E3S Web of Conferences **28**, 01021 (2018) https://doi.org/10.1051/e3sconf/20182801021
Air Protection in Theory and Practice

Environmental issues and process risks for operation of carbon capture plant

Radosław Lajnert[1,*], *Martyna* Nowak[1] and *Jolanta* Telenga-Kopyczyńska[1]

[1]Institute for Chemical Processing of Coal, Zamkowa 1 St., 41-803 Zabrze, Poland

Abstract. The scope of this publication is a presentation of environmental issues and process risks connected with operation an installation for carbon capture from waste gas. General technological assumptions, typical for demonstration plant for carbon capture from waste gas (DCCP) with application of two different solutions – 30% water solution of monoethanoloamine (MEA) and water solution with 30% AMP (2-amino-2-methyl-1-propanol) and 10% piperazine have been described. The concept of DCCP installation was made for Łaziska Power Plant in Łaziska Górne owned by TAURON Wytwarzanie S.A. Main hazardous substances, typical for such installation, which can be dangerous for human life and health or for the environment have been presented. Pollution emission to the air, noise emission, waste water and solid waste management have been described. The environmental impact of the released substances has been stated. Reference to emission standards specified in regulations for considered substances has been done. Principles of risk analysis have been presented and main hazards in carbon dioxide absorption node and regeneration node have been evaluated.

1 Introduction

Implementation of carbon dioxide (CO_2) capture technology into existing coal power plants is more and more real, because of European Comission decisions in the field of greenhouse gases emission reduction. The main part of such systems is a CCP (Carbon Capture Plant) installation, in which the CO_2 is captured. One of the technologies of carbon dioxide reduction commonly applied in the industry, is amine absorption process [1]. The technology of CO_2 capture and storage (CCS) is a key element, which helps to fulfill the requirements imposed by current legislation (EU ETS directive, CCS directive, RED II directve, non-ETS decision) in the field of CO_2 emission reduction into atmosphere. This solution fits in the CCS directive. Implementation of CCS technology allows for significant carbon dioxide emission reduction, and hence reduction of CO_2 emission costs within the European Union Emission Trading Scheme, established by the EU ETS directive [2]. This article presents the environmental conditions and process risks of such installation.

* Corresponding author: rlajnert@ichpw.pl

2 General technical and technological assumptions

The base used for analysis in the article is a demonstration installation of CO_2 reduction for exhaust gases (DCCP - Demo Carbon Capture Plant) [3]. The installation has to capture CO_2 from exhaust gases, which are generated in a reference 900 MW power plant. It is predicted, that the installation will remove about 90% of the generated CO_2 per year, which is about 1.5 million tons of CO_2/year. Thanks to the research conducted on pilot installations [4,5], carried out by research team from the Institute for Chemical Processing of Coal, a concept of DCCP installation was prepared, for Łaziska Power Plant in Łaziska Górne, belonging to the TAURON Wytwarzanie S.A. The basic technological element of the DCCP installation is a CO_2 removal module with amine solution (30% water solution of ethanolamine (MEA)) [6] or water solution with 30% AMP (2-amino-2-methyl-1-propanol) and 10% piperazine (PZ) [7]. The CO_2 removal module consists of a few process parts: amine solution storage, CO_2 absorption, heat exchange and solution regeneration. The most important part is absorpion system with absorber. The exhaust gas introduced into an absorption column is in contact with the amine water solution. Heat recovery system, located between the absorber and desorber (regenerator) is also an essential part. Part of the heat present in the hot solution, which leaves the desorber is transferred into the saturated solution, directed for regeneration. The main element of the absorption solution regeneration part is a desorption column (regenerator), in which the CO_2 capture from solution takes place, thanks to the delivered heat [8]. Absorption processes are the most often selected technologies for CO_2 removal from exhaust gases, generated in fossil fuels power plants and are currently found as best for this application [9].

3 Environmental protection and hazards

DCCP installation is a potential source of hazardous substances. Most of the substances are periodically managed as waste, part of them, which circulates in the closed system, can be dangerous only in the case of accident. However, some of the substances are transferred into the exhaust gases and are emitted into the atmosphere. Among the wastes are also hazardous wastes, which are dangerous to heatlth and life or to environment, because of their origin, chemical or biological composition and other properties. These are substances which have at least one the the hazardous properties [10]. In this installation following types of such wastes can be present: flammable, harmful, toxic for reproduction, sensitizing, ecotoxic and corrosive. Specification of main hazardous materials typical for amine-based carbon capture plant together with risk type is shown in Table 1.

