two-stage countercurrent contactor [87]. Consequently, the water in the top stage contains a much lower concentration of contaminants, making the equilibrium limit on contaminant removal more favorable. This results in better performance compared to a single-stage system of the same size. Alternatively, the first water wash stage can be followed by an acid wash using diluted sulfuric acid, which is highly effective at capturing amines and ammonia due to its strong affinity for these compounds of acidic solutions. This approach further reduces emissions compared to a double water wash section of the same size. It should be noted that using an acid wash requires a supply of acids, such as diluted sulfuric acid, and generates an additional wastewater stream, which, in most cases can be managed by existing wastewater treatment facilities.

Although water wash units are highly effective in reducing vapor-based emissions, they are ineffective against submicron-sized aerosol-based emissions. Therefore, similar to the pre-treatment section, a system removing very small particles (< 0.01μ m), such as BDU or a fabric filter, can be installed after the washing section to eliminate any remaining aerosols in the outflow. This is especially required when no measures are taken in the pre-treatment section to prevent aerosol nuclei from entering the absorber. Ultimately, the optimal positioning of the units may depend on the level and size of the aerosol emissions into the absorber as well as economic considerations, e.g., if aerosol emissions are high in the flue gas, pre-treatment may be more suitable to prevent degradation of the solvent.

Emission limits for air pollutants are set according to the potential danger they pose to humans and the environment. Minimizing emissions and complying with specific emission limit values requires the appropriate design of the plant, and the cost of the plant may increase significantly due to the required measures for emission mitigation, both in terms of initial investments as well as during operation (CAPEX and OPEX). A significant reduction in operational costs can be achieved through optimized plant operation. Therefore, the optimal design for both the pre-treatment flue gas and post-absorber treatment sections should be determined on a case-by-case basis, as it depends on factors such as the properties of the flue gas, the solvent system used, and the required specifications.

Pilot projects

Several amine-based absorption pilot projects have utilized various combinations of mitigation concepts described above and have measured atmospheric emissions of pollutants of interest including NH₃, amines, carbonyls, nitramines, and nitrosamines. In order to provide an intuition of the practical efficacy of these purification systems, a summary of a set of relevant pilot test results is given. The values are transformed into parts per billion volume (ppbv) and reported in Table 3.2, and the reader is referred to the relevant literature for details on the plants, experimental campaigns, and detailed source data [47,102,103]. These studies also contain measurement results of specific degradation products, e.g., NDMA or acetaldehyde, but for the sake of clarity, these are not reported in the table.

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Pilot study	Compounds	Value ppbv	Protocol
	Ammonia	6300 to 13000	FTIR ^a
	Amines	<1000 to 2200	FTIR ^a
30% MEA flue gas from	Amines	1 to 30	PTR-TOF-MS ^a
CHP plant, two water wash	Amines	1 to 30	LC-MS ^b
sections [102]	Carbonyls	11 to 20	LC-MS ^b
	Nitrosamines	<0.04	PTR-TOF-MS ^a
	Nitrosamines	<0.02	LC-MS ^b
	Ammonia	290 to 5500	FTIR ^a
30% MEA flue gas from	Amines	1500 to 5700	LC-MS ^b
WtE plant, Water wash and	Carbonyls	333 to 523	LC-UV ^b
acid wash [47]	Nitrosamines	<38	GC-NCD ^b
	Nitramines	<1	GC-NCD ^b
P7/AMP flue	Amines	5 to 1800	PTR-TOF-MS ^a
gas from CHP plant, two wa-	Carbonyls	100 to 2000	PTR-TOF-MS ^a
ter wash sections [103]	Nitrosamines	~1	PTR-TOF-MS ^a

Table 3.2: Measurement summary of atmospheric pollutant emissions of amine-based absorption pilot projects, "<" indicates below detection limit, ^a refers to online method, ^b refers to offline method

There are large variabilities in the emissions of ammonia, amines, and carbonyls, within and also between the pilot studies. Differences between the pilot studies are related to the differences in plant design, solvents, operating conditions, and the flue gas composition. There is also variability within pilot studies themselves, which is mainly due to changing experimental conditions (e.g., solvent degradation throughout the campaign, testing the effect of operational parameters, or plant instabilities). Furthermore, the different measurement systems utilized may yield an inconsistent picture, e.g., in pilot study 1, FTIR measurements showed orders of magnitude larger amine emissions relative to PTR-TOF-MS and LC-MS, which was related to the higher detection limit of the former, giving false values. All these differences leave only a small frame for reliable comparisons.

Nevertheless, some conclusions can be drawn from these studies:

 The ammonia emissions range from ppbv to several ppmv, of which the higher measurements are around the emission limit value of the Ordinance on Air Pollution Control (OAPC) of 7 ppmv for WtE and below the limit of 42ppmv for cement plants. This allows for the conclusion that ammonia reduction measures (e.g., in the form of an acid wash section) are necessary. In the pilot studies, FTIR was used to measure ammonia successfully.

- The sum of amine and carbonyl emissions range from ppbv to several ppmv, which is around the limits allowed according to the OAPC for total volatile organic components; therefore, for reported pilot studies, further decreases are required. Furthermore, due to the potential of amines to form nitrosamines in the atmosphere, further decreases could be necessary to avoid undesired nitrosamine concentrations around a plant (see Section 3.1.6). Not all amine concentrations were successfully determined through FTIR, but measurements with PTR-TOF-MS and offline methods filled the gaps.
- Only one (offline) nitrosamine measurement was successful in approximating a quantification, which resulted in around 1 ppbv [47], other (online) measurements were below the detection limit. Current efforts in developing measurement methods focus on offline measurement of selected nitrosamine species. This requires the determination of a sufficiently long sampling period depending on the order of magnitude of the emissions in order to sample detectable concentrations [104,105]. With a higher availability of installations, the development of measurement technologies and measurement capabilities will increase.

