



# Biological treatment of effluents generated by amine based CO<sub>2</sub>-capture plants

## 生物处理由胺二氧化碳捕获设备所产生的污水

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**Abstract** - Carbon capture and storage (CCS) is a currently developed technology to fight climate change by reducing greenhouse gas emissions from large point sources. There are various capturing principles, whereas to date most of the pilot plants are based on amine absorption. One commonly used primary amine is monoethanolamine (MEA).

During the process of carbon capture, the solvent is subject to various degradation mechanisms due to oxidation, thermal strain, and unwanted side reactions within the system. After reclaiming the usable solvent for recycling, these degradation products accumulate as waste and need to be treated accordingly. Depending on the solvent, different degradation products may be found in this so called reclaimer waste, with ammonia as a dominant end product. Volatile products may also be emitted through the exhaust gas. Estimates from a full-scale amine-based capture plant predicts approximately 0.2 ppm amine and 20 ppm ammonia in the emissions. For a full-scale capture plant removing 1 million tons CO<sub>2</sub> annually, these concentrations implicate emissions of significant environmental impact.

Effluents from those various sources within the capture plant can be treated biologically to obtain nitrogen removal as well as general detoxification. Our studies have shown that MEA, as well as MEA-based reclaimer waste, can be treated with biological nitrogen removal, which is a well-established method within the field of wastewater treatment. Most important, by applying a recycled pre-denitrification reactor configuration, we have shown that the amine and its organic degradation products will serve efficiently as the carbon source needed for the denitrification step. Future development has to take these findings into consideration.

**Keywords** – Biodegradation; Carbon capture and storage; Monoethanolamine; Nitrification

## I. INTRODUCTION

Carbon capture and storage (CCS) has received much attention in the recent years. It is thought that with CCS, the global CO<sub>2</sub> emission can be reduced until society is technologically as well as morally ready to shift from fossil fuel to alternative energy sources. In fact, the public acceptance of CCS depends on a variety of factors, such as the type of information, religious faith and others [1, 2]. However, to date many knowledge gaps of the technological side need to be filled before CCS can be employed at a large scale.

CCS relies on various capture mechanisms, whereas amine based post combustion CO<sub>2</sub>-capture has been tested on more than 25 pilot plants, approaching full scale application on coal-fired plants [3]. One reason why carbon capturing from large point sources is not yet commercially viable is that such a large scale application of solvent has to carefully consider essential environmental aspects such as solvent emissions or spillage, as well as waste handling [4-9]. It is not only the solvent itself, but also various degradation products that have to be included in the assessment. The solvents used in the CCS process need to meet many criteria. For example, the solvent needs to have good thermodynamic and mass transfer properties and be stable at process conditions, while at the same time being easily degradable in the environment [10]. Monoethanolamine (MEA) is an example of a well-studied alkanolamine, as it has been applied for decades in the gas sweetening industry and also found application in CCS [11].

## II. SOURCES OF WASTE IN CCS

During the process of carbon capture, the solvent reacts with components of the flue gas. In general, the solvent is also

subject to oxidative as well as thermal degradation. In flue gas coming from a fossil fuel-fired boiler there are CO<sub>2</sub>, O<sub>2</sub>, CO, SO<sub>x</sub>, NO<sub>x</sub>, fly ash, and other impurities, which make it very complex to predict all side reactions [12]. Therefore, waste effluents of CCS may include compounds in the liquid as well as in the gas phase. During CCS operation, a slip stream from the stripper column is taken and the degraded solution containing high molecular weight compounds and heat stable salts is separated via distillation from the useful amine [13], see Fig. 1. This so called 'reclaimer waste' contains mainly amine, ammonia, heat stable salts and other degradation products. The actual composition will depend on the type of solvent, process conditions, and flue gas quality. According to recent literature the generated amount of this type of waste ranges from 1.17kg/ton CO<sub>2</sub> to 3.94kg/ton CO<sub>2</sub> depending on flue gas composition and operational conditions [9].

Another source of waste produced in CCS is the exhaust gas. To avoid unwanted emissions of volatile amines or degradation products to the environment, the exhaust gas goes through multiple water washes. These water wash sections will remove ammonia from the gas, but over time they become saturated. Therefore, the circulating water needs to be exchanged and treated.

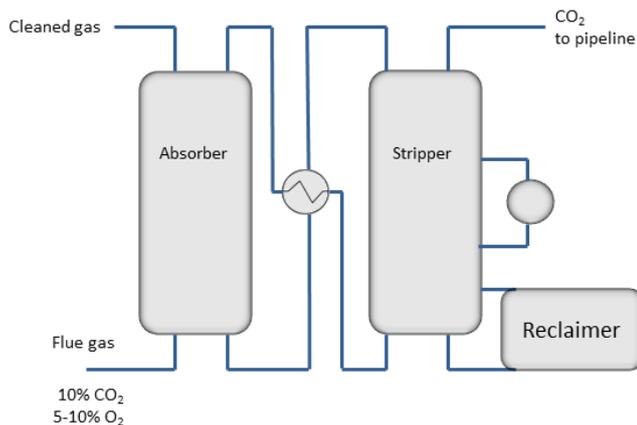
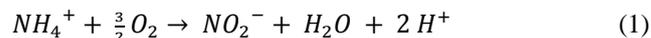


Fig. 1 Process flow diagram of typical post-combustion CO<sub>2</sub> capture by amine absorption, adapted from [13].