Table 1. Specification of main hazardous materials typical for amine-based carbon capture plant [11].

Waste code	Material	Type of risk in the case of accident
16 10 01*, 16 10 02	Residues from reclaimer	Flammable, toxic for reproducion, sensitizing, ecotoxic, corrosive
	Amine solution	Toxic for reproduction, sensitizing, ecotoxic, corrosive
	Amine decomposition	
07 01 10*	Residues from filters	
06 13 02*	Used bed, active carbon	Harmful, toxic for reproduction, sensitizing, ecotoxic, corrosive
06 02 04*	Solution of NaOH	Corrosive, harmful
16 10 03*, 16 10 04	Condensate	

Emissions from the installation include solid, liquid and gaseous susbtances as well as noise emission. All solid products, if they are not recycled to the process, must be transported into proper storage and processing site. In the case of off-site processing, the substances must be properly stored in the DCCP installation site, until they are transported off-site. Spent active carbon can be used in the plant as a fuel, together with spent active carbon used in the power plant. Therefore, it can be qualified as a side product in the administrative procedure. In such situation, the DCCP installation will not cause a significant increase of waste amount from the whole plant. All wastes generated in the DCCP installation must be included in the waste production permission update. Such permission is required, if the plant generates more than 5000 Mg of wastes per year [12].

Gaseous emission includes: emissions level directly fom the installation stack and concecntration values off-site. From the absorpion column are released NO_X, SO_X and particulate matter [11]. These are the same substances, which are emitted into the atmosphere from power plant without CCS installation. The main difference in the released gas into atmosphere is lack of CO_2. Gaseous amines degradation products are the characteristic substances for CO_2 removal process. Therefore, small amounts of amine vapors and degradation products, are transferred to the cleaned exhaust gases. Togehter with amine absorption process development by selection of new sorbents, which increases the CO_2 removal efficiency and decreases the energy consumption, attention is paid on amines and their degradation products emissions (Table 2). During the installation exploitation losses of sorbent (amine) occur, which results from thermal and oxidative degradation, and also physical phenomena, like evaporation or entraintment by flowing gas stream. As a result of sorbent degradation, compounds, which lower its active concentration, are formed. Besides, a lot of the substances are highly volatile and are released with the cleaned gas into atmosphere and cause environmental pollution.

Table 2. Main compounds formed as a result of degradation of described amines [13-15].

MEA degradation	AMP degradation	Piperazine degradation
– ammonia – ethanolamine – 3-hydroxyethylamine – N-hydroxyethyl-propanamide – 4-hydroxyethyl-2-piperazine – 2-hydroxyethylamine – N-hydroxyethyl-acetamide – metal cations – salt anions	– 2-methyl-2-(methylamine)-1-propanol – 4,4-dimethyloxazolidine – 3,4,4-trimethyloxazolidine – 1-(2-hydroxy-2-methylpropyl)-4,4-dimethylimidazolidine	– ethylenediamine – formic acis – N-nitroso-piperazine – N,N-di nitroso-piperazine

During DCCP installation exploitation emission level of the amines into atmosphere will not have a significant impact on the environment. It is proved by amine installation of this type commonly applied in refinery and petrochemical industries. According to literature [13], the amine concentration in the emitted exhaust gases after CCP proces can be lower than 0.2 ppm.

The allowable emission levels is determined by emission standards. DCCP installation is integrated with power plant and that is why the emission standards [16] are refered to the whole plant, as industry object and its all emitors. The emission exhaust gases without CO_2 is not a stream which DCCP installation adds to the general balance, but emission from the power plant, and cannot exceed the values determined in regulations. According to the

regulation [16], emission standards for existing power plant, for which the building permit was established before 1st of July 1987, with nominal thermal power of Łaziska power plant – 196 MW are (for hard coal combustion, with 6% O_2):
- 250 mg/m_u^3 for SO_2,
- 25 mg/m_u^3 for PM10