In Pilot 2, pollutant concentrations before and after the wash section were measured, revealing significant reductions in emissions. Specifically, ammonia concentrations decreased by a factor of 7, while amine concentrations were reduced by a factor of 4. This demonstrates the effectiveness of the wash section (water and acid wash) in mitigating these particular emissions. Another pilot study [106], which employed only a single water wash, showed a more modest reduction in ammonia emissions, with a decrease by a factor of 2. This comparison suggests that the addition of an acid wash has a substantial impact on reducing ammonia emissions, improving the overall purification efficiency beyond that of a single water wash. A direct comparison of emission reductions for other compounds between these pilots is challenging due to differences in the solvents used in each study, resulting in varying emission compositions. This highlights the need for consistent experimental setups when assessing the effectiveness of different wash configurations across a range of compounds.

It is hypothesized that a substantial fraction of emissions is due to aerosol formation that are generally poorly captured by wash sections (although it is difficult to quantify their exact contribution). To mitigate this issue, alternative or additional measures are needed when integrating the CO_2 capture plant. Studies have investigated the implementation of a BDU prior to the absorber, preventing aerosol nuclei from entering, which has been shown to reduce aerosol exiting the absorber by a factor of 10 [101]. In addition, other pilot studies [107,108] measured the impact of implementing a BDU after the washing section, which demonstrated a 95% reduction in aerosol-related amine emissions. Both studies suggest that the implementation of a BDU (or alternative techniques with the same effect), either before the absorber or after the washing section (the latter being more common), plays a crucial role in decreasing aerosol emissions and improving overall environmental compliance.

3.1.2.2. CO₂ product stream (II)

In the desorption section (stripper), volatile components evaporate into the gas phase alongside the CO_2 . These components mainly consist of water vapor, solvent amines, and, to a lesser extent, degradation products similar to those found in the absorber. It should be mentioned that aerosols are not of concern here, as the mechanism of formation relies on the presence of nuclei from incineration processes [87], which are not present in the stripper. Typically, these components are separated from the CO_2 through condensation, with the resulting condensate – comprising water vapor, solvent amines, and degradation products – being partially returned to the stripper and partially purged (see Section 3.1.5).

However, even after condensation, the gas will still contain small amounts of impurities, particularly the most volatile components from the solvent loop. Depending on the purity specifications required and the impurities present, one or more purification steps may be necessary, which are typically achieved using adsorption or active filtration systems. High-purity CO₂ is essential to ensure the mechanical and operational integrity of the transport system, maintain health and safety standards, and safeguard the reliability and integrity of storage capacity [109].

3.1.2.3. Slurry waste (III)

Most degradation products formed during the process are not volatile and may be divided into two groups. First, there is the formation of heat-stable salts (see Section 3.1.1), and second, there are large low-boiling molecules formed through several thermal and oxidative degradation steps (see Section 3.1.1). Both components negatively affect the properties of the solvent, thereby decreasing CO_2 uptake capacity and kinetics, increasing viscosity. Thus, they have to be removed to preserve proper plant operation [110].

It is suggested to carry this out primarily through thermal reclaimers, as the conventionally applied "Bleed and Feed" strategy has been shown to be ineffective at high degradation rates [89]. Thermal reclaimers recover amine via the addition of a strong base that dissolves the parent amine from the HSS, and thereafter evaporation of volatile compounds, including the parent amines. This leaves behind a pumpable slurry with only the degradation products, while the evaporated amine can be reused in the solvent loop after condensation. The amine slurry, containing low concentrations of nitrosamines and other toxic compounds, is classified as hazardous waste requiring adequate treatment.

The simplest solution is to combust the slurry in a controlled environment, such as a waste incineration plant designed for this type of waste. It is suggested that a WtE or cement plant itself may be utilized to destroy the hazardous slurry by co-combustion, however, the practical evaluation of this method needs further investigation [111]. Other pathways like biological treatments or chemical conversions are proposed in an attempt to valorize this waste flow [112]. Specifically, biological pathways, where

microbes transform the amine waste into biofuels or other useful chemicals, show great potential but are yet to be commercialized. The amount of this slurry waste should be minimized as all amines have to be replenished to keep operation steady, which is costly. Currently, the size of this flow is in the order of kilograms per ton of CO₂ captured, i.e., for a typical capture plant capturing 100kt/a, this would result in a slurry waste flow in the order of 100t/a. Nevertheless, it has been shown that careful selection of the solvent system and appropriate washing steps can bring down the degradation rate by an order of magnitude [113], and research efforts are ongoing in further minimizing this.

3.1.2.4. Wastewater (IV)

The wastewater stream, or effluent, consists typically of two or three parts, respectively, as shown in Figure 3.4, namely:

- IV A. The water from the DCC or pre-scrubber, resulting from the condensation of the flue gas. The flow rate is given by the change in temperature, assuming the flue gas entering the cooler is saturated. The components are typically dust and sodium plus sulfite ions. Although this flow is often already part of a WtE or cement plant, if the decision is made to further reduce the flue gas pollutants operationally when implementing the CO₂ capture process, this will increase the pollutant load in the effluent.
- IV B. (Only in case of acid wash) Wastewater from an acid wash, which will contain volatile degradation products and sulfite ions, and may include toxic components like nitrosamines or nitramines.
- IV C. Wastewater from the condensate, which is utilized to purge the volatile degradation components from the solvent loop (in some plant designs, this purge stems from the water wash section). The condensation essentially works as a purification step to concentrate the volatile degradation components before purging. This waste is a new addition to the total effluent and potentially contains toxic components like nitrosamines or nitramines.

Most of the generated wastewater arises from the condensation of water in the flue gas, and the amount produced can be estimated by calculating the difference between the water content of the flue gas entering the plant and that leaving the plant. However, providing a general statement about the concentrations of specific pollutants is more complex, as it depends on various factors, including the composition of the raw flue gas, the solvent amines used, and the design of the flue gas treatment and post-absorption treatment sections. Still, it can be stated that besides amines itself, a myriad of byproducts will also be present in the wastewater stream.

