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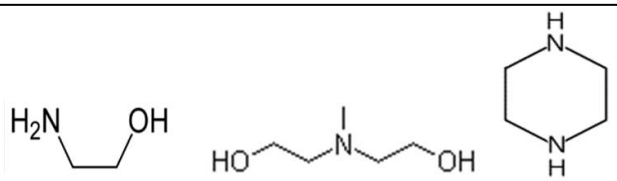
Amines Used in Carbon Capture: Potential Human Health Issues



Chemical structure of Monoethanolamine, Methyldiethanolamine, and piperazine, commonly used amine solvents for post-combustion carbon capture.

Value to the Industry

A better understanding and knowledge of the possible health impacts and environmental issues associated with amine-based post-combustion carbon capture (PCCC) technologies and its by-products in particular can provide the electric power industry, technology developers, regulators and the public with information that will be helpful in many respects. Technology vendors will have an early warning system for potential chemicals of concern and can potentially modify their processes at an early stage. Utilities could avoid potentially large costs through the use of "end-of-pipe" controls that could be installed as retrofits if problems with emissions are discovered once the technology is commercially applied. Regulators and the public will be benefit from a well-developed literature and testing to ensure regulations are well founded and the public is protected.

Introduction and Overview

A leading technology for PCCC at fossil fueled power plants is the amine-based scrubbing of carbon dioxide (CO_2) from the flue gas. Amines are organic compounds derived of ammonia (NH_3), wherein one or more hydrogen atoms have been replaced by a hydrocarbon group. Several common amines used in PCCC are monoethanolamine (MEA), methyldiethanolamine (MDEA), and piperazine. Although current PCCC designs recycle amines, loss of amines has been observed by direct emissions to the air mainly through the facility's stack, and to a lesser extent from other emission points related to the PCCC technology.[1] Besides natural sources, amines are also emitted from animal husbandry, internal combustion engines (mainly on- and off-road diesel vehicles), and various industries (food, manufacturing). After release into the atmosphere amines can a) be involved in the formation of secondary pollutants and secondary aerosols[2]; b) be degraded into aldehydes and amides, such as formaldehyde, acetaldehyde and acetamide; and c) photochemically react with nitrogen oxides forming nitrosamines. Although PCCC's efficacy of CO_2 emission reductions, cost of implementation, and full-scale technology readiness are well-studied, its potential impact on human health and the environment through emissions of amines and related degradation products to the atmosphere and other environmental media has received much less research attention. Hence, there is an urgent need to better understand amines' atmospheric photochemistry after release and to assess if these emissions due to PCCC pose a risk to human health and the natural environment.

Basic Toxicological Science of Amines and Related Degradation Products

Environmental or community exposures to amines themselves likely pose little risk to human health and the environment. For piperazine and MEA there are a few indications of reproductive and developmental toxicity; further, none of the amines used in PCCC have been reported to be carcinogenic. However, amines do have irritant and corrosive properties, and piperazine is reported to be sensitizing. In occupational settings, these materials may therefore be of more concern.

Amines can degrade in the capture system as well as in the atmosphere to form various degradation products. Some of these products may cause health effects at certain

concentrations. However, in risk assessment the emitted concentrations must be considered jointly with toxicological information and population exposures to reach conclusions about the potential risk to the public. In the atmosphere, nitrosamines can be formed from the reaction of ambient nitrogen oxides (NOx), oxygen (O_2), and nitrous acid (HONO) with amines. Gas phase nitrosamine formation in the atmosphere should not pose a significant health hazard due to the low concentrations (sub-ppm), but it remains unclear if heterogeneous formation on atmospheric particles (e.g. aerosols) could result in a significant health risk.

