ENVIRONMENTAL ASPECTS OF AFFF AND AR-AFFF

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INTRODUCTION

Debates over the effectiveness and environmental safety of different foam agents are confusing. To decipher the rhetoric, it helps to start from the beginning. There is a great deal of information – and unfortunately some misinformation – regarding the use of foam agents for flammable liquid firefighting. The following information should help when making decisions regarding the purchase and use of Class B foams.

HISTORICAL PERSPECTIVE

Understanding the history of the regulations affecting the use of certain solvents in the making of aqueous film-forming foam (AFFF) and alcohol-resistant, aqueous film-forming foam (AR-AFFF) helps to explain the current situation. Until 1990, most foam manufacturers used a solvent in their formulations known as diethylene glycol butyl ether, most commonly known by the trade name of Butyl CARBITOL® or DB.

Butyl CARBITOL is part of a family of chemicals known as glycol ethers which are commonly used to control the drying rate of paints, coatings, and inks. Because these chemicals are designed to evaporate into the air, the Environmental Protection Agency (EPA) included all glycol ethers on the Hazardous Air Pollutants (HAPS) list in the Clean Air Act Amendments (CAAA) of 1990. At that time, glycol ethers also became subject to reporting requirements under Section 313 of the Emergency Planning and Community Right to Know Act (EPCRA) and the Superfund Amendments and Reauthorization Act (SARA) Title III. In making this ruling, the EPA did not test the glycol ethers, but rather placed the entire chemical family into the default category based on the toxic chemistry of the Methyl and Ethyl CELLOSOLVE® homologues. Chemicals in the default category are automatically assigned a Reportable Quantity (RQ) of one pound (0.45 kg). That meant that the release of one pound (0.45 kg) or more of any glycol ether (having the general formula, R-$(OCH2CH2)_n$-OR'; where n = 1, 2 or 3, R= alkyl or aryl groups, R' = R, H) into the environment was a reportable event to the EPA.

In June of 1995, the EPA issued a final rule adjusting the reportable quantities (RQ) for glycol ethers. This rule eliminated the one-pound (0.45 kg) default quantity and assigned a no reporting requirement for glycol ethers. Consequently, there is no reportable quantity for <u>the release</u> of any of the glycol ethers used as solvents in any foam product manufactured today.

In response to the CAAA of 1990, at least two manufacturers of foam concentrate reformulated their products to use a solvent that was not on the reporting list. This solvent is Dipropylene Glycol Monomethyl Ether (DPM) which is a propylene oxide based glycol ether. Ironically, an actual comparison of the environmental data from material safety data sheets clearly shows that DPM has no environmental advantage over DB. Nevertheless, these manufacturers have continued to claim that their foams are more environment-friendly even though it has been shown that the propylene glycol-based solvents are less biodegradable than DB. For example, the 20-day biodegradation (BOD/COD) of DB is 85%, while the 20-day biodegradation of DPM is only 32%.

The EPA still requires any facility that has <u>in storage or other use</u> 10,000 pounds (4536 kg) of any reportable chemical to file a "Form R" of SARA Title III. This includes the DB that is used as a solvent in firefighting foams. To determine if your facility needs to file Form R, first determine the number of gallons of foam you have in inventory and then multiply that number by the amount of DB contained in each gallon. The amount of DB contained in a gallon of foam can be found on the MSDS for the foam product.

ENVIRONMENTAL METERS OFAFFF AND AR-AFFF

The U.S. EPA regulates the properties of materials released into the environment. Some of these properties include foaming, oxygen demand (BOD and COD) and aquatic toxicity (LC_{50} and EC_{50}).

AFFF and AR-AFFF consist of essentially the same ingredients. These typically include fluorosurfactants, hydrocarbon surfactants, solvents, inorganic salts, corrosion inhibitors, water; and in the case of AR-AFFF, a polymer which is typically a polysaccharide. All of the ingredients will biodegrade, some more completely than others. But currently, no foam containing a fluorosurfactant is 100% biodegradable, including fluoroproteins and film-forming fluoroproteins.

In considering the overall environmental picture, there are four categories that must be considered: toxicity, biodegradability, nutrient loading and treatability.