In many cases (but not always), there are industrial wastewater treatment plants (WWTP) as part of the WtE or cement plants directly discharging into waters, which may be able to treat such wastewater. However, the removal of typical amines and byproducts thereof requires total nitrogen removal and organics degradation simultaneously, which is known to be a challenge for industrial wastewater treatment facilities [114]. But alternative customized treatment options are possible and need to be thoroughly evaluated. In other cases, WtE or cement plants discharge their pretreated industrial wastewater into the public sewer system, which is finally treated in central WWTPs together with municipal wastewater. Central WWTPs are not designed to treat amines and byproducts emitted from industrial processes. Therefore, the industrial wastewater must be pretreated before being discharged into the public sewer system.

Furthermore, selected central WWTPs are being upgraded with micropollutant removal processes such as activated carbon treatment or ozonation [116]. Ozonation is known to generate harmful byproducts including nitrosamines, particularly in cases with a relevant industrial pollutant load such as amines, i.e., flows B and C. Biological post-treatment steps such as sand filtration, granular activated carbon, or fluidized beds is obligatory after an ozonation to partly eliminate such harmful byproducts. Among them, sand filtration has shown promising results in significantly reducing nitrosamine concentrations, while further investigations are recommended to evaluate the effectiveness of other processes [115]. In any case, the wastewater's treatability with ozone must be thoroughly assessed on a case-by-case basis to validate if the facilities in place are sufficient to handle the wastewater and the pollution load.

3.1.3. Atmospheric chemistry and dispersion

When the flue gas is eventually emitted from the stack into the atmosphere, the components are dispersed through wind and diffusion, while at the same time, chemical reactions occur, causing species to disappear and new ones to be generated, and dilution occurs. This process has a significant influence on the actual exposure relative to the concentration at which they are emitted, and thus on the impact of the emissions on human health and the environment. Understanding the atmospheric effects of the components involved is important as it provides the relation between the emission limits that should be imposed in order not to cause the exposure risks on the ground (see Section 3.1.1).

In particular, due to the carcinogenic nature of nitrosamines, exposure must be minimized as a precaution. Thus, the atmospheric chemistry that causes the formation of nitrosamines and nitramines from primary, secondary and tertiary amines is relevant. In the presence of OH radicals and NO_x, which are present around a flue gas stack, amines are partially converted into nitrosamines and nitramines, while daylight breaks down nitrosamines. This chemistry is illustrated in Figure 3.5 for the secondary amine PZ. Thus, when amines are emitted from a stack into the atmosphere, one has to understand which fraction ends up as nitrosamines or nitramines in the environment; similarly, one has to understand how many of the nitrosamines emitted are broken down in the atmosphere. This may be done using reactive-dispersive modeling or through simpler methods like applying a dilution factor and assuming a conversion rate. Results from reactive-dispersive modeling for a demonstration capture plant in Norway, for which the emissions at the stack were assumed, showed that the exposure around the site is well below advised exposure limits (see 3.1.1). However, the actual results obtained with this gaussian model are not directly applicable to Switzerland due to the vastly different topography and weather conditions requiring a Lagrangian model. This leads to the conclusion that for every installation, reactive-dispersion modeling has to be carried out to assess the exposure situation at particularly vulnerable sites in the vicinity of installations (e.g., settlements, schools, and offices, drinking-water catchment areas). As long as reliable emission data from projects are missing, this has to occur on the basis of emission projections by the plant engineers.



Figure 3.5: The atmospheric chemistry of amines, nitrosamines, and nitramines, illustrated for secondary amine PZ [117].

3.2. Other absorption technologies

Inorganic salt solutions (specifically HPC) and aqueous ammonia are appealing alternatives to amines due to the absence of amine degradation issues. However, certain environmental challenges may still arise and should be carefully considered.

3.2.1. Inorganic salt solutions

Although inorganic salt solutions, such as pure potassium carbonate in the HPC process, are nonvolatile and do not cause issues regarding flue gas emissions, the kinetics are slow. As mentioned earlier, catalysts called promoters can be used to enhance the reaction kinetics. These promoters include the typical compounds used for absorption, e.g., amines or amino acids, but also several inorganic compounds, e.g., boric acid and arsenous acid [36]. Again, precautionary measures are required (on a much smaller scale) as described in Section 3.1.2. Similar to ammonia-based absorption, impurities such as NO_x and SO_x will enter the system and have to be purged from time to time. Thus, a wastewater stream containing potassium, nitrate, and sulfate will arise, which must be managed by a water treatment system.

3.2.2. Aqueous ammonia

Due to the high vapor pressure of ammonia, the primary concern with aqueous ammonia systems is ammonia evaporation and slippage into the atmosphere (similar to flow I in amine-based absorption). To address this, a variety of plant designs have been developed, as outlined in Section 2.1.2 [38]. Some designs incorporate complex ammonia (NH₃) recovery systems, which consist essentially of an entire dedicated absorption unit, recycling all evaporated ammonia – though this comes with a significant energy penalty. Other designs feature less efficient recovery systems but employ an acid wash before the flue gas is released to capture remaining evaporated NH₃, resulting in a wastewater stream containing ammonium sulfate (analogous to flow IV B in amine-based capture).

