

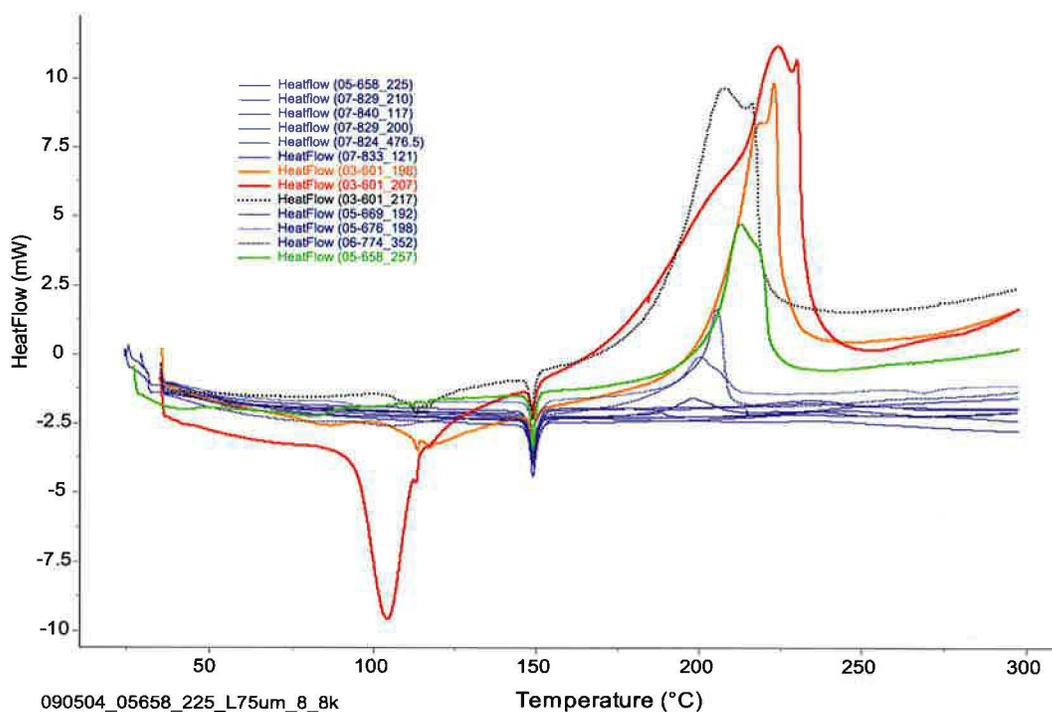
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*Adding amines to steam humidification systems*

*Case Study: Lead monitoring*

*Measuring changes in UCLA's lab safety program*



*Ranking the risk of hazardous thermal reactions*

# Adding amines to steam for humidification

Humidity control is required in all health care facilities. Direct injection of steam from a central boiler plant is the most economical humidification system. The steam carries neutralizing amines—corrosion-inhibiting chemicals—that are added to boiler feedwater to prevent pipe corrosion. When the steam condenses, the amines neutralize the resulting carbonic acid and raise the pH of the condensate, which helps reduce, slow down, or prevent corrosion to the condensate system. This technical review compares the use of ‘clean steam’ to ‘utility’ steam and discusses the health effects, regulation, and control of three of the most commonly used amines in ‘utility’ steam: morpholine, cyclohexylamine (CHA), and diethylaminoethanol (DEAE) to make the point that proper application, control, monitoring and oversight of amines in a ‘utility’ steam system of a health care facility is safe, feasible and economical.

By Farhad Memarzadeh

## INTRODUCTION

In this technical review, we examine the use of ‘utility’ steam containing neutralizing amine additives under controlled conditions in support of the use of ‘utility’ steam in healthcare facilities. Humidity control is required in all health care facilities and many other facilities where people spend large segments of their day.

Direct injection of steam from a central boiler plant is the most economical humidification system for many commercial and industrial facilities. Direct steam-injection systems are subject to corrosion. The U.S. Federal Highway Administration (FHWA) released a study in 2002 on the direct costs associated with metallic corrosion in 26 U.S. industry sectors. The study determined that the annual cost of corrosion in the United States at that time was estimated to be greater than \$300 billion. In the pharmaceutical industry, the total annual direct cost of corrosion was estimated at \$1.7 billion per year (8 percent of total capital expenditures). Although the costs of corrosion related to the health care industry or specifically to direct injection of steam used in humidification systems were not listed, the study provided data to support the need for a combination of safe, effective and less expensive corrosion prevention measures and improved application and monitoring systems.<sup>1</sup>

The use of direct steam-injection humidification has advantages and disadvantages. Briefly, some of the advantages include a relatively low purchase and installation cost; the ability to produce excellent vapor/steam quality i.e., the impurities in the steam have been removed; a large amount of steam can be introduced from a relatively small system; the system is responsive to control because a direct steam humidifier has a variety of control valves sized for the system; it typically has reliable performance and a long life-span; and a direct-injection steam humidifier is perhaps the most reliable and low maintenance type of commercial humidifier.<sup>2</sup> The high temperatures of the steam used in direct steam-injection kills fungal and bacterial organisms that can otherwise cause occupant illness or discomfort and is thus the system of choice in many facilities.

The disadvantages, though off-putting to some users, are very manageable. They primarily revolve around the toxicity of the corrosion prevention chemicals injected into a closed loop system. These chemicals typically have an offensive odor that is detectable well below the regulated exposure limits. The evidence suggests that in the reported case studies where people were affected by the presence of the chemicals in the indoor air or deposited on surfaces, the chemical injection or dilution process was faulty, the steam delivery system was defective, the indoor ventilation was inadequate

or inappropriate for the facility, or some other technical or human error occurred to cause elevated levels of the chemical in the surroundings. Furthermore, the measured levels of the chemicals, despite the fact that they were reported to have caused symptoms including respiratory irritation, nausea, vomiting, or contact dermatitis, were all below the allowable levels as regulated by the Food and Drug Administration (FDA), Occupational Safety & Health Administration (OSHA), National Institute for Occupational Safety and Health (NIOSH), the American Conference of Governmental Industrial Hygienists (ACGIH) and other regulatory entities.

## TYPES OF HUMIDIFIER SYSTEMS

Although direct injection of steam from a central boiler plant is commonly used for the humidification system in many commercial and industrial facilities, there are alternate means of humidification. Among the alternatives are steam-to-steam heat exchangers and stand-alone humidifiers. Design engineers should clarify the quality of the steam and confirm if there is any direct impact to the product or risks to the users and others who might be exposed directly or indirectly to the steam, before undertaking the design. This clarification will minimize the risk of product contamination or potentially hazardous human exposures and may also save money by

using a lower-cost type of steam. The design engineer must take into account the potential level of impurities, including boiler additives (amines and hydrazines) and other impurities that may be present in the steam system that could find their way into the final end product when humidifying a process airstream. The design engineer should look specifically for areas where open processing takes place, and where the steam could possibly contribute significantly to the contamination of the end product. In these cases, a purer grade of steam (clean steam) should be selected and applied.