and for NO_X the individual value for Łaziska power plant is 600 mg/m_u^3 (up to 31st of December 2017). The emission values, which are adequate for allowable emission standards for hard coal combustion for each emitors are presented in an integrated permit. For Łaziska power plant the permissible emission values of SO_2 and PM10 are less rigorous in the permit than in the emission standards [16]. The regulation does not define emission standards for MEA, AMP, PZ and ammonia, but their emission values can be assessed by actual emissions from insdustrial objects. The biggest installation of CO_2 removal by chemical absorption method in Europe - „CO_2 Technology Centre Mongstad" in Norway has a permit for following emissions [17]:15 and 23 mg/m_u^3 for MEA and NH_3 respectively. According to de Koeijer [18], for the abovementioned instalation following design emissions were defined respectively 2.5 and 3.6 mg/m_u^3. It is expected, that the actual emissions will be 1.3 and 1.8 mg/m_u^3. A simulation prepared for the abovementioned installation shows, that for 25% of AMP and 15% of piperazine solution, following emission values are obtained [13]:
- for NH_3 – 0,012 ÷ 1,3 g/Mg CO_2,
- for AMP – 16 ÷ 1340 g/Mg CO_2,
- for PZ – 0,6 ÷ 25 g/Mg CO_2,

depending on gas temperature and the CO_2 molar charge nad removal efficiency. Additionally, in Commission Recommendation [19] information about piperazine monitoring are presented: *„[...] The competent authorities in the Member States concerned lay down conditions, emission limit values or equivalent parameters or technical measures regarding piperazine in the permits issued under Council Directive 96/61/EC [...]".* This term recommends inclusion of piperazine emission in the integrated permit, but the act includes only the concentration values in working environment. According to the directive [20] and regulation [21], the highest allowable levels in working environment of piperazine are (for 293.15K and 101.3 kPa):
- 0.1 mg/m_u^3 – the highest allowable concentration referred to an average working time,
- 0.3 mg/m_u^3 – the highest temporary allowable concentration.

Similarly, the values for ammonia are 14 and 28 mg/m^3 and for MEA 2.5 and 7.5 mg/m^3.

Although, the regulation [16] does not define emission standards for amines and ammonia. To determine an impact on the environment off-site, pollutants propagation calculation should be performed and should include the background of considered pollutants. The regulation [22] does not define allowable amines concentration, but in the regulation [23] there are presented subtances, characteristic for CO_2 removal by absorption method – ethanolamine (for MEA solution) and ammonia (for both solutions). According to the regulation [23], the reference levels of substances concentration of-site are:
- for ethanolamine – 30 μg/m_n^3 average for one hour and 1.6 μg/m_n^3 average for the year,
- for ammonia – 400 μg/m_n^3 average for one hour i 50 μg/m_n^3 average for the year.

Corresponding standards for the basic substances are:
- for NO_X – 30 μg/m_n^3 average for the year,
- for NO_2 – 200 and 40 μg/m_n^3 average for one hour and for the year, respectively,
- for SO_2 – 350, 125 and 20 μg/m_n^3, average for one hour, day and the year,
- for PM10 – 50 and 40 μg/m_n^3, average for the day and the year.

Because of the wastewater, generated in the installation, all process areas in which amines are applied, must be equipped in trays and each area should have its own drainage with wastewater tank. The assessment procedure for the liquid utilization is based on a list from annex to the regulation [24], which contains substances, which are particularly harmful for water environment, which introduction into sewage system requires water permit or inclusion in the integrated permit.

During CCP installation exploitation there will be new noise sources, such as a compressor, a pump room with amine pumps and chemicals pumps (in this rooms, the noise should not exceed 85 dB (A)) and electrical appliances in a electric building (65 dB (A)). Predicted noise emission of the DCCP installation during exploitation will be negligible for the surrounding.

4 Hazard studies

Process hazards are an inherent part of technological processes. Chemical or physical phenomena present during the installations exploitations can cause damage to property and environment. Assessment of potencial hazards identification is targeted at limiting the possibility of occurence and propagation of hazards from the experimental installation, appliances, objects etc. The identificaion procedures are focused at [25]:

- identification of all process hazards, which have an impact on technical safety,
- analysis of all elements, which have an impact on technical safety level,
- finding solutions in order to eliminate the occurence of lapses and errors.

Hazard studies give the possibility of identification and assessment of hazards, which can occur during the installation designing, building, commissioning and exploitation. Information in process design are the basis for hazard study development. Depending on the investment hazard study, persons responsible for its realization undertake appropriate safety measures, in order to avoid, reduce, accept or transfer the hazard.In the following part, the hazard study with HAZID, HAZOP and SIL methods is shortly described.

HAZID (Hazard Identification) study is a method, which aims at full understanding of basic risk related to the process. In this method, potential events, frequency of their appearance and hierarchical control, which manages this risk are considered [26]. The aim of the HAZID analysis is identification of key hazards and thanks to it, there is a possibility of their elimination at the design step. It should be underlined, that the HAZID analysis is a node-by-node study, not line-by-line assessment. The nodes are selected in a way to include a big area of the installation, in which different chemical processes in similar conditions are conducted instead of analyzing similar areas.