Additionally, while impurities such as NO_x and SO_x from the raw flue gas do not cause solvent degradation, they must be periodically purged from the system to prevent accumulation, which could lead to undesired precipitation or other negative impacts on process performance (similar to flow IV C in amine-based capture). In summary, the effluent produced from ammonia-based absorption will contain a mixture of ammonia, nitrate, and sulfate, with concentrations depending on the specific plant design, all of which must be managed by a wastewater treatment system. An alternative to the plant designs discussed is the addition of inhibitors to prevent ammonia evaporation. Suggested inhibitors include specific amines, such as AMP (2-amino-2-methyl-1-propanol) and other amino alcohols [37]. While the introduction of these compounds into the solvent can help reduce ammonia evaporation, it also brings environmental concerns associated with their use as described in Section 3.1, though to a lesser extent due to their lower concentrations. Thus, precautionary measures must be taken when using amines as additives, as outlined in Section 3.1.2, albeit on a smaller scale.

3.3. Adsorption and membranes

Both adsorption and membrane processes are gas-solid operations, meaning no liquids are circulated. As a result, the nature of the waste streams changes, with no slurry or wastewater expected from the separation processes themselves. However, there are still environmental concerns associated with these technologies that warrant discussion.

3.3.1. Adsorption

On the one hand, adsorbents utilizing physical interactions, e.g., silicas, zeolites, polymeric membranes, etc., have a high chemical stability. This stability of the solid phases ensures that no emissions of toxic compounds, as with amine or ammonia absorption processes. However, these materials require the gas to be dried and will thus create an effluent containing dissolved NO_x and SO_x and other impurities from the flue gas. As all water has to be removed, the effluent volume can easily be determined from the water content in the raw flue gas. On the other hand, amine-functionalized adsorbents (see Section 2.2.3) are known to be chemically unstable [68–70], which is an active topic of research as it is associated with functionality loss. Severe decreases in functionality are reported due to reactivity with NO_x or SO_x, however, it is at this moment not clear what the exact reaction products are, and thus unknown if these are volatile and/or toxic. If these reaction products are indeed toxic and volatile, measures similar to those for amine-based absorption, i.e., a washing section and aerosol removal, would be required before the flue gas is emitted into the atmosphere. Hence, when aminefunctionalized adsorbents are used, it is prudent to use characterization methods that can accurately identify potential toxic compounds in the gases released into the atmosphere.

3.3.2. Membranes

Membranes use materials similar to those in adsorption processes, and the same environmental principles outlined in Section 3.3.1 should be applied. For membranes that rely on physical interactions, no emissions of toxic compounds are expected. However, monitoring and measurement systems must be implemented to detect any potential toxic compounds in the gas streams for amine-functionalized membranes.

3.4. Oxyfuel and cryogenics

The main addition in oxyfuel operation is the pre-combustion ASU, which is generally cryogenic distillation and requires a cooling technology; cryogenics requires similar technology. This type of cooling technology is well established, with predictable environmental effects unrelated to those described in Sections 3.1 to 3.3, and is therefore beyond the scope of this report.

3.5. The regulatory landscape

In relation to emissions into the environment, the two key pathways, stack emissions (airborne pollutants) and wastewater discharges are governed by regulatory frameworks aimed at mitigating environmental and health impacts. This section provides an overview of the current regulatory landscape for each, including a discussion of potential gaps.

3.5.1. Atmospheric emissions

Emissions of airborne pollutants must be limited based on Article 11 Paragraphs 1 and 2 of the Environmental Protection Act as a precautionary measure and through measures at the source, to the extent that this is technically and operationally possible and economically viable. If excessive emissions are expected from the installation, the emission limits must be tightened. In Switzerland, the OAPC sets emission limit values (ELV) for industrial installations e.g., WtE plants and cement works. The emitting installation and the PCC unit are to be qualified as a single plant due to the functional dependency of the latter on the combustion plant. ELV for pollutants related to absorption processes, e.g., ammonia and various volatile compounds, are compiled in Table 3.3. Emission limit values refer to emissions from the stack into the atmosphere and not to exposure, i.e., the concentration on the ground around an installation (see Section 3.1.3 for the relation between those). For substances for which no ELV exists, emissions shall be regulated through Article 4 of the OAPC: "Emissions for which no limit is specified in this Ordinance or for which a particular limit is declared not to apply shall be limited preventively by the authorities as far as is technically and operationally feasible and economically acceptable". This implies that emission limits will be imposed through individual permits for each installation.

Pollutant	Cement [mg/m ³] Annex 2 No 1	WtE [mg/m ³] Annex 2 No 7	General preventive emission limit*	
NO ₂	200	80	Annex 1 No 6	
Ammonia and ammoniums	30	5	Annex 1 No 6	
SO ₂	400	50	Annex 1 No 6	
Gaseous organic substances	50	20	Annex 1 No 7	
Dust	10	10	Annex 1 No 4	
Mercury	0.05	0.05	Annex 1 No 5	
Cadmium	0.05	0.05	Annex 1 No 8	
Lead and Zinc (total)	1	1	Annex 1 No 5	
Dioxins and furans (sum)	0.1×10 ⁻⁶	0.1×10 ⁻⁶	-	
Hydrogen chloride		20	Annex 1 No 6	
Hydrogen fluoride		2	Annex 1 No 6	
Carbon monoxide		50	-	
Carcinogens ELV for specific compounds in Annex 1 No 8				

Table 3.3: The emissions limit values from the Ordinance on Air Pollution Control (OAPC) for the classes and compounds relevant for carbon capture installation. *General preventive emission limits refer to installation types not specifically listed in Annex 2 OAPC.

In the following, each of the potentially affected compounds is discussed in relation to the ELV; it is highlighted if extra regulations are required.

Ammonia

Ammonia is part of the class "ammonia and ammonium compounds", which is regulated through OAPC Annex 2 No 1 and Annex 2 No 7 for cement plants and WtE plants, respectively. The emission limits are clearly defined.