Toxicity

Toxicity testing relates the dose-response severity of a product on a population over a period of time. Toxicity can be expressed as either an LC_{50} or an LD_{50}. An LC_{50} is a calculated concentration of a substance in air, exposure to which, for a specified length of time, is expected to cause the death of 50% of an entire defined experimental animal population. An LD_{50} is a calculated dose of a substance that is expected to cause the death of 50% of an entire defined experimental population. It is determined from the exposure to the substance by any route other than inhalation. The number that precedes the LC or LD symbol represents the number of hours or days the exposure was conducted. As an example, a notation of $96LC_{50}$ would mean that the lethal concentration for 50% of the test specimens occurred in 96 hours.

It is important to test for toxicity at various levels of the food chain to ensure that a substance is not toxic to a species that represents a food source for another species present in the same environment. It is not sufficient to test only species at the top of the food chain when the organisms they feed on die from the same chemical contamination.

Because most firefighting foams enter an ecosystem via water, the accepted method for measuring toxicity is by using a series of tests that involve microorganisms, algae or various species of fish. This is done by analyzing how long certain species survive after having been dosed with a specific amount of chemical. The toxicity is expressed as a LC_{50} concentration. The higher the number, the less toxic the chemical is to the species. Typical ratings are as follows:

< 0.1 mg/L	(0.0007 oz./gal.)	Extremely Toxic
< 1.0 mg/L	(0.007 oz./gal.)	Highly Toxic
1-10 mg/L	(0.007-0.07 oz./gal.)	Moderately Toxic
10-100 mg/L	(0.07-0.7oz./gal.)	Slightly Toxic
100-1000 mg/L	(0.7-7.0 oz./gal.)	Practically Non-Toxic
>1000 mg/L	(7.0 oz./gal.)	Insignificant Hazard

For example, consider a chemical that has a LC_{50} of 1 mg/L (or 1 part per million). One gallon of this chemical spilled in a river and diluted with one million gallons of water could potentially kill 50 percent of the fish in the immediate area of the spill.

Although firefighting foams are generally discharged on land, they could reach a waterway via runoff into a stream or the foam can migrate through the soil into the groundwater with the possible release to a waterway. The potential for this to happen is a function of the volume of firefighting foam discharged, the soil type, and the depth and volume of ground water. As a measure of environmental responsibility, steps should be considered to abate the flow of the foam/water solution to the ground water. An area where this has become a recognized problem is at training sites where the use of foam has gone on for a long time without containment and where the water table is close to the surface.

Biodegradability

A second area of consideration is biodegradation, the measure of how completely a substance breaks down in the environment. The biodegradability of a chemical is expressed as a percentage determined by dividing the BOD by the COD and multiplying by 100. The chemical oxygen demand, COD, is the amount of oxygen needed to completely break a chemical down to its most oxidized state (for example: CO_2, H_2O, and HF) and is a measured analytical value. The biochemical oxygen demand, BOD, is an empirical test that measures a relative oxygen requirement. This test measures the oxygen required for the biochemical degradation of organic and inorganic material. The test may also measure the oxygen required to oxidize reduced forms of nitrogen. For firefighting foams, this test is conducted for 20 days as opposed to the usual five days for other chemicals because the bacteria requires a longer time to acclimate to the test solution of the foam. As stated earlier, biodegradation is the percentage ratio of BOD/COD. If that resulting number is higher than 50%, the chemical is determined to be readily biodegradable. If it is below 15%, the chemical is determined to be not biodegradable. The U.S. Mil Spec F24385F requires all approved AFFF on the QPL have a minimum of 0.65 (65%).

If BOD / COD > 50%, then biodegradable

If BOD / COD < 15%, then NOT biodegradable

Nutrient Loading

Nutrient loading is a third area of concern. This can become an issue with firefighting foams if the foam is allowed into a waterway. The two biggest contributors to nutrient loading are nitrogen and phosphorous. Organic carbon must also be considered, however there is usually enough organic material occurring in natural waters that the minimal amounts of organic carbon from firefighting foams does not upset the balance of nature. AFFF and AR-AFFF do not contain appreciable amounts of either nitrogen or phosphorous. Nutrient loading is not considered an environmental attribute of AFFF or AR-AFFF. However, protein foams do contain a considerable quantity of organic nitrogen. Release of a protein-based firefighting foam into an ecosystem could result in a nutrient overload or shock to that system.

Treatability

The last area to consider is the treatability of a firefighting foam as it enters a wastewater treatment facility. Since most everything in a firefighting foam is biodegradable, an activated sludge wastewater treatment facility provides an acceptable means to dispose of firefighting foams after use. Foaming is the main concern for any activated sludge treatment facility when accepting a foam solution. When too much firefighting foam is sent to a waste treatment facility, the action of the aeration basin will cause foaming. When foaming occurs, the activated sludge will float and be discharged by the plant. Regardless of the reason, foaming in a waste discharge stream is a violation of local, state and federal water and wastewater guidelines and is cause to revoke a discharge permit.

