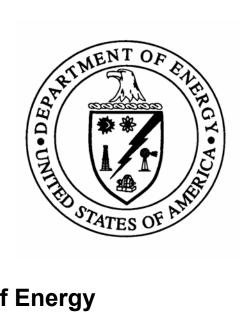


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## **DOE HANDBOOK**

# CHEMICAL MANAGEMENT (Volume 1 of 3)



U.S. Department of Energy Washington, D.C. 20585

**AREA SAFT** 

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Page / Section	Change
p. iv / Table of Contents	Added reference to new Appendix D
p. 4 / Acronyms and Abbreviations	Added new acronyms consistent with new
	Appendix D
p. D-1 / Appendix D	New appendix added: Appendix D, Life Cycle
	Management of Shock Sensitive Chemicals
Throughout	Page numbers updated and "intentional blank"
	pages deleted.

#### Foreword

DOE

This non-mandatory Handbook is designed to assist Department of Energy (DOE) and contractor managers in assessing chemical hazard management and is approved for use by all DOE Components and their contractors. Examples of best practices and real life examples needed to institute high-quality chemical management within the context of a site's Integrated Safety Management System (ISMS) are provided.

ISM

DOE P 450.4 DEAR DOE Policy 450.4, "Safety Management System Policy," and Chapter 9 of Title 48 of the Code of Federal Regulations (CFR), Department of Energy Acquisition Regulation (DEAR), call for systematic integration of safety into management and work practice at all facets of work planning and execution. Material acquisition, handling, and final disposition are some of the key elements of management systems to which the Integrated Safety Management (ISM) Core Functions are applied. Consideration of environment, safety, and health risks for these elements is, in principle, the same for all hazards, whether chemical, radiological, or physical. Therefore, a quality chemical management program is merely part of a site's ISMS and need not call for new or additional requirements.

This Handbook is comprised of two Volumes. Volume 1 contains the core material. Chapter 1 presents a discussion of how chemical management fits into ISM. The ISM Core Functions (Define the Scope of Work, Analyze the Hazards, Develop and Implement Hazard Controls, Perform Work within Controls, and Provide Feedback and Continuous Improvement) provide the structure needed to ensure all work activity is undertaken safely.

**OSHA** 

**EPA** 

DOE-STD-3009-94

DOE O 440.1A

A number of DOE, Occupational Safety and Health Administration (OSHA), and Environmental Protection Agency (EPA) directives, standards, and requirements address chemical management both directly and indirectly. DOE examples include DOE-STD-3009-94, "Preparation Guide for U.S. Department of Energy Nonreactor Nuclear Facility Safety Analysis Reports," and DOE Order 440.1A, "Worker Protection Management for DOE Federal and Contractor Employees." Chapter 2 discusses the elements of a quality chemical management program. The elements are presented in a logical sequence and each section includes information on applicable DOE, OSHA, and EPA directives, standards, and requirements.

The Appendixes to Volume 1 contain sample lines of inquiry, which may be used for ISM verification, lessons learned to allow readers an opportunity to learn from the experiences of their peers, and a listing of program resources.

ACC Responsible Care

MSV pilot

Supplemental to the core Handbook, Volume 2 presents site approaches to chemical management programs from across the DOE complex and the chemical industry to illustrate chemical management program implementation. For example, the American Chemistry Council's (ACC) Responsible Care ® program was found to be a useful tool in chemical management at a recent Management System Verification (MSV) pilot project at the Hanford Plutonium Finishing Plant (PFP).

The Handbook is designed to serve as a general reference for chemical management.

It is formatted to allow quick and easy access to its content and useful references. For example, the oversized left margin contains annotations to key points presented in the text. In addition, in the electronic version, these annotations are active links which allow navigation to web sites for more detailed information on specific topics. An expanded version of this document with the most recent collection of best practices and lessons learned will be maintained on the DOE Chemical Management

Web Site at http://www.eh.doe.gov/web/chem\_safety/.