Amines and carbonyls

Amines and carbonyls are part of the class "gaseous organic substances" regulated through the OAPC Annex 2 No 1 and Annex 2 No 7 for cement plants and WtE plants, respectively. Furthermore, a set of specific amines and carbonyls are regulated through OAPC Annex 1 No 7. To prevent exposure to amines and carbonyls, the ELVs are defined, and no changes or specific adaptations are required. However, due to amines serving as the precursor for the transformation into nitrosamines and nitramines in the atmosphere, stricter limit values may be required for amines. In a first step, this is likely to be regulated by the cantonal authorities through OAPC Article 4 until sufficient scientific evidence on the emission behavior of different plants is gathered to set ELV (note that this requires knowledge of the atmospheric chemistry and dispersion effects around a capture plant).

Nitrosamines and Nitramines

Nitrosamines and nitramines are known carcinogens at very low concentrations. For carcinogenic molecules listed under OAPC Annex 1 No 8, ELV are set. However, nitrosamines and nitramines are not part of this list yet. These ELV do not apply to unlisted carcinogenic molecules, emissions of which must be limited preventively according to OAPC Article 4, i.e., ELV should be set as strict as technically and operationally feasible and economically acceptable. The exposure of humans and of the environment has to be restricted by limiting the emissions at the stack. In a first step, this is likely to be regulated by the cantonal authorities as well through OAPC Article 4 until sufficient scientific evidence is gathered to set ELV for the installations concerned. To set appropriate emission limits requires knowledge of the emission behavior of the plant as well as atmospheric chemistry and dispersion effects around a capture plant.

3.5.2. Wastewater disposal

To protect waters and the public sewer system, respectively, against harmful effects, discharged wastewater must be treated on the basis of Articles 6 and 7 of the Waters Protection Ordinance (WPO). The requirements for industrial wastewater for discharge are set in Switzerland in Annex 3.2 in the WPO. In principle, the necessary measures according to the state of the art must be taken in

the production process and in the treatment of wastewater in order to discharge as few substances as technically and operationally possible and economically viable (Annex 3.2 Point 1 No 2). Annex 3.2 Point 2 sets requirements for certain pollutants but many of the species expected in wastewater from CO_2 capture (e.g., nitrosamine or amines) are not listed, hence the following applies according to Annex 3.2 Point 1 No 6:

"If Nos 2 and 3 contain no requirements for specific potential water pollutants, the authorities shall specify the necessary requirements based on the state of the art in the authorization. In so doing they shall take account of international or national standards, directives published by the FOEN or standards drawn up by the industrial sector concerned in collaboration with the FOEN."

In addition, it is mandatory to check in a second step whether the requirements concerning water quality of surface and underground waters set in Annex 2 WPO are fulfilled. The water quality of surface waters must fulfill the requirements of the drinking water regulation after "appropriate" treatment processes for drinking waters, while groundwaters used for drinking water production must do so after "simple" treatment processes (Annex 2 Point 11 No 1 letter c and Annex 2 Point 22 No 1 WPO). In addition, water pollutants must not have a negative impact on sensitive aquatic organisms (Annex 2 Point 11 No 1 letter f WPO). This implies that the requirements for wastewater will be imposed through individual permits of the cantonal authorities for each installation based on the state of the art. The following points must be evaluated during the permitting process:

- Amount of wastewater per time
- Concentrations and loads of all water pollutants in the specific wastewater, including amines, N-nitrosamines and other combustion products
- Treatment processes to remove these water pollutants from the industrial wastewater based on the state of the art before discharge to waters or the public sewer system
- In the case of discharge into the public sewer system: check whether the central WWTP is equipped with ozonation and whether harmful by-products are formed as a result.
- Evaluation of the effects of the remaining emitted water pollutants even if treatment processes based on the state of the art are applied – in terms of drinking water quality and ecotoxicity. In case drinking water and ecotoxicological criteria are not fulfilled, the discharge limits must be tightened accordingly. It should also be noted that lake water treatment plants also use ozonation to produce drinking water from lake water.
- Definition of a monitoring and intervention concept

Practical experience concerning these points does not exist yet and cannot be evaluated based on theoretical considerations. This is why the permitting process must include pilot tests with measurements to evaluate the real concentrations and loads of water pollutants.

4. Technology performance assessment

This chapter provides an overview of the performance of the processes in terms of cost, economies of scale, capture efficiency, and energy utilization; in the appendix, a table can be found with the values extracted from the literature that were used in the analysis.

4.1. Cost assessment

4.1.1. Absorption, adsorption, and membranes

Cost assessments should be interpreted with caution as their outcome is highly reliant on assumptions like energy prices, etc. Nevertheless, the statistical presentation of the outcome of such analyses can provide an intuition of ranges of price levels according to the scientific literature. Figure 4.1 gives the



Figure 4.1: Cost assessment in CHF per ton CO₂ captured according to literature, the data and references can be found in the appendix

ranges of price levels that were found in literature studies, where the bar indicates the standard deviation, and the point gives the mean. The selected data points are for capture efficiencies of at least 90%, and for flue gas compositions and flowrates in the same order of magnitude as is typical for WtE and cement plants.

Most of the available literature discusses absorption, adsorption, and membrane technologies, among which absorption utilizing PZ as solvent has the lowest cost estimation. This advantage is partly due to the TRL, e.g., due to the improvements of solvents, but there are additional factors to consider. First of all, moisture presents a challenge for the membranes and sorbents considered, necessitating a costly drying step. Additionally, the economies of scale differ between absorption and other technologies, as illustrated in Figure 4.2(a), showing data extracted from an earlier analysis [56]. The complexity of typical process schemes of absorption-based separation introduces high capital expenditure and makes them less attractive for small-scale applications. However, their economies of scale are better than those of the other technologies, making absorption favorable for larger-scale applications like cement and most WtE installations. On the other hand, adsorption-based and membrane-based processes are characterized by relatively simple process schemes (e.g., no flowing liquid phase, fewer auxiliary streams, and fewer pieces of equipment), making them cost-competitive at small scales. Also, components like adsorption columns and membrane modules are generally limited in their maximum size and thus benefit less from economies of scale [56,118]. It should be mentioned that Figure 4.2(a) represents the economies of scale for a specific case, i.e., capture efficiency, flue gas conditions, etc. Although it is commonly understood that there exists an intersection point in such a plot, the specific capacity at which this point lies differs per case.