#### **Self-contained electric humidifiers**

Potable water is used to generate steam without any chemical additives. At least two major designs are available. City water is sent to a sealed plastic tank and heated with an electrode-type heating element. Electric current passing through the water, causing it to boil, generates steam. The steam is delivered to the duct through a variety of dispersion systems. The disadvantage of this design is that dissolved minerals in the city water build up in the tank, reducing output and eventually requiring replacement. No type of pretreatment can be used; deionized or demineralized water is not conductive enough for the heating element to work, and softened water is often too conductive, which may lead to arcing inside the unit. If a stainless steel evaporating chamber with a submerged heating element is used instead, city water can still be used but it can be pretreated to soften, demineralize, or deionize the water. With these higher quality waters, the units last much longer. All electric units require large amounts of power and add considerably to a facility's electric bill, a factor that should be considered when an adequately sized boiler is already available. Electric humidification system must be on emergency power so additional costs of emergency power generators and related switchgear present a disadvantage. As a result, electric-type humidifiers are used mostly in the existing facilities where only a few units are needed and where the emergency power system has sufficient capacity.

#### **Steam-to-steam converters**

Perhaps the best option for those who already have a steam boiler providing humidification is the steam-to-steam converter. The chemical-laden steam provided by the boiler is put through a tube-type heat exchanger that is immersed in a tank of city water. The boiler steam heats the city water through the exchanger and returns it to the boiler. The city water, which has not come in contact with chemical additives, becomes the source of steam for humidification. In this way, steam is used, and there is no increase in energy consumption as with electric units. The chemical additives amines never reach the air stream.

#### **Ultrasonic humidifiers**

Ultrasonic humidifiers are more efficient and require less maintenance than competing humidifier technologies such as indirect steam-to-steam. The greatest energy and cost savings from ultrasonic humidifiers occur in applications requiring simultaneous cooling and humidifying. The types of facilities where this technology is best used are computer rooms for data processing centers, communication centers with large amounts of electronic switching equipment, clean rooms for electronic and pharmaceutical manufacturing, and hospital operating rooms. They do not require anti-corrosive additives that affect the IAQ of buildings using direct-steam humidifiers. There are two potential disadvantages of ultrasonic humidifiers. They must use mineral-free, deionized water or water treated with reverse osmosis. Treated water reduces maintenance costs because it eliminates calcium deposits, but increases other operating costs. Also, the cool mist from ultrasonic humidifiers absorbs energy from the supply air as it evaporates and provides a secondary cooling effect. This cooling is beneficial in applications where simultaneous humidification and air conditioning are required, but detrimental when heating and humidifying. Ultrasonic humidifiers are also well suited to applications requiring tight controls on humidity (1%) due to their instantaneous response. Ultrasonic humidifiers have the highest benefit when energy,

maintenance costs, sensitive humidity control, and cleanliness are high priorities. The technology has a cost and large energy saving advantage over other humidification technologies when simultaneous cooling and humidification is required. Ultrasonic humidifiers were judged to have notable potential and to be life-cycle cost-effective in the proper applications.

#### **Direct-injection type humidifiers**

Direct-injection humidifiers offer the lowest initial and operating costs, and the most efficient and best level of controls with precise control of output. These types of humidifiers may be used to disperse the steam from the central boiler plant. In a "clean" steam system with direct injection type humidifiers, clean steam is generated in a dedicated gas-fired boiler, steam-to-steam converter, or electric steam generator. The disadvantages of the clean-steam system include the need for stainless steel steam and condensate system components, and the make-up water must be treated in the reverse osmosis or de-ionization equipment.

#### **'CLEAN STEAM' VS. 'UTILITY' STEAM**

Steam is available and produced in different grades depending on its application. 'Clean' steam is used in the pharmaceutical and health care industries where moist-heat sterilization is critical and in processes where the steam may come in contact with ingestible or parenteral products or their packaging. According to the California Mechanical Code<sup>3</sup>, humidification is required in operating rooms, cystoscopy, cardiac catheter labs, delivery rooms, recovery rooms, newborn nursery, intensive care newborn nursery, and in intensive care rooms. 'Clean' steam is also used in humidification of clean rooms in pharmaceutical manufacturing plants in the manufacture of sterile compounds for injection or wound application and for ingestible medications. In these environments, entrained contaminants may affect downstream products and processes exposed to the humidification system such as open aseptic processing. Some forms of 'clean' steam

may be used in the food production industry. Historically, these industries have used filtered steam for sterilization. However, in demanding ever-higher levels of purity assurance these sectors have migrated to the adoption of 'clean' steam. 'Clean' steam is now used as standard in a range of quality-critical processes at risk from plant steam contaminants.

To create 'clean' steam, a secondary generator with controlled feed water is used. The design of the steam distribution network, material selection, and installation practices are all critical for minimizing steam degradation thus ensuring acceptable purity and quality at the point of use. By using 'clean' steam, manufacturers know there will be no boiler additives, volatiles, and particulates that could taint, blight, or contaminate final products. In addition, 'clean' steam is often used not only to remove contaminants, but also to ensure the quality control of critical attributes such as dryness, superheat, and production of non-condensable gases, all of which could adversely affect the process and equipment.

It is costly to use 'clean' steam. The cost is increased primarily by two factors: (1) it is expensive to purify water to the necessary specifications prior to its being introduced into the boiler system and (2) the non-corrosive conduit components that should be used in a 'clean' steam system are of very high quality and expensive to purchase and maintain.

Although the use of 'clean' steam is determined by Good Manufacturing Practice (GMP) as detailed in the Code of Federal Regulations (CFR 21, Part 211),<sup>4</sup> specific recommendations for steam composition or its condensate are lacking. The water used to produce the steam in the pharmaceutical industry, so as to generate a 'clean' product at the point of use, is regulated by the US Pharmacopoeia (USP).<sup>5</sup> The USP does not define criteria for 'clean' steam. Steam purity is determined by individual pharmaceutical manufacturers so as to meet the GMP requirement to avoid product contamination.

The USP defines Purified Water (PW) and Water for Injection (WFI) – the two grades of water primarily used for pharmaceutical manufacture.

Purified water must meet specific criteria for conductivity, total organic carbon and microbial colony forming unit (CFU) limits. Conductivity, the tendency of water that contains ions to conduct electricity, is used to measure feed water and lower qualities of treated water. The more ions present in the water, the higher the conductivity. It is measured as the Siemen(S), microsiemens/centimeter ( $\mu\text{S}/\text{cm}$ ) or micro-mho/cm.<sup>6</sup> Total Organic Carbon (TOC) is a the concentration of all organic carbon atoms covalently bonded in the organic molecules of a given sample of water. TOC is typically measured in parts per million (ppm or mg/L). Microbial colony forming units (CFU) are a measure of microbial content in water samples that are plated on a growth media, incubated and counted microscopically. Although most microbial species are destroyed under the intense heat and pressure of a steam process, the endotoxin by-products they produce are stable under these same conditions and are the contaminating factor of concern in the pharmaceutical industry.

Water for injection (WFI) has more stringent CFU limits, as well as endotoxin limits and production specifications than PW. Water for injection is produced by reverse osmosis and distillation to remove organics, bacteria and pyrogens.<sup>7</sup>

Pharmaceutical quality 'clean' steam does not contain corrosion inhibiting additives and because of its low conductivity water or condensate, it is corrosive to materials commonly used in 'utility' steam systems.<sup>8</sup> The metal components for 'clean' steam systems must be of extremely high quality and are usually AISI 316L stainless steel, titanium<sup>9</sup> or nonmetallic materials such as ethylene propylene diene monomer (EPDM) rubber<sup>10</sup> and polytetrafluoroethylene (PTFE).<sup>11</sup>

Even in a 'clean' steam system a form of corrosion called 'rouging' can occur. When 'rouging' occurs, the system must be shut down to perform a chemical cleaning process to remove possible contaminants to the final product.<sup>12</sup>

The most economical humidification system is direct injection of the steam from the central boiler plant.