HAZOP (Hazard and Operability) study is a method intended to provide a detailed assessment of the proposed design, such that suitable and sufficient prevention, control and mitigation measures can be included to reduce the risk to a tolerable level [26]. The benefits of this method are, increase of installation work reliability, lower exploitation costs, reduction of losses associated with downtime, full range of identified hazards, high effectiveness and early detection of hidden hazards.

SIL (Safety Integrity Level) assessment is a structured, logical, team-based approach to the determination of the requirement for safety instrumented functions necessary to ensure that risks from industrial activity are tolerable. Safety integrity is a probability, that the system related to safety will properly perform the required safety functions in particular conditions and time interval [26].

5 Hazards assessment

The following Table 3 presents scenarios of main and characteristic for DCCP installation hazards during accidents in key nodes, such as absorption and regeneration nodes.

Table 3. Assessment of the main risks in absorption and regeneration nodes [26].

Risk scenario	Causes	Potential impact on humans	Potential impact on environment
Absorption node			
CO_2 emission to the environment	Installation shut-downs, emergency venting	Potential suffocation	Minimal
Loss of tank/pipeline tightness – amines leakage	Corrosion, tank or pipeline failure, collision, tank overflow, pump seal failure	Vapors can irritate skin, eyes and the respiratory system. Contact can additionaly cause serious skin burns and eye damages	Can have a significant impact on the environment, if amines are released outside the tank/pipeline/ installation. Potential contamination of groundwater
Absorption column failure	Incorrect structural design, column overflow	Potential fatalities caused by installation failure and hazardous materials release	
Clogged gas inlet - implosion	Gas congestion during fast cooling and auxiliary fan operation		
Absorber leakage - hot exhaust gases and amine derivatives release	Corrosion caused by accumulated corosive substaces, expansion joint failure	Exposure to hot exhaust gases, potential suffucation or thermal shock. Injuries caused by falling parts	Limited impact on the environment, if the acids derivatives are released into drainage
Regeneration node			
Amines release into condensate during starts or shut-downs. Corrosion of turbine/boiler	Leakage in heat exchanger, malfunction of vapor valves system, which cause vacuum	Staff exposure to vapor leak – potentially fatal	Potential leak into sewage system. Possibility of amine contamination of the local environment
Vacuum on vapor, condensate and heat exchanger nodes	Extraction on low and medium pressure below 25% of efficiency, water vapor condensation in tanks	Vapors can cause skin and eyes irritation, respiratory sensitization. Contact with hot amine can cause serious skin burns and eye damage	Potential impact on local environment
Leakage of pipeline with cold or hot amine	Regeneration column or pipeline/heat exchanger damage, pump or reclaimer	Exposure to hot materials and vapors. Can cause skin and eyes irritation, respiratory	Potentially significant impact, if amines are released off-site. Potential

	leakage, corrosion, amine pipeline failure	sensitization	contamination of ground waters

6 Summary

Air emissions from described installation will not be harmful for the environment. Process waters and waste waters are also not problematic, because the process areas in which amines are applied are equipped with trays and each are will have their own drainage with waste water tank. In the worst, but less likely case of such leak, there can be soil contamination and hence amine penetration into ground water. Wastes generated in the installation will be segregated and safely stored on the DCCP site until they are managed in appropriate place. Predicted noise emission of DCCP installation during exploitation will not have a significant impact on the surrounding.
According to rules applied in HAZID, HAZOP and SIL studies, the most important technological nodes of the DCCP installation were analyzed and risks to humans occurs only during emergency situation. Most of the identified hazards are typical for industrial installations, such as fire, electrocution, fall from a height, unsealing because of appliances structural integity decrease, resulting in vapor or water leak and splinter falling. There are also hazards characteristic for the DCCP installation, related to amine solutions and their deivatives presence. Hazardous substances forming during the installation exploitation are: amine solution, amine degradation products, residues from the reclaimer, residues from filters, sodium hydroxide and condensate. The described hazards can cause ground water contamination, if the amines are released off-site. Environmental protection and hazards issues in case of AMP and PZ solutions application do not differ significantly in case of MEA solution application.

Presented research results were obtained during realization of research project no 11.16.008 „Monitoring of national and community regulations and actions supporting municipalities and industry within environmental protection", financed by the Ministry of Science and Higher Education within dotation for research potential maintenance.