Figure 4.2: Cost assessment in CHF per ton CO₂ captured according to literature, the data and references can be found in the appendix

All three technologies have the ability to achieve high capture efficiencies, i.e., more than 90%, as shown in Figure 4.2(b), which shows costs as a function of the capture efficiency [56]. For absorption, the costs per unit CO_2 captured decrease as a function of the capture efficiency. This is due to the fact that increased capture efficiency is achieved by an approximately linear increase in energy expenditure, without increasing plant size and thus diluting the capital expenditure per ton of CO_2 captured. For TSA adsorption, the costs also decrease up to a certain point (96% in this case) for similar reasons as for absorption. Moreover, costs are penalized due to a large increase in regeneration times required for further increasing the capture efficiency, which decreases the plant's productivity. It should be mentioned that with VPSA, it is more challenging to achieve high capture efficiencies, and the cost optimum lies at lower values. Membranes have an optimum in a wide range of capture efficiencies (between 50 to 80 percent in this case), after which the cost increases [56]. This increase is because high capture efficiencies require high pressures to push all the CO_2 through the membranes, for which a high energy penalty is paid. Although this analysis was performed for a specific case, similar behavior is expected in other cases.

4.1.2. Oxyfuel and cryogenics

The limited studies available for oxyfuel cement production (none are available for WtE) exhibit costs comparable to the best-performing absorption technologies, although these data should be interpreted with care as this technology has yet to prove itself at scale. Also, oxyfuel will be less favorable for WtE than for cement, as more costly oxygen has to be generated per ton of captured CO₂: only one third of the CO₂ generated in cement manufacturing comes from fuel oxidation (the rest coming from calcination of limestone), whereas in WtE all CO₂ comes from fuel oxidation and thus requires significantly more oxygen generation per ton of CO₂ captured.

The results published for a cryogenic process utilizing an external cooling loop are promising [82]. However, there are few details available on the process and underlying calculations. An independent economic analysis of this process has yet to be found in scientific journals, and the reported results should be interpreted with significant care.

4.2. Energy requirements

As energy is one of the main cost drivers, research focuses on decreasing the regeneration energy required for CO₂ capture processes, which differ in nature. Figure 4.3 shows the median values of required heat and electricity consumption of the relevant processes from literature (with the bar indicating standard deviation). Here, too, the energy consumption values for cryogenics are very promising, but as with the economic findings, these should be interpreted with care and have thus been highlighted by an open-circle marker in the figure.

It shows that amine-based absorption processes and temperature-swing adsorption processes both require significant amounts of high-grade heat to regenerate the solvent or the adsorbent, which is generally delivered in the form of steam. This is a major cost driver for these processes, and if the heat, i.e., steam, is not available, these options can become less attractive as a separate investment for steam generation would be required. It is clear that newer solvents with lower energy demand, like PZ, are more favorable as they result in better process economics. In many cases, part of the heat required for PCC can be recovered, which can reduce the effective heat demand of the capture process. This is particularly advantageous in facilities with existing low-temperature heat requirements, such as WtE plants that often provide heat to local district heating networks [119]. Therefore, it is important to consider not only the specific heat demand of a PCC process but also its potential for heat recovery to minimize overall energy consumption.

All other processes are electrically driven, with membranes showing the largest electricity consumption due to the large pressures required to push the large amounts of CO₂ through the membranes. Analogous to the other processes, there are continued efforts to improve the permeability of membranes to decrease energy demand, while not decreasing their selectivity (see Section 2.3). When excluding cryogenics due to the limited information, oxyfuel shows the lowest electricity consumption among the electrically driven processes; however, this is specific for application to a cement plant. For WtE plants it is expected that the energy requirement, which mostly comes from oxygen generation, is about 3 times higher (see Section 4.1).



Figure 4.3: Heat and power requirements of different PCC technologies in GJ per ton CO₂ captured according to literature

4.3. Hybrid processes

So far, CO₂ capture processes have focused on single separation technologies (absorption, adsorption, membranes, cryogenics). However, to overcome the challenges of standalone CO₂ capture technologies, hybrid processes may be a good alternative. They usually consist of two or more conventional technologies in series, but other types of integration, e.g., parallel processes and recycling loops, are also possible. A challenge for any hybrid process is the additional equipment required due to the complexity of these systems, which in general leads to high capital expenditure. Discussing each technology here is beyond the scope of this work; however, the authors feel it is worth mentioning two of them due to their commercial availability or presence in literature.

4.3.1. Adsorption – cryogenics

This concept first utilizes VPSA, to obtain a gas with increased CO₂ content (40-80%), and then utilizes a second cryogenic step to further purify and simultaneously liquify the CO₂. It overcomes the weakness of VPSA (expensive at high purity/recovery), while utilizing the strength of cryogenics (works efficiently at high CO₂ concentrations). It is said to optimize energy expenditure (electricity only) and is claimed to be superior to standalone adsorption or cryogenics [120]; detailed technoeconomic data has not been found in the scientific literature.

4.3.2. Membrane – Absorption

This concept is also referred to as a membrane contactor, or membrane gas absorption, and merges membrane technology with absorption technology. The flue gas stream and a liquid absorbent usually flow counter-currently on both sides of a porous hydrophobic membrane, i.e., the absorber is integrated into the retentate side of the membrane (see Figure 2.3 and Figure 2.5 for an illustration of a normal absorption process and a normal membrane, respectively). This provides essentially two advantages:

- 1. As the absorbent continuously sweeps away the CO₂ at the retentate side, it means no pressure at the retentate side is required for the driving force, saving electrical energy.
- 2. The membrane (hollow fibers usually) provides a larger contact surface than seen in conventional packed columns, which makes the process more compact.