Typically, humidification is achieved in two stages: primary and secondary. The primary humidifier, installed in the air-handling unit, adds moisture to maintain relative humidity in non-critical patient areas of the facility at approximately 35 percent relative humidity. The secondary humidifiers are located downstream of the final filters and downstream of the terminal unit with the reheat coil serving each space where individual temperature and humidity controls are required.

This steam is referred to as 'utility' steam. Typically, the water supplying the boiler is pre-treated to remove or adjust contaminants such as salts and dissolved gasses, but pre-treatment doesn't necessarily remove all contaminants and may not be economically feasible.

'Utility' steam from a conventional boiler contains anti-corrosion chemicals that help prevent equipment failure, lower maintenance costs, and improve maintainability, efficiency, reliability, treatment, system life and safety of the boiler and cooling systems. A steam/condensate system is subject to corrosion due to the carbon dioxide ( $\text{CO}_2$ ) present in the steam. Carbon dioxide is produced when carbonate and bicarbonate alkalinities in boiler feed water thermally decompose in the boiler. Carbon dioxide is driven off as a gas and is carried with the steam. It then dissolves in the condensate to form carbonic acid, which causes corrosion in condensate piping, receivers, and traps, commonly composed of carbon steel, gunmetal, and bronze. Some of the  $\text{CO}_2$  dissolves in the condensate and reacts with water to form carbonic acid having a pH of about 4.5–5.5, which can severely damage the entire condensate system and corrosion by-products are carried back to cause fouling and deposition in the feed water tank and boiler. The presence of oxygen from make-up water and leakage into the system can cause the formation of iron oxide to varying degrees that result in pitting. In the presence of acidity caused by  $\text{CO}_2$ , corrosion products are dissolved causing further damage to the system. Corrosion may manifest as a thinning or grooving of the condensate pipe or degradation of pipe threads.

Neutralizing amines, volatile alkaline compounds that are carried with the steam, are added to boiler feed water to prevent such corrosion. When the steam condenses, the amines neutralize the resulting carbonic acid, raising the pH of the condensate and preventing corrosion to the condensate system. Neutralizing amines are fed into a boiler system to maintain a moderately alkaline pH range from 8.2 to 9.2. The amines found in steam used for humidification are carried via humidifiers into room air, where they are inhaled and/or inadvertently ingested via hand to mouth contact of surface deposits. These amines, have been implicated, mostly based on anecdotal evidence, as the causative agents for adverse health effects such as eye, upper respiratory, and skin irritations in humans and animals. The chemicals are carried via humidifiers into room air, where they are inhaled and/or ingested. When amine-treated steam is used for direct humidification of human occupied space, some amount of the volatile amines may be present in the humidified air supply.

The adverse health events attributed to neutralizing amine exposure from additives in 'utility' steam systems have often been inadequately researched and interpreted, leading to the false assumption that it is necessary to use 'clean' steam in the health care environment. The California Code Application Notice (CAN) #4-408.1.5<sup>13</sup> in part, reads: "If steam from a central boiler plant will be injected directly into air stream, it is recommended, but not required that the design professional verify that the boiler water will not be treated with chemicals or contain minerals which are known to be hazardous to health or which might contribute to an indoor air quality problem."<sup>13</sup>

The Environmental Protection Agency (EPA) has issued warnings regarding boiler chemicals: "Heating system steam should not be used in the HVAC humidification system, as it may contain potentially harmful chemicals such as corrosion inhibitors."<sup>14</sup> "Steam humidifiers should utilize clean steam rather than steam created from chemically treated boiler water, so occupants will not be exposed to chemicals."<sup>15</sup>

## CHARACTERISTICS OF NEUTRALIZING AMINES

In order to maintain a safe indoor air quality (IAQ), design engineers and owners should be knowledgeable about the chemical additive properties with respect to their purpose, use and toxicity as each has different properties, toxicities, advantages and disadvantages.

Neutralizing amines are organic compounds that behave as weak bases and have a strong, characteristic, fishy or ammonia-like odor. They are classified by their (1) neutralizing capacity – a measure of how much amine it takes to neutralize a given amount of acid, expressed as the parts per million (ppm) of carbonic acid neutralized per ppm of neutralizing amine; (2) alkalinity or pH and (3) vapor/liquid distribution ratio (V/L) defined as the tendency of the chemical compound to condense with the steam condensate. For neutralizing amines, the V/L represents the amines interaction between the liquid and steam phases and the pressure, temperature and pH of the steam/condensate environment. The higher the ratio the more likely the amine will stay with the steam in a distribution system, while an amine with a lower ratio will condense earlier depending on its chemical properties and the variables of pressure, temperature and pH. A higher ratio product therefore is a better choice for a larger/longer system while a lower ratio product is best for a smaller system.

The neutralizing amines are corrosive in and of themselves before they chemically react with an acid to neutralize that acid and they must be handled judiciously. Although there are alternatives to using neutralizing amines in certain situations, the use of neutralizing amines remains the method of choice in many facilities because of its reasonable cost and general ease of use and monitoring.<sup>16-19</sup>

Neutralizing amines each have different chemical properties so that a combination of appropriate amines may be necessary to address the corrosion effects on different segments of the system. In addition to selecting a neutralizing amine or combination of amines based on these characteristics

the cost, consumption rate, length of the condensate lines, amount of carbon dioxide generated in the boiler and thermal stability must be considered as well. Because of the complexity of combined amine additive interactions and the systems for which they are selected, sophisticated computerized modeling techniques may be used to predict the amine distribution and pH profile across the system.

The most commonly used neutralizing amines in boiler systems are, cyclohexylamine (CHA), diethylaminoethanol (DEAE), morpholine, ammonia methoxypropylamine (MPA), monoethanolamine (ETA) because, used individually or in combination, they are capable of preventing corrosion in systems of various lengths, and it is fairly easy to control their indoor air concentrations well below accepted exposure limits through the use of standard operating procedures and practices. Of these, CHA, DEAE and morpholine are the most commonly used neutralizing amines in steam boiler humidification systems in health care facilities. This is primarily because they have been approved by the FDA for use in food processing applications or in other words, for ingestion. The USDA permits the use of the amines in meat and poultry plants. As described in the section '*Regulation of Neutralizing Amines*', FDA, OSHA, and ACGIH exposure limits are significantly higher than any levels that have been found in the classic exposure case studies reported in the literature. Since no Federal government regulations exist governing the use of amines in direct steam humidification systems (other than in the food industry in which all the existing standards and guidelines are based on ingestion) the water treatment industry tends to follow FDA limits for amine levels in steam used for direct steam humidification systems. However, lacking better or more current scientifically based criteria, this is all the guidance currently available to manufacturers and regulators.