EH-5 Chemical Management Web site

Feedback

We invite everyone to share their experiences by submitting exemplary chemical management practices or lessons learned via our Web Site Feedback page at <a href="http://www.eh.doe.gov/web/chem\_safety/">http://www.eh.doe.gov/web/chem\_safety/</a>. In addition, beneficial comments on this Handbook (recommendations, additions, deletions) and any pertinent data that may improve this document should be sent to: Director, DOE Office of Worker Health and Safety (EH-5), U.S. Department of Energy, Washington, D.C. 20585, by letter or by sending the self-addressed Document Improvement Proposal Form (DOE F 1300.3), available at <a href="http://www.explorer.doe.gov:1776/pdfs/forms/1300-3.pdf">http://www.explorer.doe.gov:1776/pdfs/forms/1300-3.pdf</a>

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## Glossary

The following definitions are based on existing DOE directives:

**Authorization Basis**—Safety documentation supporting the decision to allow a process or facility to operate. Included are corporate operational and environmental requirements as found in regulations and specific permits, and, for specific activities, work packages or job safety analyses.

**Contractor**—Any person under contract (including subcontractors or suppliers) with DOE with the responsibility to perform activities or supply services or products.

**Enhanced Work Planning**—A process that evaluates and improves the program by which work is identified, planned, approved, controlled, and executed. The key elements of enhanced work planning are line management ownership; a graded approach to work management based on risk and complexity; worker involvement beginning at the earliest phases of work management; organizationally diverse teams; and organized, institutionalized communication.

**Environmental Management System**—That part of the overall management system that includes organizational structure, planning activities, responsibilities, practices, procedures, processes, and resources for developing, implementing, achieving, reviewing, and maintaining the environmental policy.

**Facility**—The buildings, utilities, structures, and other land improvements associated with an operation or service and dedicated to a common function.

**Hazard**—A source of danger (i.e., material, energy source, or operation) with the potential to cause illness, injury, or death to personnel or damage to a facility or to the environment (without regard to the likelihood or credibility of accident scenarios or consequence mitigation).

**Hazard Analysis**—The determination of material, system, process, and plant characteristics that can produce undesirable consequences, followed by the assessment of hazardous situations associated with a process or activity. Largely qualitative techniques are used to pinpoint weaknesses in design or operation of the facility that could lead to accidents. The Safety Analysis Report (SAR) hazard analysis examines the complete spectrum of potential accidents that could expose members of the public, on-site workers, facility workers, and the environment to hazardous materials.

**Hazard Controls**—Design features; operating limits; and administrative or safety practices, processes, or procedures to prevent, control, or mitigate hazards.

**Integrated Safety Management Core Functions**—The core safety management functions for DOE P 450.4, "Safety Management System Policy," which are to: (1) define the scope of work; (2) analyze the hazards; (3) develop and implement hazard controls; (4) perform work within controls; and (5) provide feedback and continuous improvement. These functions are also identified in DEAR 48 CFR 970.5204-2(c).

**Integrated Safety Management System**—A Safety Management System to systematically integrate safety into management and work practices at all levels as required by DOE P 450.4, "Safety Management System Policy," and the other related Policies: DOE P 450.5 and DOE P 450.6.

Occurrence Report—A documented evaluation of an event or condition that is prepared in sufficient detail to enable the reader to assess its significance, consequences, or implications and to evaluate the actions being proposed or employed to correct the condition or to avoid recurrence.

**Performance Indicator**—Operational information indicative of the performance or condition of a facility, group of facilities, or site.

**Pollution Prevention**—The use of materials, processes, and practices that reduce or eliminate the generation and release of pollutants, contaminants, hazardous substances, and waste into land, water, and air. For DOE, this includes recycling activities.

**Risk**—The quantitative or qualitative expression of possible loss that considers both the probability that a hazard will cause harm and the consequences of that event.

**Safety Analysis**—A documented process to (1) provide systematic identification of hazards within a given DOE operation; (2) describe and analyze the adequacy of the measures taken to eliminate, control, or mitigate identified hazards; and (3) analyze and evaluate potential accidents and their associated risks.

Voluntary Protection Program—The Department of Energy Voluntary Protection Program (DOE-VPP), which promotes safety and health excellence through cooperative efforts among labor, management, and government at DOE contractor sites. DOE has also formed partnerships with other Federal agencies and the private sector for both advancing and sharing its Voluntary Protection Program (VPP) experiences and preparing for program challenges in the next century. The safety and health of contractor and federal employees are a high priority for the Department.