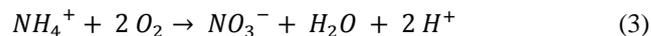
Maximum atmospheric emissions from simulations of a coal fired MEA based capture plant are reported with 5.5 and 1.14 mg/Nm<sup>3</sup> (dry CO<sub>2</sub> lean Flue gas) for MEA and NH<sub>3</sub>, respectively [14]. Other reported volatile compounds are diethanolamine (DEA), formaldehyde, acetaldehyde, acetone, methylamine and acetamide [14].

### III. BIOLOGICAL NITROGEN REMOVAL

Biological nitrogen removal is based on the sequential reduction of ammonia to inert nitrogen. It is a key process in the natural nitrogen cycle and has been applied for wastewater treatment during the last century. This two-step process can be divided into nitrification and denitrification. The first step comprises the oxidation of ammonia to nitrate via nitrite and is facilitated by two groups of bacteria, namely the ammonia oxidizing bacteria (AOB) and the nitrite oxidizing bacteria (NOB), in two steps (Eqs. (1) and (2)):

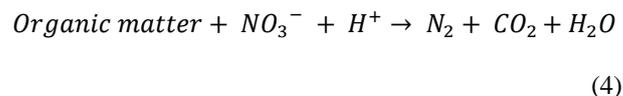


Commonly expressed by the total sum (Eq. (3)):



Both of these phylogenetically unrelated bacteria groups are chemolithoautotrophic, meaning they use inorganic compounds such as NH<sub>4</sub><sup>+</sup> and nitrite as energy source while utilizing carbon dioxide as the carbon source. Due to the low energy yield, they grow very slow compared to the denitrifying bacteria in the following step.

In the next step, the generated nitrate is stepwise reduced to molecular nitrogen by denitrifying bacteria, as shown in Eq. (4).



In the absence of oxygen, some bacteria may use nitrate as the terminal electron acceptor for respiration instead of oxygen. Most denitrifying bacteria are facultative, meaning they can switch their respiration from oxygen to nitrate. Denitrification occurs then only under severe oxygen limiting conditions, because oxygen is energetically more favorable than nitrate [15].

Denitrifying bacteria are heterotroph, meaning they need organic carbon for energy metabolism, as well as for growth. The denitrifying bacteria belong taxonomically to various subclasses of the *Proteobacteria*. However, the ability to denitrify can also be found among archaea and core enzymes have even been found in fungi [15].

### IV. BIODEGRADATION

Many natural occurring compounds have a functional role in at least one or more microbial metabolic pathways. This means that bacteria utilize them as a carbon source, or in their energy metabolism. Xenobiotics are man-made compounds, which do not occur naturally. However, many of these compounds may also be utilized by microbes if they can be made available to the bacteria and the conditions are right.

The persistency of a compound will depend on the chemical structure, the concentration and the environmental conditions for degradation. Monoethanolamine (MEA) is an easily degradable alkanolamine, but at high concentrations it was shown to persist for decades in soil [16]. Another aspect to consider when treating undefined mixed waste is that certain compounds might act synergistic or antagonistic in combination [17].

In general, biodegradation depends on chemical reactions catalyzed by extra- and intra-cellular enzymes. Larger molecules are hydrolyzed to smaller compounds before cellular uptake and the final oxidation to carbon dioxide. In the absence of an external electron acceptor, reduced products such as methane will accumulate. Thus, MEA based reclaimer

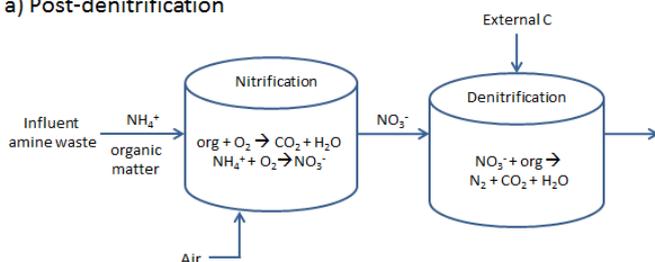
waste has been successfully degraded even under anaerobic conditions for biogas production [18-21].