### Cyclohexylamine

Cyclohexylamine (CHA), a colorless to yellow liquid with a strong fishy odor, is used primarily for boiler water

treatment in low pressure systems (50 down to 5 psi) and also for systems with long condensate systems where it is used in combination with other neutralizing amines. It has a high vapor-liquid distribution ratio of 4.7:1 (i.e., cyclohexylamine will place 4.7 times the material in the vapor phase as in the water phase). CHA is unique among the neutralizing amines approved for steam boiler systems in that it will stay with the steam as pressure is reduced. Cyclohexylamine is a mutagen and a corrosive chemical that can be an acute and chronic irritant to the lungs, skin, and eyes. Inhalation exposure can cause dizziness, light-headedness, anxiety, nausea and vomiting. It is also a flammable liquid and a fire hazard.

#### **Morpholine**

Morpholine is the amine of choice for direct sterilization systems and short run systems. It must be blended with either DEAE or CHA for use in longer systems since it drops out of the steam early. It has a low boiling point and low distribution ration (0.4 parts morpholine in the steam; 1.0 part morpholine in the condensate). There are no data available on levels of morpholine in ambient and residential indoor air and in drinking water.

#### **Diethylaminoethanol (DEAE)**

Diethylaminoethanol (DEAE), a colorless liquid with a nauseating, ammonia-like odor, has a vapor-liquid distribution ratio of 1.7, which is between cyclohexylamine and morpholine. It is a good choice in a medium length system where either morpholine or cyclohexylamine used separately would not provide complete protection. DEAE is not effective in low pressure systems because of its high boiling point. DEAE can be compared to morpholine as a primary irritant.<sup>20</sup>

#### **OTHER NEUTRALIZING AMINES**

##### **Ammonium hydroxide**

Ammonium hydroxide is a colorless liquid with a pungent suffocating odor and an acrid taste. Unlike the previously mentioned volatile amines, which are manufactured, the ammonium ion is

found in nature. Ammonia is sometimes used in steam lines where the steam contains a large amount of carbon dioxide or where there is significant steam loss from the condensate system. Although ammonia is relatively inexpensive, it cannot be used in systems containing copper, nickel or zinc. Ammonia is also more difficult to adjust correctly between pH 5.5 and 6.5 but it can neutralize carbon dioxide to pH 8.5–9.0 when the steam condenses. However, it is very volatile and neutralizes only at the end of the condensation rather than as required during the whole condensation.

Other neutralizing amines sometimes used for corrosion inhibition include: methoxypropylamine (MOPA) used primarily in the oil industry in anticorrosion of petroleum lines; dimethylpropylamine (DMPA) used mainly in the foundry industry, as a tertiary amine catalyst for the production of sand cores (cold box process); monoethanolamine (MEA), similar to morpholine, is used for corrosion control in steam cycles of power plants, including nuclear power plants with pressurized water reactors. It is sometimes selected because it does not accumulate in steam generators (boilers) and crevices due to its volatility, but rather distributes relatively uniformly throughout the entire steam cycle.

#### **EVIDENCE OF HEALTH RISKS ASSOCIATED WITH EXPOSURE TO CORROSION-INHIBITING AMINES**

##### **Acute exposure**

High concentrations of neutralizing amines in ambient air are suspected to have adverse health effects on humans and animals. Brief exposure has caused nausea, dilated pupils, slurred speech, anxiety, vomiting, and narcosis. Occupational exposure to CHA has been reported to cause headache, nausea, dizziness, vomiting, and rapid and irregular heartbeat. Acute exposure of animals resulted in extreme mucous membrane irritation, gasping, tremors, clonic muscular spasms, lung hemorrhage, opaque corneas, vascular lesions, and hemolysis.<sup>21</sup> DEAE and CHA are both acute

mucosal irritants at high exposure levels. Ingestion of CHA and DEAE may result in abdominal pain and diarrhea. Dermal contact with DEAE may lead to redness, pain, burns, and blisters.<sup>22</sup>

The evidence of adverse events caused by exposure to neutralizing amines in the indoor environment is mostly anecdotal with an occasional scientific study that provides evidence to support the accepted regulatory limits for exposure rather than human exposure to concentrations well below these limits. Well-designed scientific studies related to the neutralizing amines are scarce. The classic workplace examples used as evidence of exposure and adverse effects to neutralizing amines reflect inadequate ventilation, inadequate research and improper ventilation.

The effects of amine exposure have been found to depend on the exposure concentration. The greatest (dose-dependent and statistically significant) increase in mean systolic and diastolic blood pressure was observed 1 h after administering cyclohexylamine in single doses of 5 or 10 mg/kg body weight to healthy male volunteers. A slight drop in heart rate accompanied the vasopressin effect. The plasma cyclohexylamine levels correlated to the increase in mean arterial blood pressure. The authors estimated that a cyclohexylamine level of 0.7–0.8 µg/ml plasma was still able to produce a significant hypertensive effect.<sup>23</sup>

The human olfactory threshold for diethylamine is 0.14 ppm. In a study on perceived acute sensory effects, Lundqvist et al.<sup>24</sup> determined that there was an increase of nose and eye irritation, and odor perception, with gradually increasing DEAE concentrations of 12 ppm over 60 min [time-weighted average concentration of 10 ppm]. In order to minimize such irritation symptoms, a 15-min short term exposure limit (STEL) of 10 ppm is recommended. The European Commission, in its recommendation on occupational exposure limits for diethylamine note that the outcome of the Lundqvist study suggests that some symptoms of eye and nose irritation might start to occur with DEAE exposures of about 10 ppm.<sup>25</sup>

There are no known methods of directly measuring concentration of amines in the air; hence, measurement is derived from the concentration of amines in the condensate and related amount of supply air. Possibly as a result of this, many of the available case studies, particularly the earliest reported cases, lack good data. Adding to the difficulty in associating exposures to symptoms is the shortage of reported and recorded information for many incidents such as the three occupational exposures to CHA reported by Watrous and Schulz in 1950.<sup>26</sup> One brief exposure of about 1 h involved a worker who noticed a strong fishy smell. He reported symptoms of nausea, light-headedness and anxiety as well as loss of appetite, throat irritation and rapid heartbeat. Air samples were not taken immediately nor were details such as location of the incident or other worker exposures noted. Air samples taken at an unspecified time showed 4–10 parts per million (ppm) of CHA. Another exposure was the result of a worker splattered with an unknown concentration of liquid CHA dissolved in an unidentified caustic solution. The individual developed a rash described as coagulative necrosis on the face and experienced nausea and vomiting 1–3 h after the exposure. Other symptoms included slurred speech and widely dilated pupils. The individual appeared to recover completely within 24 h of exposure. The third exposure in the Watrous and Schulz<sup>26</sup> report was of a supervisor in a CHA plant who was exposed to CHA vapors and experienced classic nausea and vomiting symptoms. Again, there were no details reported for the incident.

The National Institute for Occupational Safety and Health (NIOSH) has investigated several cases related to exposure to boiler steam containing corrosion-inhibiting chemicals. NIOSH uses environmental evaluation criteria that are intended to suggest levels of exposure to which most workers may be exposed up to 10 h per day, 40 h per week for a working lifetime without experiencing adverse health effects, even though there may be exceptions to these time frames because of individual susceptibility, a

pre-existing medical condition, and/or a hypersensitivity (allergy). There are a variety of factors that are not accounted for in these criteria including that several substances may act in combination with other workplace exposures, and may be absorbed by direct contact that may increase the overall exposure.

