Date: Wed, 18 Nov 1998 13:56:12 -0600
From: Meredith Brown <racer@lanl.gov>
Subject: Yelllow Alert: Trimethylamine Gas Released from Resin

Title: **Trimethylamine Gas Released from Resin**
1998-ID-INEEL-467

**Executive Summary:**
Three reactor auxiliary operators were exposed to higher than allowed levels of trimethylamine gas while recharging anion exchange resin.

**Lessons Learned Statement:**
MSDSs may not indicate product instability or breakdown products. Unwanted chemical changes may occur when product is kept in a temporary staging area for longer than anticipated. Inventory and storage control (e.g., time, temperature) may reduce or eliminate safety hazards. Safety hazards posed by trimethylamine gas may be reduced or eliminated by using an eductor.

**Discussion**:
On June 30, 1998, three reactor auxiliary operators were exposed to trimethylamine gas concentrations that were well above the Threshold Limit Value-Short Term Exposure Limit (TLV-STEL) (limit for a 15-minute exposure). The odor of trimethylamine gas is similar to ammonia. Operators were recharging an anion exchange resin bed in the INEEL's Advanced Test Reactor M-19 Bypass Demineralizer tank. The task had been successfully performed--without incident--several times a year for more than 30 years. The procedure they followed addressed known hazards and was written in accordance with the Material Safety Data Sheet (MSDS) provided by the resin manufacturer. Procedural controls were designed to prevent injuries from lifting the heavy (450-lb) barrels or slipping if resin beads were spilled on the floor. However, the MSDS gave no indication of product instability or breakdown products such as trimethylamine gas. (The resin used was Type 1 Anion Exchange Resin manufactured by ResinTech, Inc. This type of resin is also supplied by numerous other manufacturers.) The procedure called for emptying nine barrels, each containing 7 cubic feet of anion resin, into an open resin addition tank. The tank is located in the Primary Coolant Pump Motor Area. Typically, resin is staged in the area for no more than 24 hours before the procedure. The resin is stored for up to 1 year at the Test Reactor Area (TRA) 669 warehouse. In the procedure, the lid of the first barrel is removed, the barrel is lifted approximately 5 feet above the floor using a barrel hoist, and then the barrel is manually upended to empty the resin into the tank. Each barrel takes about 90 seconds to empty once it is upended. Barrels continue to be opened, lifted, and upended until the tank is full.

When the first barrel was opened, the operators noticed an ammonia odor. However, when the resin was emptied into the tank, the operators realized the odor was much stronger. When a second barrel was opened and emptied, the odor was so strong during the last 20 seconds that the operators discontinued the job and sought technical assistance.

The Advanced Test Reactor Chemistry Coordinator and the Industrial Hygienist generated a Safe Work Permit that prescribed the use of full-face respirators equipped with an MSA

chemical cartridge to complete the job. Air sampling equipment measured the concentrations of trimethylamine gas in the workers' breathing zone while a third barrel of anion resin was emptied. Measurements revealed concentrations of trimethylamine on the order of 300 ppm, well above the ACGIH TLV-Time Weighted Average (TWA) of 5 ppm (limit for an 8-hour exposure) and the ACGIH TLV-STEL of 15 ppm for trimethylamine gas.

Measurements taken in the area approximately 10 minutes later showed that the concentrations of trimethylamine were no longer measurable. None of the workers exhibited any symptoms of respiratory problems and no medical treatment was necessary. The workers were cleared to return to work without any work restrictions.

**Analysis:**
Discussions with the resin manufacturer indicated that buildup of trimethylamine gas in the barrels is dependent upon the age of the resin and temperature at which the resin is stored. The anion resin had been staged in the primary Coolant Pump Motor Area for approximately 2 weeks. The three operating 2,000-horsepower pump motors raise temperatures in the area to between 110 and 130 degrees Fahrenheit. To determine whether staging the resin at elevated temperatures in the Primary Pump Motor room caused chemical changes in the resin, air samples were drawn from anion resin barrels stored at the Test Reactor Area warehouse. The level of trimethylamine gas in the breathing air zone with the lid removed was below the TLV limit of 5 ppm. However, levels at the surface of the resin and inside the resin containers were found to be equally high as that sampled in the Primary Pump Motor room. Levels of trimethylamine gas at the surface of the resin barrels quickly dissipated after opening the barrels, but increased as the sampling probe was pushed toward the bottom of the resin barrel. This measurement suggested that presence of trimethylamine vapors will be a continuing problem, but that the vapors can be easily drawn off by improved local ventilation when the barrels of resin are emptied into the resin fill tank. An engineering evaluation was performed. The manufacturer indicated that the optimum storage temperature for the resin is 40 degrees Fahrenheit, but the anion resin was stored at elevated temperature in the Primary Pump Motor room. The ion exchange capacity of the resin and level of trimethylamine gas are dependent upon both storage temperature and age of the resin. The normal storage temperature range for the resin to retain a 5-year shelf life is 40 to 90 degrees Fahrenheit. The engineering evaluation concluded that the resin should still be used.

A temporary field change to the procedure was developed and approved for completing addition of the remaining six barrels of resin staged in the Primary Pump Motor room. The field change specifies use of a portable exhauster unit to ventilate the barrels of resin when the lids are removed and when the barrels of resin are emptied into the resin fill tank. As specified in a Safe Work Permit, workers will be required to wear breathing air protection until air samples in the breathing air zone confirm that the portable air exhauster is effective in protecting the workers.

Air sampling results taken during this next evolution will be used in developing a recommendation for making a permanent change to the procedure for future anion resin additions to the ATR Bypass Demineralizer. If the portable air exhauster successfully protects the worker without need for supplied airline respirator protection, it will be used in the future. If supplied airline respiration protection is required (even with the portable air exhauster in use),

the resin addition system will be modified to use an eductor. An eductor is used at the ATR Warm Waste Treatment Facility and should work equally well for the ATR Bypass Demineralizer system. To use an eductor, the product would be turned into a water slurry and transferred to the receiving container using a hose or pipe. Use of an eductor will help in three areas. First, since trimethylamine is miscible in water, it will significantly reduce the amount of gas exposure to the operators. Second, it will eliminate potential safety hazards from lifting and handling the heavy drums of resin. Finally, it will reduce safety hazards associated with potential resin spills.

**Recommended Actions:**

1. Store product according to the manufacturer's recommendations (for resin, at 40-90 degrees Fahrenheit).

2. Fill resin barrels with water and use an eductor to charge the resin tanks.

3. Use a portable air exhauster to protect workers. If necessary, also use supplied airline respirator protection.

Originator: Lockheed Martin Idaho Technologies Company, Test Reactor Area
Contact: David R. Quigley, (208) 526-0046, dq1@inel.gov; Alan Johnson, (208) 533-4555, AJQ@inel.goc
Authorized Derivative Classifier: Dale Claflin
Reviewing Official: Dale Claflin
Keywords: trimethylamine gas, MSDS, anion, resin
Priority Descriptor: YELLOW/Caution
Reference: ORPS Report: ID--LITC-ATR-1998-0014