Two economic assessments were performed utilizing this concept outside of WtE or cement [121,122], which resulted in a similar or higher costs compared to traditional processes, in this case absorption or adsorption. It should be mentioned that this concept is not yet at a TRL of conventional separation processes, and improvements are likely to be made in the future [123].

5. Discussion and conclusions

Carbon capture will play a crucial role in achieving net-zero emissions in Switzerland, with numerous technologies already being developed to support this goal. Based on their TRL and suitability for WtE and cement plants, the five technologies evaluated are absorption, adsorption, membranes, cryogenics, and oxyfuel combustion. Each was assessed in terms of general advantages and disadvantages, recent developments, environmental impacts, energy requirements, and cost-effectiveness; a summary of this analysis is provided in Table 5.1. Among the five technologies analyzed, amine-based absorption is the most mature (TRL 8-9) and offers one of the most favorable cost estimates, particularly when using the latest proprietary amines. As a result, it is highly likely to be implemented, especially for larger-scale PCC operations e.g., in the WtE sector. However, it presents a set of environmental concerns that must be addressed. Over time, amines degrade, forming volatile toxic compounds such as the amines themselves, ammonia, carbonyls, and nitrosamines and nitramines – well-known carcinogens. These volatile compounds can be released into the atmosphere through the flue gas, either by evaporation or by condensation on aerosols. Mitigating these emissions is crucial and can be achieved through the following measures:

- Thorough treatment of the flue gas to remove NO_x and SO_x, using existing technologies, is
 essential as both compounds accelerate degradation processes in the absorber, with NO_x
 contributing to nitrosamine formation. These steps are already installed in existing WtE and
 cement facilities to comply with environmental regulations.
- Additionally, preventing the entry of aerosol-forming nuclei over the entire size distribution into the absorber – e.g., by using a BDU – can significantly reduce emissions associated with aerosols. The BDU can be implemented either before or after the absorber; the optimal position will depend on the plant-specific emission characteristics.
- Operating the plant with a stable, non-volatile solvent, maintaining moderate temperatures and CO₂ loading, and adequate purging of the solvent loop can all contribute to a significant reduction in emissions.
- Implementing a post-absorption gas treatment process with one or more wash sections, including an acid wash, helps remove amines, ammonia, carbonyls, and less volatile nitrosamines and nitramines. Additionally, incorporating an aerosol removal unit to capture any

remaining aerosols exiting the absorber is highly recommended, if not unavoidable, especially when no extra precautions are taken in the pre-treatment to capture aerosol nuclei.

Since different amines produce varying emission profiles (arising from the diverse chemical behaviors of each amine), measuring and regulating these emissions becomes challenging. Currently, ELV for nitrosamines and nitramines are not listed in the OAPC, as regulating their emissions was of no concern in the past. Until a generally applicable level of BAT can be established on a representative set of installations, it is likely that emissions, particularly for the first installations, will be regulated on a case-by-case basis through permits from the authorities. Activities to establish guideline documents are ongoing.

Furthermore, amine absorption generates several wastewater streams that contain the amines and their degradation products, potentially including nitrosamines. This poses a significant challenge for industrial and central wastewater treatment systems, as it requires the removal of total nitrogen and the breakdown of organic compounds. If ozonation is used at central WWTPs for micropollutant removal, it must be considered that the treatment may inadvertently enhance nitrosamine formation due to the amine-containing wastewater, thus requiring careful assessment on whether existing wastewater treatment facilities can manage the additional pollutant load. If necessary, the industrial wastewater must undergo separate pretreatment using alternative technologies.

Ammonia absorption offers the advantage of being resistant to the degradation processes commonly seen in amine absorption. However, its high vapor pressure leads to evaporation and the potential release of ammonia into the atmosphere, which is a major concern. One approach to mitigate ammonia emissions is to implement an ammonia recovery unit downstream of the absorber (with various designs available), while another approach involves operating at very low temperatures. Both options, however, significantly increase the costs of the CO₂ capture process. It remains uncertain whether this technology will become widely viable.

Absorption based on potassium carbonate in the HPC process is an attractive alternative to amines as it has reasonable cost estimates and, moreover, no environmental concerns associated with it. When a pure potassium carbonate solution is utilized, the solvent is non-toxic and non-volatile, meaning there are no issues with emissions into the atmosphere. As the process relies on a pressure swing to carry out the separation, it is mainly driven by electricity and exhibits significantly lower heat duties than amine-based processes. A downside is the resulting high electricity duty as well as low kinetics that remain a challenge despite the elevated operating temperatures of HPC. It should be noted that non-volatile catalysts have been developed to improve the slow kinetics of the potassium carbonate solution. However, these catalysts often introduce additional challenges, e.g., corrosion, which may be considered acceptable depending on the trade-offs involved. Both adsorption and membrane technologies using non-functionalized materials have less favorable cost and energy profiles compared to other carbon capture technologies at the scale of WtE and cement plants. Currently, their potential is more promising for smaller-scale operations, such as biowaste treatment (e.g., aerobic and anaerobic digestion). A key advantage of these materials is their high chemical stability, which ensures no emissions of toxic compounds, unlike amine or ammonia absorption processes. The use of amine-functionalized materials improves CO₂ capacity and reduces energy requirements, potentially lowering costs significantly. However, these materials are still at a low TRL. Their chemical instability leads to degradation, which diminishes their effectiveness too quickly to be viable for industrial applications. Furthermore, if the degradation products are toxic and volatile, similar to amine-based absorption, mitigation measures such as a washing section would be required after the absorber unit to treat the flue gas before it is released into the atmosphere.