In March 1981, NIOSH investigators determined that dermatitis and other employee reported symptoms in the office area of a pharmaceutical production building were the result of exposure to a condensation or reaction product of DEAE that had been added to the air-handling system. The specific agent could not be identified despite environmental air and surface sampling. However, results of sampling suggested the presence of a conjugated amine that possesses acidic properties. Environmental and medical evaluations indicated the source of the reported symptoms to be the air-handling system.<sup>27</sup>

Similarly, in 1982, there was an investigation at a Cornell University museum in Ithaca, New York. Forty employees reported eye irritation and dermatitis. DEAE had been added to a humidification system. Air sampling detected minimal DEAE concentrations in only two of 14 samples collected. The detected DEAE concentrations were three orders of magnitude less than the OSHA permissible exposure limits (PEL) of 10 ppm. It was concluded that dermal contact with released DEAE that had subsequently condensed on surfaces was the exposure pathway rather than inhalation because symptoms did not begin to develop until about two years after the introduction of DEAE into the museum humidification system. NIOSH recommended that DEAE be wiped from surfaces.<sup>28</sup>

A confirming follow up study conducted by Battelle, Columbus, Ohio and reported by Edgerton et al.,<sup>29</sup> took consecutive measurement of amines in an indoor office/laboratory that is steam-humidified by a system in which amines were added for corrosion control. The average room concentrations of DEAE and CHA at 42% relative humidity (RH) are 0.6 and 0.7 ppb, respectively. At 61% RH, the average

DEAE and CHA concentrations are 2.4 and 0.8 ppb, respectively. During the final hour when the humidifier was shut off, the concentrations of both compounds decay to 50% of their steady-state values at 61% RH. Of 14 samples, DEAE was detected in only two, at concentrations of 8 and 10 ppb with a detection limit of 8 ppb. The amine concentrations measured in this study are significantly lower, by about a factor of 10, than those reported in the NIOSH study. The author postulates that the museum in the NIOSH study had a very limited supply of fresh air and relied primarily on recirculated air. This study suggests that the concentrations of these amines in indoor steam-humidified air remain low enough that they do not present any hazard to health. The primary fate of the amines that are input into the room air from steam humidification is probably removal to surfaces.

In 1988, NIOSH investigated Cincinnati Electronics Corporation after 64% of the employees reported an ammonia like odor and filed complaints of rashes, headaches and eye, nose, and throat irritations while working where amine-treated steam was used in direct humidification.<sup>30,17</sup> Investigators determined that four times the recommended amount of combined CHA and DEAE had been added to the humidification system. Air samples were not taken until four days after the incident was reported. During the time between the outbreak and sampling, the boilers had been flushed with an estimated 25,000–75,000 l of makeup water containing normal amounts of corrosion inhibitors. Inability to recover CHA or DEAE suggests that the levels fell below the NIOSH method's detection limit; however, an accurate measure of the amine concentration at the time of the incident was never obtained.<sup>30,17</sup>

In 1988, NIOSH also investigated a complaint involving hospital staff at a neonatal intensive care unit and nursery. According to a CDC report, nurses experienced upper respiratory distress and burning eyes after the corrosion inhibitors CHA and morpholine were added to boiler water used to humidify the wards (NIOSH, unpublished data). Associated follow

up reports for this particular incident were not found in this literature search so chemical concentrations and any other circumstances cannot be identified.

A laboratory worker removing animals from an inhalation chamber was inadvertently exposed for less than 30 s to DEAE at an estimated concentration of 100 ppm (480 mg/m<sup>3</sup>). The individual developed nausea and vomiting within 5 min. Other persons in the same room also complained of a nauseating odor but showed no ill effects.<sup>31</sup>

In September 1993, NIOSH conducted a Health Hazard Evaluation (HHE) at the Veterans Administration Medical and Research Center, White River Junction, Vermont. There had been employee complaints of fatigue, allergy symptoms, and eye, nose and throat irritation and it was known that morpholine and CHA had been used in the boiler system. Air, surface wipe and steam samples were obtained from research laboratories for the two anti-corrosion chemicals. A small sheet of plastic, which had been hanging in a research laboratory for several months, was also analyzed for the presence of these compounds. Several months later additional samples were taken to include testing for morpholine, CHA and formaldehyde. Morpholine and CHA were not detected in either the air or wipe samples at concentrations which exceeded minimum detectable concentrations of 0.002 parts per million (ppm), and 0.005 ppm respectively but they were detected on the plastic sheet and in steam condensate samples. Very low levels (<0.01 ppm) of formaldehyde were also detected in the area air samples from the research laboratories. Formaldehyde concentrations were at or below what is generally considered 'background'. The report does not indicate whether or not formaldehyde was used in any form in the sampled laboratory. The environmental sampling results indicate that employees are not exposed to airborne morpholine or CHA at concentrations above the minimum detectable concentrations for these compounds. NIOSH recommendations included discontinuing direct injection of boiler condensate for humidification.<sup>32</sup>

One of the more scientifically sound studies on how amine concentration may affect IAQ was reported by Lao.<sup>16</sup> The study assessed exposure to CHA from a steam humidification system at the East Carolina University School of Medicine Greenville, North Carolina. Use of a gas chromatograph fitted with a flame ionization detector allowed for a lower detection limit of 0.08 µg CHA per air sample. The results were compared to a material balance calculation designed to model the CHA concentration in room air to predict situations that could lead to a toxic event and make recommendations based on findings. The methodology and scientific approach provide a model that shows that air concentrations derived by gross material balance can be used to predict measured values. Lao notes that in this study a manual or malfunctioning dosing system could result in a CHA concentration that significantly exceeds the 10 ppm OSHA standard and might result in a toxic event to those exposed.<sup>16</sup>

In 1996, the International Chemical Workers Union (ICWU) requested that NIOSH conduct a Health Hazard Evaluation (HHE) at Agrium U.S., Incorporated, Homestead Nitrogen Operations (formerly Cominco Fertilizers, Inc.), located in Beatrice, Nebraska.<sup>33</sup> Employees reported adverse health affects that included rashes, headaches, upper respiratory irritation, skin irritation, vomiting, and disorientation. The symptoms were attributed to exposure to a combination of diethylhydroxylamine, N-isopropylhydroxylamine, cyclohexylamine (CHA), and diethylaminoethanol (DEAE) used in the boiler feed water prior to Agrium management attempting to alleviate the problem by using alternative chemical additives. Symptoms abated after initiating the use of alternative chemical additives but since no analysis was done until after the change was made to the alternative chemical additives, the initial cause of the symptoms could not be determined. The alternative additives contained oxides of nitrogen (NO<sub>x</sub>) and other compounds of which there were also health concerns. So NIOSH proceeded to evaluate potential employee exposures to NO<sub>x</sub>, nitrosamines,

ammonia, inorganic acids, and volatile organic compounds (VOCs) present in the system at the time of sampling. One of the alternative additives contained morpholine which can react under certain conditions with NO<sub>x</sub> to form N-nitrosomorpholine (NMOR). The sampling results indicated that NO<sub>2</sub> concentrations did not exceed the 8-h time weighted average (TWA) evaluation criteria. However, employees might sporadically be exposed to NO<sub>2</sub> concentrations which exceed both the NIOSH recommended ceiling limit and the OSHA and ACGIH short term exposure limit (STEL). The environmental sampling also indicated that the potential for NMOR formation existed during this process. All the air concentrations determined for NO, nitric acid, and ammonia were below their relevant exposure limits. The results of this investigation suggest that elimination of DEAE and CHA from boiler cures alleviates symptoms.