The following subsections outline the primary health concerns associated with several common degradation products in PCCC systems. It should be noted that these compounds are expected to be present at very low concentrations, and exposure to human populations will be influenced by a number of factors. For example, nitrosamines are not stable in sunlight and in fact have atmospheric lifetimes on the order of minutes to hours; this is important in determining the population risk of these materials. Similarly, compounds like formaldehyde and acetaldehyde are present at relatively higher concentrations in vehicular exhaust compared to what is likely to be observed in the PCCC systems, and the relative exposure from different sources will be important to determine.

Formaldehyde: When inhaled, formaldehyde reacts rapidly at the site of contact and is quickly metabolized in respiratory tissues. The most common effects of formaldehyde exposure are various symptoms caused by irritation of the mucosa in the eyes and upper airways. Formaldehyde is genotoxic,[3] but only when it is actual toxic to the targeted cells. Formaldehyde vapor can induce development of tumors in the nasal cavity and it is classified as a potential human carcinogen.

Acetaldehyde: Although acetaldehyde can be absorbed through the lungs and gastrointestinal tract, the general population is mainly exposed to it due to its production in the liver as a result of alcohol/ethanol metabolism. Nevertheless, acute exposure to acetaldehyde vapor causes irritation of the eyes, skin and respiratory tract, but effect levels are above the reported odor threshold (0.09 mg/m3). Acetaldehyde is classified as possibly carcinogenic to humans. The mechanism of carcinogenicity observed with acetaldehyde is likely similar to that of formaldehyde, but higher doses are required to observe the same effects. Although toxicological studies on inhaled acetaldehyde vapor are currently lacking, oral exposure of acetaldehyde induces developmental toxicity, direct teratogenic (i.e., can cause anomalies in the developing fetus) effects, and it may contribute to the abnormalities seen in human fetal alcohol syndrome.

Acetamide: This chemical causes mild skin irritation in humans from acute exposure. Acetamide is considered a non-genotoxic carcinogen. Although no studies on the potential carcinogenic effects of acetamide on humans are known to exist, several animal studies have reported liver tumors from oral exposure to acetamide and the International Agency for Research on Cancer (IARC) has therefore classified acetamide as a Group 2B, possible human carcinogen.

Nitrosamines: Nitrosamines are known to be toxic and suspected to be carcinogenic in humans. Besides photochemical formation in the atmosphere, exposure to nitrosamines occurs mainly through our diet, through use of tobacco, cosmetics, and pharmaceutical products. The particular structure and molecular weight play an important role in determining nitrosamines' acute toxicity. Liver injury, in the form of liver necrosis and liver damage, is the most common result of acute toxicity for a number of nitrosamines, such as N-nitrosodimethylamine (NDMA) and N-nitrosodiethylamine (NDEA), but these compounds appear to exhibit a low to moderate acute toxicity otherwise. Other acute effects of nitrosamines include irritation of eyes, lungs and skin, and also vomiting, lung damage and convulsions. However, nitrosamines are extremely potent mutagens and induction of mutagenesis by nitrosamines has been reported. Nitrosamines have also been studied extensively in laboratory animals for carcinogenicity. In general, the predominant sites of tumor formation include organs like the kidney, lungs, heart, liver, pancreas, urinary bladder and esophagus, as well as nasal and oral cavities, brain and nervous system, and skin. Animal studies have shown that the optimal conditions for nitrosamine tumor induction occur via exposure to low levels over long periods of time; i.e. chronic exposure. It has been reported that piperazine can be metabolized by microorganisms in the gastrointestinal tract to two nitrosamines: N-mononitrosopiperazine (NPZ) and N,N'-dinitrosopiperazine (DNPZ), which have been found to be carcinogenic in rodents. Most nitrosamines are suspected to be human carcinogens since direct causal associations have not yet been reported, but human liver tissue appears to metabolize nitrosamines similar to that of rodents.