Work Planning—The process of planning a defined task or activity. Addressing safety as an integral part of work planning includes execution of the safety-related functions in preparation for performance of a scope of work. These functions include: (1) definition of the scope of work; (2) formal analysis of the hazards bringing to bear in an integrated manner specialists in both environment, safety and health (ES&H) and engineering, depending on specific hazards identified; (3) identification of resulting safety controls including safety structures, systems, and components, and other safety-related commitments to address the hazards; and (4) approval of the safety controls.

Work Smart Standards Process—The Work Smart Standards (WSS) process is used to reach agreement between DOE and its contractors with regard to the applicable standards to be followed for safe work. WSS was approved for use in January 1996 and issued as policy in DOE P 450.3, "Authorizing the Use of Necessary and Sufficient for Standards-Based Environmental, Safety and Health Management." The process for applying the WSS is described in DOE M 450.3-1, "The Department of Energy Closure Process for Necessary and Sufficient Sets of Standards."

## **Acronyms and Abbreviations**

ACC American Chemistry Council

ACGIH American Conference of Governmental Industrial Hygienists

ACIS Automated Chemical Inventory System

ARAC Atmospheric Release Advisory Capability

ASA Auditable Safety Analysis

ATSDR Agency for Toxic Substances and Disease Registry

BHI Bechtel Hanford Incorporated
BIO Basis for Interim Operation

BNL Brookhaven National Laboratory

CAMEO Computer-Aided Management of Emergency Operations

CERCLA Comprehensive Environmental Response, Compensation, and Liability Act

CFR Code of Federal Regulations

CGITS Cradle-to-Grave Information and Tracking System

CHEMTREC Chemical Transportation Emergency Center

CO2 Carbon Dioxide

CSTC Chemical Safety Topical Committee

DEAR Department of Energy Acquisition Regulation

DOE Department of Energy

DOE-VPP Department of Energy Voluntary Protection Program

DOT Department of Transportation
EA Environmental Assessment

EH-5 DOE Office of Worker Health and Safety

EIS Environmental Impact Statement

EM DOE Office of Environmental Management

EM&R Emergency Management and Response

EPA Environmental Protection Agency

EPCRA Emergency Planning and Community Right-to-Know Act

ES&H Environment, Safety and Health

EWP Enhanced Work Planning

FEMA Federal Emergency Management Agency

FEMIS Federal Emergency Management Information System

HASP Health and Safety Plan

HAZMAT Hazardous Materials

HEPA High Efficiency Particulate Air

HF Hydrogen Fluoride

HMIS Hazardous Materials Information System

HAZWOPER Hazardous Waste Operations and Emergency Response

ISM Integrated Safety Management

ISMS Integrated Safety Management System

ISO International Organization for Standardization

LDR Land Disposal Restriction

LOI Lines of Inquiry

MARPLOT Mapping Applications for Response and Planning of Local Operational Tasks

MIN Materials In Inventory

MSDS Material Safety Data Sheet

MSV Management System Verification

NaK Sodium Potassium

NEPA National Environmental Policy Act

NETO National Environmental Training Office

NFPA National Fire Protection Association

NIOSH National Institute for Occupational Safety and Health

NSC National Safety Council
OE Operating Experience

ORPS Occurrence Reporting and Processing System

OSHA Occupational Safety and Health Administration

PEL Permissible Exposure Limit
PFP Plutonium Finishing Plant

PNNL Pacific Northwest National Laboratory

PPE Personal Protective Equipment

RCRA Resource Conservation and Recovery Act

RMP Risk Management Plan RQ Reportable Quantity

SAR Safety Analysis Report

SARA Superfund Amendments and Reauthorization Act

SBMS Standards-Based Management System

SLG State and Local Guide

SME Subject Matter Expert

SNL Sandia National Laboratory

S/RIDs Standards/Requirements Identification Documents

SRS Savannah River Site

SSC System, Structure, or Component

TLV Threshold Limit Value

TQ Threshold Quantity

VPP Voluntary Protection Program

WSS Work Smart Standards

## **Introduction and Scope**

Why a DOE Chemical Management Handbook?

attributed to radiation.