NIOSH was asked to investigate employee complaints of building-related employee illnesses at Riverside County Regional Medical Center, Riverside, California. It was believed that the illnesses were caused by DEAE present in boiler steam used to humidify air in patient care units in the hospital. Symptoms included skin irritation, eye irritation, runny or stuffy nose, headaches, and increased allergies. The tests did not detect any DEAE in the air. However, several interesting facts support the premise that improper practices and/or design of the humidification system can result if the system is not working properly or if proper standard operating procedures are not followed. The boiler mechanics wore gloves made of neoprene and latex rubber while handling DEAE. These materials will not keep hands from being exposed to DEAE. The building had diesel-powered generators and it is possible that diesel exhaust re-entered the building's ventilation system and affected the hospital's air quality. Despite the fact that there was insufficient data to positively link DEAE exposure with reported symptoms, the employee's symptoms were consistent with DEAE exposure. NIOSH investigators recommended that humidification with boiler steam

containing DEAE be discontinued.<sup>18</sup> The NIOSH reports notwithstanding, no Federal government regulations exist governing the use of DEAE or other amines in direct steam humidification systems.

Most of the time, exposures to volatile amines become apparent from NIOSH Health Hazard Evaluation (HHE) reports. In light of how many building steam systems use anti-corrosion amines, exposure incidents are rare occurrences and to date it appears that they have been due to either human error or a defective ventilation system. There are very few scientific studies to prove the correlate that proper procedures result in a safe environment. The literature clearly indicates that the actual concentration of amines in the indoor air is measured in parts per billion (ppb) versus parts per million (ppm). Grattan<sup>19</sup> described a study that was conducted by a chemical product manufacturer to determine amine levels in room air humidified with morpholine, CHA and DEAE. The results were published in a peer reviewed journal. Temperature and relative humidity were maintained at about 50% RH and 22–23 °C (71.6–73.4 °F). In general, increasing the concentration of amine in the steam resulted in higher airborne amine concentrations. The maximum air concentration never exceeded 0.66 ppm amine which is substantially below OSHA/ACGIH exposure limits. From this study, Grattan<sup>19</sup> notes that proper feed, dosage, and control of amine condensate corrosion inhibitors are critical to assure compliance with FDA, OSHA, and ACGIH guidelines regarding the levels of amine permissible in steam-humidified room air. Control is required to minimize corrosion in steam and condensate systems; to prevent unscheduled outages; and to optimize boiler efficiency by reducing the corrosion byproducts returned to the boiler via the condensate return system. Unfortunately, there is no standard that can protect anyone from a situation where standard operating procedures are not followed or from gross error in system operations.

Primary injection steam constitutes a very small fraction of the mass flow of the humidified air stream. Consequently, the concentration of

neutralizing amines in the humidified air stream is usually less than one-tenth of the regulated concentration in the steam. An independent risk assessment study conducted for the Alkyl Amines Council of the American Chemical Society determined that when DEAE was properly applied to a boiler system, the concentrations were consistently below 10 ppb in room air humidified with DEAE-treated steam and 100 ppb of DEAE was an acceptable air concentration.<sup>54</sup>

### HEALTH RISKS OF CHRONIC EXPOSURE TO CORROSION-INHIBITING AMINES

Animal studies have been conducted to observe chronic exposure to neutralizing amines. No significant increase in the incidence of tumors was seen in two strains of mice, one strain of rats, and one strain of hamsters that were tested for carcinogenicity by oral administration of morpholine. Morpholine inhalation exposure in rats did not increase the incidence of tumors over that in controls and no data were available from studies in humans on the carcinogenicity of morpholine. The World Health Organization (WHO) identifies morpholine as “not classifiable as to its carcinogenicity to humans.”<sup>35</sup> NIOSH established an immediately dangerous to life or health (IDLH) concentration for morpholine of 1400 ppm.<sup>36</sup>

Under certain conditions, it is theoretically possible that DEAE (or related compounds) in boiler water may be converted to nitrosamines, which are suspected human carcinogens. No experimental evidence exists to indicate whether this occurs.<sup>37</sup> In a 14-week study in which rats were exposed to 0, 11, 25, or 76 ppm DEAE, temporary signs of mild to moderate respiratory irritation were found to be dose dependent and the no-observed-effect-level was found to be 10 ppm. There were no signs of any systemic toxicity.<sup>38</sup> DEAE has a NIOSH IDLH of 100 ppm.<sup>36</sup>

On the basis of animal toxicity studies, the principal health hazard from accidental exposures to morpholine is a moderate to severe irritation/corro-

sion of the eyes, skin, and mucous membranes, exposure to appreciable concentrations of morpholine vapors can result in irritation to the eyes, nose, and throat, and may produce temporary and reversible hazy or blurred vision. These symptoms disappear when exposure to morpholine is terminated. Adequate ventilation should be provided where a large quantity of product is exposed, or where mists or vapors are generated.

Conaway<sup>39</sup> conducted a study to evaluate the subchronic toxicity of morpholine in Sprague-Dawley rats to help further define potential long-term effects of lower concentrations, and to determine a maximum tolerated dose (MTD). The inhalation toxicity of 25, 100 and 250 ppm morpholine was investigated by 6 hr/day, 5 day/week exposures for 13 weeks. A maximum tolerated dose for a rat 2-year chronic morpholine study was established at 150 ppm on the basis of the data.

A similar study of morpholine was conducted using Sprague-Dawley rats at exposure concentrations of 0, 10, 50, and 150 ppm for 6 h per day, 5 days per week, over a period of 104 weeks. Gross pathology, and histopathology were normal in the exposed groups and comparable to the control animals. There were no exposure-related adverse changes any internal organ or tissue. The incidences of neoplasia were comparable among all groups (including controls), and were typical for the strain and age of rat used in this study. The results of this chronic exposure study demonstrated that morpholine is neither carcinogenic nor systemically toxic although these exposures did result in local (ocular, nasal, and dermal) irritation, consistent with the known irritation properties of morpholine. At the reported levels of the present occupational and environmental exposures, morpholine does not seem to create any significant risk of systemic toxic effects. Local effects (irritation) of the eyes and respiratory tract may occur in non-controlled occupational and incidental exposures to high concentrations of airborne morpholine, and skin irritation may result from contact with liquid (even diluted) morpholine.<sup>40</sup>

Cyclohexylamine is suspected to have chronic toxicity as an animal or human mutagen although the ACGIH Threshold Limit Value (TLVs<sup>®</sup>) Appendix A4 states that it is 'Not Classifiable as a Human Carcinogen'. CHA is not listed on National Toxicology Program (NTP), International Agency for Research on Cancer (IARC) or OSHA lists as a cancer-causing agent. The chemical is well known to be pharmacologically active, having sympathomimetic activity.<sup>41,42</sup> However, no data are available on human health risks associated with long-term, low-level airborne exposure to these amines and data to support that CHA is a suspected teratogen, mutagen, and carcinogen are inconclusive.