A common measure for the biodegradability of a compound is the so called biological oxygen demand (BOD). During this test the microbial aerobic degradation of a compound is determined by measuring the oxygen consumption during degradation over a set time frame, such as 7 days in the standardized OECD Test No. 301 [22]. For solvents used in CCS, a lot of work has been invested to test the biodegradability of amines in seawater [23], whereas data on freshwater is yet scarce. We are currently testing amine biodegradability in freshwater with both oxygen and nitrate as alternative electron acceptors for oxidation.

## V. PROCESS CONSIDERATIONS

For biological nitrogen removal there are multiple alternative process solutions available. The post- and pre-denitrification set-up illustrated in Fig. 2 have recently been tested for treatment of MEA [24]. A post-denitrification set-up is beneficial if the influent contains ammonia and only low amounts of organic matter. The aerated nitrifying reactor will convert ammonia to nitrate that serves as an electron acceptor in the second denitrifying step. Amine waste contains substantial amounts of ammonia, but also vast amounts of organic matter.

### a) Post-denitrification



### b) Pre-denitrification

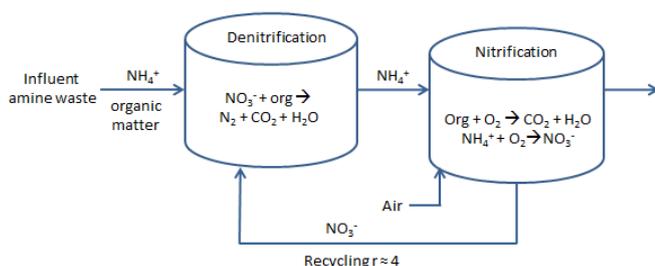


Fig. 2 Alternative process configurations.

This may be utilized aerobic by heterotrophic competing with the nitrifiers for oxygen, thus decreasing the nitrification efficiency. In an open system, autotrophic nitrifying bacteria are always accompanied by heterotrophic bacteria, and their competition for space and oxygen is a well-known phenomenon, particularly in biofilm systems [25]. For the nitrogen removal efficiency this does not have to play a major role, but in terms of economy, the additional feed of organic

matter in the following denitrifying step may be of significance.

The obvious solution is to feed the heterotrophic denitrifying bacteria with the available organic matter in the amine waste. This can be achieved with the pre-denitrification set-up where the amine waste reaches the anoxic denitrification reactor first, see Fig. 2b. Here the amine can be biodegraded, resulting in ammonia and other organic compounds. The organic matter represented by the amine itself serves as a carbon source, while the bulk fraction of ammonia continues into the aerated nitrifying reactor (Fig. 2b). Ammonia will there be biologically oxidized to nitrate, which then has to be recycled to the denitrifying bacteria, to serve as the electron acceptor for their respiration. One disadvantage of this set-up may be that there will always be some nitrate lost in the effluent. However, the cost saving advantage of not needing any additional carbon source is the most important factor. We have recently successfully treated MEA as well as real reclaiming waste from an amine based CO<sub>2</sub>-capture plant with this set-up [24, 26].

Another crucial factor in bioprocess engineering is the retention of the biocatalyst in a continuous flow. Losses have to be minimized so that bacterial growth can compensate to maintain a steady state activity. This is of particular importance for the slow-growing nitrifiers, with a doubling time of 1 day or more. We have applied so called moving bed biofilm carriers to achieve successful retention and activities [24, 26].

The corresponding diffusion transport dominated micro-environment of the biofilm has been found to determine the actual organic loading capacity as well as toxic inhibition of such a system, work is in progress to understand and model those essential process parameters in detail.

## VI. NEW SOLVENTS

Developing new capture solvents is currently an ongoing research topic [27]. As mentioned above, the solvent must show stability during process conditions, as well as be easily degradable in the environment. According to Hoff et al. [10] most of the first generation post combustion solvents belong to one of the following groups: Two-component buffer plus promoter systems (activated AMP or MDEA), single component amine system with high molecular efficiency (MEA, Piperazine), amino acid systems using strong base or amine as neutralizing agent (KOH + Glycine), or promoted carbonates (K<sub>2</sub>CO<sub>3</sub> + activator) [10]. All of these solvent groups show more or less chemical degradation during process condition. Volatility is another important aspect. Amino acids show low volatility [10], and in terms of biodegradability in marine environment, amino acids show low toxicity and high biodegradability. However, tertiary amines, compounds containing quaternary carbons and some solvents (such as AMP and MDEA) did not degrade easily in sea water [23]. Researchers are currently working on third generation solvents, aiming on improving their energy efficiency.

## VII. CONCLUSION

Biodegradability tests of solvents need to be applied before large scale utilization in CCS can be done. For many solvents data exist, but not for all relevant environments. A limitation of the BOD testing is that just the aerobic degradation is determined and not the anoxic degradability which is crucial in biological waste treatment as illustrated.

Efficient waste and effluent treatment must be integrated in the evaluation and choice of future solvent systems. We have shown how this can be tested in lab scale to develop suitable compact bioprocess plants for this purpose [24, 26].

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