Oxyfuel combustion offers highly favorable energy and cost characteristics for cement production, although its TRL is lower than absorption processes. For WtE plants, less is known, but it is expected to be less advantageous due to the need for approximately three times more oxygen compared to cement production, making the process both costly and energy-intensive. Oxyfuel operation does not introduce any significant environmental concerns; in fact, it could even reduce current pollutant levels in WtE or cement plants. This is because the absence of nitrogen during combustion leads to a reduction in thermal NO_x formation. However, the major drawback of oxyfuel technology is that it cannot be easily retrofitted to existing plants, making it suitable only for those willing to undergo extensive adaptations or newly constructed facilities. This limitation constrains its potential for immediate large-scale implementation.

Cryogenic technologies encompass several concepts, some of which are theorized to offer high performance. However, these technologies are currently at a low TRL, and detailed information about them remains limited. Their performance has yet to be validated by the scientific community, and they are not expected to be implemented at large scale in the near future, particularly in sectors like WtE or cement plants.

All in all, amine and HPC absorption are expected to play a crucial, if not the most significant role in the near- and medium-term future of carbon capture in Switzerland. However, clear empirical data is still lacking, making it difficult to accurately predict the industry's evolution and how to best tackle regulatory and environmental challenges. Therefore, it is essential to execute demonstration or even commercial projects as soon as possible (within safe regulatory constraints) to gather the necessary insights and accelerate the development of the carbon capture industry. This will be key to bringing the industry closer to achieving net-zero emissions in line with Switzerland's strategy.

Technology	Advantages	Disadvantages	Notes
Absorption			
Amines	 TRL 8-9 Good cost assessment and energy requirements, especially for large scale applications 	 Emissions of amines and degradation products into the air are of major concern A variety of waste streams containing amines, N-nitrosa- mines and other combustion products High steam require- ments 	 Emissions mitigation by two wash sec- tions, of which proba- bly one acidic Crucial to capture aerosols (< 0.01 µm) with filtration system e.g., BDU, and via operational measures
HPC	 TRL 7-8 Little environmental concern Reasonable cost and energy assessment 	 Large columns required due to low kinetics High electricity requirements 	
Ammonia	TRL 6-7No solvent degradation	Ammonia emissions to the air are of major concern	 Mitigation requires complex designs in- creasing cost and en- ergy requirements
Adsorption and me	embranes		
Non- functionalized	TRL 6-7Little environmental concerns	 Poor performance at large scale Requires dry gas	
Amine functionalized	 High theoretical per- formance relative to non-functionalized 	 Low TRL Amines degrade in- ducing functionality loss and environmen- tal concerns 	
Oxyfuel	 TRL 7-8 for cement Good cost assessment and energy demand No environmental concerns 	 No retrofitting TRL for WtE is low Higher capital expenditure 	
Cryogenics	 High theoretical per- formance 	Low I RL, little is known	

Table 5.1. Tabular summary of the analysis performed	1: Tabular summary of the analysis performed	1
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Figure 6.1: Schematic of a cement plant with oxyfuel combustion, with optional flue gas recycle [83]

Technology	CO ₂ vol% in flue gas	Capture rate [kt/day]	Capture efficiency [-]	Costs [CHF/t]	Heat duty [GJ/t]	Electricity duty [GJ/t]	Reference
Absorption (PZ)	0.12	0.5	0.9	33	3.75	0.35	S.E. Zanco, et al. [56]
Adsorption (TSA)	0.12	0.5	0.9	75	5.7	1.1	S.E. Zanco, et al. [56]
Membrane	0.12	0.5	0.9	74	0	2.3	S.E. Zanco, et al. [56]
Absorption (PZ)	0.12	0.5	0.9	37	3.0	0.35	J.F. Pérez-Calvo, et al. [51]
Absorption (PZ)	0.2	1.1	0.9	32	2.6	0.3	J.F. Pérez-Calvo, et al. [51]
Absorption (MEA)	0.2	2.6	0.9	57	5.49	1.58	S. O. Gardarsdottir, et al. [124]
Membrane	0.2	2.6	0.9	72	0	3.22	S. O. Gardarsdottir, et al. [124]
Oxyfuel	0.2	2.6	0.9	42	0	1.3	S. O. Gardarsdottir, et al. [124]
Absorption (PZ)	0.23	4.6	0.9	22	2.57	0.21	C. Tsay, et.al. [125]
Absorption (PZ)	0.13	2.9	0.9	23	2.96	0.19	C. Tsay, et.al. [125]
Absorption (MEA)	0.12	3.8	0.99	50	-	-	M.F. Hasan, et al. [118]
Membrane	0.12	3.8	0.95	95	-	-	M.F. Hasan, et al. [118]
Adsorption (PSA)	0.12	3.8	0.95	70	-	-	M.F. Hasan, et al. [126]
Adsorption (TSA)	0.12	3.8	0.95	58	-	-	M.F. Hasan, et al. [126]
Absorption (MEA)	0.2	3.8	0.99	60	-	-	M.F. Hasan, et al. [118]
Membrane	0.2	3.8	0.95	70	-	-	M.F. Hasan, et al. [118]
Adsorption (TSA)	0.2	3.8	0.95	49	-	-	M.F. Hasan, et al. [126]
Adsorption (PSA)	0.2	3.8	0.95	40	-	-	M.F. Hasan, et al. [126]
Absorption (MEA)	0.2	2.5	0.9	65	2.0	0.236	S. Roussanaly, et al. [127]
Adsorption (PSA)	0.2	3.8	0.9	100	0	1.96	D. Danaci, et al. [128]
Adsorption (PSA)	0.12	5.9	0.9	150	0	2.4	D. Danaci, et al. [128]
Cryogenics	0.15	10.0	0.9	27	0	0.9	C. Hoeger, et al. [82]
Absorption (HPC)	0.12	1.7	0.9	60	0	1.9	V. Becattini, et al. [129]
Oxyfuel	-	2	0.9	51	0	1.93	C.C. Cormos [130]

Table 6.1: Summary of performance of different post-combustion capture technologies

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