### REGULATION OF NEUTRALIZING AMINES

The criteria for regulation of neutralizing amines in steam boiler systems falls within environmental evaluation criteria for the workplace. The federal agencies responsible for these regulations are (1) NIOSH for recommended exposure limits (RELs), (2) ACGIH for Threshold Limit Values (TLVs<sup>®</sup>), and (3) OSHA for permissible exposure limits (PELs).

The OSHA regulates the maximum PEL's in humidified air for two of the three chemicals: diethylaminoethanol and morpholine promulgated for the protection of industrial workers. They are not intended to protect members of the general public, which may include children, the elderly, those in ill health, and others who may be particularly sensitive to the effects of these substances. NIOSH RELs relate to the prevention of occupational disease.<sup>37</sup> The ACGIH has published threshold limit values (TLV's) for all three neutralizing amines. The limits are slightly different; the PELs for these chemicals are based on an 8-h day and 40-h week.<sup>36,43,44</sup>

A time-weighted average (TWA) exposure is the average airborne concentration of a substance during a normal 8–10 h workday. In relation to the establishment of an 8 h time weighted average (TWA) limit value (average exposure on the basis of a 8 h/day, 40 h/week work schedule) the key

study was taken to be that of Lynch et al.<sup>44</sup> Using the 1983 summary report by NIOSH of the pathology seen in this study, 25 ppm was a Lowest Observed Adverse Effect Level (LOAEL). In order to minimize irritation symptoms, a 15-min STEL of 10 ppm is recommended.<sup>44</sup>

Short-term exposure limits (STEL) supplement the TWA where there are recognized toxic effects from higher exposures over the short-term. A STEL is defined as a 15-min TWA exposure which should not be exceeded at any time.<sup>45</sup>

The FDA has approved morpholine, cyclohexylamine, and diethylaminoethanol for use in steam boilers whose steam comes in contact with food except for milk and milk products. The Code of Federal Regulations 21 CFR 184.1139<sup>46</sup> allows maximum levels of 10 ppm for morpholine and cyclohexylamine, 15 ppm for DEAE, and 3 ppm for octadecylamine. No Federal government regulations exist governing the use of DEAE or other amines in direct steam humidification systems. All existing standards are based on ingestion not inhalation. It has been a convention in the water treatment industry to follow FDA limits for amine levels in steam used for other purposes. The FDA allows 20 ppm total amine when any or all are used in combination, provided that individual limits are not exceeded.

The FDA allows only the use of ammonium hydroxide in processing plants in which treated steam contacts dairy products. Ammonium hydroxide is also included in the U.S. Department of Agriculture's (USDA) list of 'safe and suitable ingredients'. Ammonium hydroxide is a substance affirmed as 'generally recognized as safe' (GRAS) at 21 CFR 184.1139.<sup>46</sup> FDA permits its use as a leavening agent, a pH control agent, a surface-finishing agent, and as a boiler water additive. The OSHA has set a 15-min exposure limit for gaseous ammonia of 35 ppm by volume in the environmental air and an 8-h exposure limit of 25 ppm by volume.<sup>47</sup>

However, OSHA, ACGIH, and the FDA have established the allowable concentrations in air as 20 ppm for morpholine; 10 ppm for CHA and 10 ppm for DEAE based on an 8 h

day and 40 h week. The ACGIH Threshold Limit Values (TLV) are the same as the PELs for these compounds. Where steam is used for sterilization of surgical instruments, the American Society for Hospital Central Service Personnel (ASCHSP) has published guidelines for allowable amine concentrations. The ASCHSP guidelines also follow FDA limits for permissible amine levels in treated steam. Many jurisdictions encourage management to follow whichever are the more protective criteria for their operation (Table 1).

The Occupational Safety and Health Administration (OSHA Hazard Communications Standard 29 CFR 1910.1200)<sup>50</sup> states that employees have both a need and a right to know the hazards and identities of the chemicals they are exposed to in the work place. Under HCS, if a "Subpart-Z" chemical exists in the workplace, the employee must be warned of the exposure, regardless of the level of the concentration and the degree of compliance with "safe" exposure limits. HCS 29 CFR, Subpart Z lists PELs for only two out of four common corrosion-inhibitor chemicals, DEAE (10 ppm) and morpholine (20 ppm). Both are subject to the HCS rules and regulations. Clarification letters to HCS indicate that HCS does not apply to the general public and employees who may be incidentally exposed to the chemicals in trace amounts from the humidification system.

The National Research Council (NRC) has established acute exposure guideline levels (AEGs) 1–3 for cyclohexylamine over a period of 8 h of 1.8 ppm, 2.7 ppm, and 9.5 ppm; the selection of these levels was based on a comprehensive study of Sprague-Dawley rats.<sup>21</sup> AEG-1 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic, non-sensory effects that are reversible and not disabling. AEG-2 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious,

Table 1. Comparison of chemical additive regulations for steam versus milk or milk products.

Neutralizing amine	Max. conc. in steam (ppm) that contacts food or food products (FDA 21 CFR 173.310) <sup>48</sup>	Max. conc. of amine (ppm) in indoor air (OSHA 1910.1000 PEL) <sup>49</sup>	Max. conc. of amine (ppm) in indoor air ACGIH (TLV)	Limitations based on a TWA exposure of 8 h mg/cubic meter of air (OSHA)	FDA GRAS Standards – Title 21 CFR 184.1139 <sup>46</sup>
Cyclohexylamine (CHA)	Not to exceed 10 ppm in steam	Not regulated	10	40	
Morpholine	No milk or milk products Not to exceed 10 ppm in steam	20	10	70	
Diethylaminoethanol (DEAE)	No milk or milk products Not to exceed 15 ppm in steam	10	2	50	
Octadecylamine	No milk or milk products Not to exceed 3 ppm				
Ammonium hydroxide (NH <sub>4</sub> OH)	No milk or milk products				No Limitations in steam, except not used in excessive amounts; OK with milk or milk products

long-lasting adverse health effects or an impaired ability to escape. AEGL-3 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life threatening health effects or death. No AEGL levels have been established for morpholine or DEAE.<sup>21</sup>

The USDA no longer issues separate regulations for meat, poultry, egg and fish processing plants under its jurisdiction. These limitations were previously listed under older USDA guidelines, as “G6” and “G7” compounds.<sup>51</sup> These older USDA limitations have all been replaced by the limits found in Title 21, Sections 173.310<sup>48</sup> and 184.1139<sup>46</sup> of the Code of Federal Regulations. 21 CFR 173.310<sup>48</sup> lists the various boiler water additives, approved by the FDA, for use in the preparation of steam, when the steam will contact food or food packaging. This regulation also spells out the conditions where these approvals are applicable.

#### MEASUREMENT AND MONITORING OF CORROSION-INHIBITING AMINES

Measurement of CHA concentration  
The water used to generate steam for humidification originates in the

condensate holding tank. If corrosion inhibitors are needed, the condensate tank is infused with a small amount of makeup water mixed with the neutralizing amines. High-performance liquid chromatography (HPLC) or gas chromatography can be used to directly measure amine concentrations in steam samples upstream from the point of steam release into ambient air; however, they are complex and time-consuming procedures. CHA concentration can be approximated using a material balance calculation under the assumption that there is no significant internal source of humidity, no internal CHA source, and no significant internal removal of CHA. This approach does not take into account the internal removal of CHA through sorption and other unknown means.