References

1. L. Więcław-Solny, A. Tatarczuk, A. Krótki, A. Wilk, Karbo, **57**, 62 (2012)
2. L. Więcław-Solny, M. Ściążko, A. Tatarczuk, A. Krótki, A. Wilk, Polityka Energ., **14/2**, 441, (2011)
3. A. Tatarczuk, M. Stec, M. Ściążko, L. Więcław-Solny, A. Krótki, Przem. Chem., **95/11**, 2322, (2016)
4. M. Stec, A. Tatarczuk, L. Więcław-solny, A. Krótki, T. Spietz, A. Wilk, Clean Technol. Environ. Policy, **1**, (2015)
5. L. Więcław-Solny, A. Tatarczuk, M. Stec, A. Krótki, Energy Procedia, **63**, 6318, (2014)
6. A. Tatarczuk, M. Ściążko, M. Stec, S. Tokarski, Chemik, **67/5**, 407, (2013)
7. D. Śpiewak, A. Krótki, T. Spietz, M. Stec, L. Więcław-Solny, A. Tatarczuk, A. Wilk, Chem. Process Eng., **36/1**, 39, (2015)
8. T. Spietz, L. Więcław-Solny, A. Tatarczuk, A. Krótki, M. Stec, Chemik, **68/10**, 884, (2014)
9. Technology Roadmap: Carbon Capture and Storage (2013), International Energy Agency, https://www.iea.org (accessed 14.11.2017)

10. Act of 14th December 2012 on waste (Journal of Laws of 2013 item. 21, as amended)
11. UK Carbon Capture and Storage Demonstration Competition - Project HSE Report. ScottishPower CCS Consortium, (2011) https://pl.scribd.com/document/72781748 (accessed 14.11.2017)
12. Act of 27th April 2001 Environmental Protection Law (Journal of Laws of 2001 no 62 item. 627 as amended)
13. N. Dave, T. Do, P. Jackson, P. Feron, M. Azzi, M. Attalla, CSIRO, Australia, (2010)
14. A. B. Rao, E. S. Rubin, i M. B. Berkenpas, Department of Engineering and Public Policy, **1**, (2004).
15. T. Do, D. Narendra, P. Feron, M. Azzi, CSIRO, (2012)
16. Regulation of the Minister of Environment of 4t November 2014 on emission standards for installations, combustion sources and combustion appliances or waste incineretion (Journal of Laws of 2014 item. 1546)
17. Y. Maree, S. Nepstad, i G. de Koeijer, Energy Procedia, 37, 6265, (2013)
18. G. de Koeijer et al., Energy Procedia, **4**, 1207, (2011)
19. Commission communication on the results of the risk evaluation and the risk reduction strategies for the substances: Piperazine; Cyclohexane; Methylenediphenyl diisocyanate; But-2yne-1,4-diol; Methyloxirane; Aniline; 2-Ethylhexylacrylate; 1,4-Dichlorobenzene; 3,5-dinitro-2,6-dimethyl-4-tert-butylacetophenone; Di-(2-ethylhexyl)phthalate; Phenol; 5-tert-butyl-2,4,6-trinitro-m-xylene
20. Commission Directive 2000/39/EC of 8 June 2000 establishing a first list of indicative occupational exposure limit values in implementation of Council Directive 98/24/EC on the protection of the health and safety of workers from the risks related to chemical agents at work
21. Regulation of the Minister of Labour and Social Policy of 6th June 2014 on maximum admissible concentrations and intensities for agent harmful to health in the working environment (Journal of Laws of 2014 item. 817, as amended)
22. Regulation of the Minister of Environment of 24th August 2012 on admissible levels of some substances in the air (Journal of Laws of 2012 item. 1031)
23. Regulation of the Minister of Environment of 26th January 2010 on reference values of some substances in the air (Journal of Laws of 2010 no 16 item. 87)
24. Regulation of the Minister of Environment of 15th December 2008 amending the regulation on substances that are particularly harmful to the aquatic environment, which introdution into sewage system requires water permission (Journal of Laws o 2008 no 229 item. 1538)
25. T. Podczaszy, Opinia w zakresie konieczności wykonania analizy identyfikującej potencjalne zagrożenia dla bezpieczeństwa technicznego instalacji doświadczalnych i stanowisk testowych oraz środowiska naturalnego dla CCTW (2011) – unpublished
26. Kingsnorth CCS Hazard Identification (HAZID) Report (2011), http://webarchive.nationalarchives.gov.uk/20121217151014/https://www.decc.gov.uk (accessed 14.11.2017)