To prevent foaming, a metered discharge of the firefighting foam solution must be used. If hydrocarbon fuels are present in the waste resulting from the use of firefighting foams, the use of an oil/water separator is recommended. The oil fraction should be handled in accordance with local, state and federal regulations. When this pretreatment is not possible, special considerations apply. A qualified individual should evaluate these wastes to determine if volatile flammable materials are present at hazardous concentrations and review the applicability of sewer code restrictions. If volatile materials in the waste present an explosion hazard, these wastes should not be discharged to the waste treatment facility. Such wastes should receive further treatment or they should be incinerated by a facility designed to handle such wastes.

If flammable materials are not present and a qualified individual has determined that the waste meets sewer codes, the waste may be metered into the sewer that flows into a waste treatment system. It is essential that these wastes be metered into the system at a sufficiently slow rate so that the waste will not cause foaming in the aeration basin. This rate will be determined by the capacity of the waste treatment plant and will be unique to that plant. Discharges must follow all local, state and federal regulations. Since these regulations may vary, consult the necessary authorities before discharge. Waste treatment authorities must also be consulted to determine the discharge flow into the facility so that appropriate discharge rates can be determined.

The recommended discharge rates for AFFF's and AR-AFFF's are as follows…

AR-AFFF (1/3 or 3/3)	=/< 25 mg/liter of sewage
AR-AFFF (3/6)	If used at 3%: 50 mg/L (0.35 oz./gal.) of sewage
	If used at 6%: 25 mg/L (0.175 oz./gal.) of sewage
AFFF	If used at 1%: 25 mg/L (0.175 oz./gal.) of sewage
	If used at 3%: 50 mg/L (0.35 oz./gal.) of sewage
	If used at 6%: 100 mg/L (0.7 oz./gal.) of sewage

If foaming occurs or there is a need to treat more foam/water solution at a faster rate, antifoam agents may be added to the foam/water waste flow in the treatment facility. These antifoam agents may be obtained from the following suppliers.

- Dow Chemical
- General Electric
- Henkel
- Ross Chem Inc
- Union Carbide
- Wacker Silicones

The amount of antifoam required is based on the volume of foam/water solution being treated. Therefore, testing a representative sample of the foam/water solution is recommended prior to application.

CONCLUSION

The purchase and use of firefighting foam agents can sometimes be complicated. However, when a flammable liquid fire breaks out, AFFF's and AR-AFFF's are very effective firefighting weapons. The judicious use of these products will help ensure their continued availability in the future.

GLOSSARY

Biodegradability: The degree to which chemicals are broken down by microorganisms in the environment.

BOD: Biochemical Oxygen Demand. Grams of oxygen used/gram of test material in a specified number of days (useful for determining biodegradability).

CAAA: Clean Air Act Amendments (of 1990).

CERCLA: Comprehensive Environmental Response Compensation and Liability Act.

COD: Chemical Oxygen Demand. The amount of oxygen required to completely break down a chemical to its most oxidized state (useful for determining biodegradability).

DB: Diethylene Glycol as identified by Chemical Abstract Service (CAS) Number 112-34-5.

DPM: Dipropylene Glycol Methyl Ether as identified by Chemical Abstract Service (CAS) Number 34590-94-8.

EC_{50}: The effective concentration of a material needed to cause a 50% reduction in the oxygen uptake rate.

EPA: The U.S. Environmental Protection Agency.

EPCRA: Emergency Planning and Community Right to Know Act.

Form R: The form used to report quantitative information for the site on releases, transfers, treatment and waste minimization for the covered chemical or category.

HAPS: Hazardous Air Pollutants.

IC_{50}: The Inhibitory Concentration needed to cause a 50% reduction in the growth rate of algae over a 96-hour period.

LC_{50}: The Lethal Concentration needed to cause 50% mortality over a selected period of time.

LD_{50}: The Lethal Dose needed to cause 50% mortality over a selected period of time.

MSDS: Material Safety Data Sheet.

Nutrient Loading: Nitrogen or phosphorous loading of a waterway causing algae bloom.

QPL: Qualified Products List.

SARA Title III: Superfund Amendments and Reauthorization Act Title III.

Solvent: A substance, usually a liquid, capable of dissolving other substances.

Toxicity: The quality of being poisonous.

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