A simple mass balance calculation (such as that used by Edgerton<sup>29</sup>) for DEAE, CHA and morpholine shows for example, that if the room condition is maintained at 75 8F and humidity at 50% the steam concentration would need to be over 1000 ppm for CHA, 1600 ppm for DEAE, and 2000 ppm for morpholine in order to reach OSHA PELs. Studies conducted by Lao<sup>16</sup> and Edgerton<sup>29</sup> indicate that the concentration values of these

amines in room air are in parts per billion, far below the acceptable levels.

CHA concentration is positively associated with the amount of humidification and the CHA concentration in the steam, and negatively associated with the raw air temperature and humidity decreases of the room air after heating and humidifying. Fluctuations in humidification are small, but the design of some steam systems can greatly affect CHA concentration in steam. Material balance can be used for real-time modeling if the necessary variables are constantly monitored and the effect of internal removal is known.

#### CAREFUL MAINTENANCE, CONTROLS AND MONITORING

The feed rates of neutralizing amines are controlled in the field by in-plant testing for condensate pH. When maintained in a slightly alkaline range (7.5–9.0 pH), condensate will be relatively non-corrosive to system metals. However, maintaining pH in this range is no guarantee that amine levels in the steam are within acceptable limits for a regulated application. When it is necessary or desirable to determine if amine levels are in compliance with

government regulations or published guidelines, laboratory analysis of the steam is required. To assure accurate results from a laboratory amine analysis, care must be taken to follow very specific procedures for collection and shipment of steam samples.

When corrosion-inhibiting amines are added to boiler water using proper techniques and at concentrations required to prevent condensate system corrosion, studies have shown that the amine level in the steam-humidified air falls well below the PEL for the amine.

Grattan et al.<sup>19</sup> describes steam humidification tests conducted by Nalco for commonly applied amines under controlled conditions. It has determined that concentrations in room air normally are well below prescribed federal limits if sound application techniques are followed. Even when the concentration of morpholine in the steam was increased to 64.8 ppm, the airborne concentration in the humidified air remained as low as 0.018 ppm, a level far in excess of that required for condensate system corrosion inhibition; this is again far below the amine PEL.<sup>19</sup>

The recommendations from the Nalco study<sup>19</sup> discussed by Grattan included continuously monitoring for corrosion problems and process leaks in steam/condensate systems. The entire system should be sampled at multiple locations to determine system conditions. Samples should be cooled to below 90 °F to prevent flashing off the dissolved gases and amines. Condensate samples should be tested for pH, conductivity, corrosion products, dissolved oxygen, and carbon dioxide. The presence of other contaminants should also be evaluated. These might include water hardness, silica, and organics, and iron and copper levels.

The methods used to add corrosion inhibitors to boiler systems appear to affect the risk of toxic exposure. Although average amine concentrations in humidified air can be kept low, it is extremely important that volatilizing amines only be used with well-maintained automatic dosing devices to prevent toxicity. The study reported by Lao<sup>16</sup> supports the use of a material balance approach to identify the additive feed mechanism as the

control point most likely to influence the occurrence of a toxic event arising from humidification with steam containing volatilizing amine corrosion inhibitors. Lao notes that the automatic feed device should be carefully maintained and manual dosing of the boiler should not be allowed in the event that the automatic dosing equipment is inoperable. This conclusion is also supported by Malaiyandi et al.<sup>52</sup> His research shows that where intermittent manual dosing is used rather than constant mechanical dosing, the level of corrosion inhibiting amines in condensate can rise over 10,000 ppm for periods of more than 10 h.

In order to assure compliance with FDA, OSHA, and ACGIH guidelines regarding the levels of amine permissible in steam-humidified room air, minimize corrosion in steam and condensate systems, and prevent unscheduled outages and optimize boiler efficiency by reducing the corrosion byproducts returned to the boiler via the condensate return system, it is critical to monitor the proper feed, dosage, and control of amine condensate corrosion inhibitors. Feed rate controls include tank level sensors, pump controllers and flow sensors. pH and conductivity of the steam can be measured using on-line analyzers. Coupons or sample ports placed strategically, allow for frequent checking for corrosion products. The point of chemical injection should be located in an accessible area. Coupons, however, allow water to be lost from the system, and oxygen is added, every time the coupon rack is opened. Other control techniques include continuous feeding of chemicals via metered feed pumps; not permitting slug feeding; daily checking and adjustment of the feed rates.

## CONCLUSION

The most common neutralizing amines used in steam boiler humidification systems in health care facilities are cyclohexylamine (CHA), diethylaminoethanol (DEAE), and morpholine. Used individually or in combination, they are capable of preventing

corrosion in systems of various lengths. It is fairly easy to control their indoor air concentrations well below accepted exposure limits through the use of standard operating procedures and practices.

The Environmental Protection Agency (EPA) has issued strong warnings regarding boiler chemicals.<sup>14,15</sup> Steam used for humidification is not ingested but inhaled. Since no Federal government regulations exist governing the use of amines in direct steam humidification systems (other than in the food industry in which all the existing standards and guidelines are based on ingestion) the water treatment industry tends to follow FDA limits for amine levels in steam used for direct steam humidification systems for other purposes.

The literature is full of examples where the concentration of amines in the indoor air is measured in parts per billion (ppb) versus parts per million (ppm), the measurement used by U.S. regulatory agencies for allowable concentrations in air. The evidence strongly suggests that the concentration of amines in indoor air where humidification is controlled using steam created with 'treated water' is negligible, far below the acceptable PEL levels currently adhered to for IAQ and not a health risk to building occupants when the chemical additives are injected automatically; in industry accepted concentrations; and monitored regularly per standard operating procedures.

The way in which corrosion inhibitors are added to boiler systems appears to affect the risk of toxic exposure. It is recommended that volatilizing amines be used in systems with well-maintained automatic dosing devices. Manual dosing should not be allowed when automatic dosing equipment is inoperable because of the possibility of human error. Investigators should consider applying the material balance calculations in the design of hospital steam humidification systems to avoid loss of the amine additive through volatilization. The material balance may be used for real time modeling if the appropriate variables are constantly monitored and the effect of internal removal is known.

Low ambient air amine concentration levels can be effectively managed with careful maintenance and monitoring, including metered introduction of the treatment chemicals into the steam system. Practical considerations to achieve low ambient air amine concentration levels include:

- Continuous feeding of chemicals via metered feed pumps
- Not permitting slug feeding
- Daily checking and adjustment of the feed rates
- Measure pH and conductivity using on-line analyzers
- Providing coupons and/or sample ports to enable frequent checking

Unfortunately, there is no standard that can protect anyone from a situation where standard operating procedures are not followed or from gross error in system operations. When corrosion-inhibiting amines are added to boiler water using proper techniques and at concentrations required to prevent condensate system corrosion, studies have shown that the amine level in the steam-humidified air falls well below the PEL for the amine. With careful monitoring of water chemistry, along with direct testing for amine levels in the humidified air space, and careful risk assessment operators of steam humidification systems can be assured that room air amine levels will be well below that necessary to cause adverse effects in humans.

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