Potential Impact

Although there are currently no U.S regulations regarding permissible exposure levels via air for amines released from fossil fueled power plants with PCCC technology and nitrosamines (formed in the atmosphere due to photochemical

oxidation of amines), IARC has classified NDMA and NDEA as group 2A carcinogens (probable human carcinogens), and other nitrosamines, such as NPZ and DNPZ, as group 2B carcinogens (possible human carcinogens). In addition, currently there are no established exposure limits in the workplace in the U.S. Given that nitrosamine formation is theoretically possible from amine-based PCCC systems, and limited data actually suggest that NAs are emitted, a rigorous evaluation of NAs in emissions from PCCC facilities and a corresponding in-depth health risk evaluation are warranted. Evaluation of other degradation products is also important.

Current Understanding and Knowledge Gaps

The health effects of specific amines and some selected degradation products, such as formaldehyde, are relatively well-understood. However, we lack a full understanding of the complex mixture of degradation products; in particular, composition, concentrations, and how both of these may change over the operating time of a power plant, are not clear.

A number of significant knowledge gaps need to be addressed to identify potential health risks associated with amine-based PCCC technology. First, toxicological data are lacking for many of the specific compounds expected to be generated in PCCC systems, although it is likely that the more obscure compounds for which information is not available are likely to be present in emissions at extremely low concentrations. Second, a complicating factor is that many solvents are proprietary; therefore, the identity and concentrations of degradation products are not known. Data related to amine functional groups in general (e.g., primary, secondary, tertiary, sterically hindered amines) can be evaluated and useful information gleaned, but ultimately knowledge of specific hazards is dependent upon the exact chemical makeup. Moreover, additives are typically present in solvent mixtures for corrosion control and other purposes; these are also proprietary, and we currently have little – if any – data on the toxicity of these materials and their possible interactions with the solvent itself. Third, public health risk due to nitrosamines can only be accurately determined through measurement of these compounds in emissions from pilot- or demonstration-scale operating facilities as well as understanding their atmospheric formation and chemistry, and background ambient concentrations.

Research by EPRI and Others

Several research groups worldwide are actively investigating aspects of the health and environmental impacts of amines used in PCCC. For example, several entities, including the Commonwealth Scientific and Industrial Research Organization (CSIRO) in Australia as well as various groups in Norway, are evaluating measurement methods and amine photochemistry. EPRI is studying this issue in a highly multidisciplinary manner, with physical scientists, environmental health scientists, and occupational hygienists working side by side.

EPRI is currently leading several efforts to better understand potential health risks due to amine-based PCCC technologies. Laboratory toxicology studies are being conducted to determine the health effects of specific amines and their degradation products. Methods are being developed for sampling and analysis of amines and their degradation products, and emissions measurements of these materials are being made at appropriate facilities. Modeling of the partitioning behavior of amines in the atmosphere is also ongoing. All of these activities are expected to significantly advance our knowledge of amine chemistry and toxicology.

Contact Information

For more information, contact the EPRI Customer Assistance Center at 800.313.3774 (askepri@epri.com).

Technical Contact

Annette Rohr at 425.298.4374 (arohr@epri.com)

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[1] For example solvent evaporation, removal by waste water, etc

[2] A secondary pollutant or aerosol is a pollutant that is formed by atmospheric reactions of primary emissions. An example of a secondary pollutant is ozone, the primary component of smog, produced in the atmosphere from organic vapors and NOx. The organic vapors (primary emissions) are released into the atmosphere; reacting with sunlight and NOx to form ozone. The control of secondary pollutants and aerosols is complicated because a) it requires the identification of the precursor compound(s); b) the precursor source(s); and c) an understanding of the chemical reaction(s) that produce the secondary pollutant/aerosol.

[3] An adverse action on a cell's genetic material. Genotoxic substances can be potentially mutagenic or carcinogenic, ultimately affecting the cells entire integrity.

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Electric Power Research Institute
3420 Hillview Avenue, Palo Alto, California 94304-1338 • PO Box 10412, Palo Alto, California 94303-0813 USA
800.313.3774 • 650.855.2121 • askepri@epri.com • www.epri.com