Chemicals are ubiquitous in DOE's nuclear and non-nuclear operations. Given their wide application, it is not surprising that chemical incidents or exposures continue at a rate of approximately one a day. With respect to major accidents, chemicals are the second leading cause of DOE Type A & B accidents, exceeded only by those

All chemical exposures have the potential for health consequences. Depending on the toxicology and concentration, the effects of chemical exposures may be immediate (acid burns) or long term (chronic beryllium disease or cancer). In any case, chemical exposures may result in life threatening outcomes. Chemicals may cause physical damage such as explosions or fires resulting in serious injury and facility damage. Facility and mission related effects might include corrosive actions that degrade equipment performance (like mercury on copper nickel alloys and aluminum) and residual contamination that limits the future use of facilities and equipment. Environmental issues may arise as a result of spills, releases, or waste chemical inventories. In addition to the health effects, physical damage, or environmental effects that may result from a chemical incident, there will be a need to apply scarce resources to the mitigation of the incident.

Chemical Vulnerability Working Group Report

DOE

Management Response Plan Despite the 1994 Chemical Vulnerability Study and the management response plan developed to address its findings, the chemical incident rate to date at DOE has remained essentially unchanged. To effectively reduce both the number and magnitude of incidents, DOE needs to effectively use its safety resources to raise the awareness of chemical hazards and improve chemical safety management. These resources include expanded use of chemical management best practices, lessons learned, and existing guidance.

There are numerous DOE, OSHA, and EPA standards, rules, orders, etc., which contain chemical management requirements as well as lessons learned (Appendix B) and best practices. Field operations need to ensure chemical management is

fully incorporated into ISM programs, consolidate these requirements and best practices, and avoid duplication to focus on what is truly essential. This Handbook will provide guidance and examples, such as successes in integrating chemical management into existing ISM programs.

Use of the guidance, best practices, and lessons learned contained in this Handbook will result in safer operations, greater productivity, and a reduced need for costly interruptions to operations.

## 1.0 Chemical Management as part of Integrated Safety Management

DOE P 450.4 (ISM)

This chapter presents a discussion of the five ISM core functions from the perspective of chemical management. To accomplish work safely and protect workers, the public, and the environment, the safety system functions to identify hazards and establish controls. These hazards range from commonly encountered workplace hazards to one-of-a-kind process hazards found in existing newly designed to old, non-operational facilities. For personnel who plan tasks involving chemicals, the goal is to ensure that safety documentation for the facility, procedures for conducting the task, and supporting hazard identification and analysis adequately address the full range and scope of chemical hazard(s).

#### 1.1 Define the Scope of Work

Translating a mission into work is the first step to planning and accomplishing work tasks safely and effectively. Planning considers the entire life cycle of a mission, and as such, the entire life cycle of chemicals required to accomplish the work must also be considered.

Defining expectations for the scope of work addresses the goals and objectives for both DOE and the contractor to accomplish the work. At this step in planning, issues relating to chemicals that could be considered include, but are not limited to, efficacy versus toxicity, engineering controls, chemical disposal, emergency response, medical monitoring, personnel training and exposure, facility and equipment contamination, and release to the environment. The impact of these issues should be weighed against performance expectations and resolved to support the mission and the allocation of resources.

If a site's mission involves the use of chemicals, then some of the contractual requirements address chemical management, i.e., chemicals used to accomplish work, chemicals in storage or transportation, or chemicals as waste materials.

When a change in the scope of work, or in requirements or regulations affects a site's chemical management, the sufficiency of the set of contractual chemical management requirements must be evaluated. As a mission matures and the work

moves from one phase to another, incorporates evolving technologies, or adjusts to changes in prioritization and budget, the set of contractual requirements for chemical management should be continuously evaluated as a part of the ISM self-assessment process. DOE G 450.3-3, "Tailoring for Integrated Safety Management Applications," can be used to guide the review and evaluation of work controls for managing chemicals.

DOE G 450.3-3

#### 1.2 Analyze the Hazards

DOE G 450.4-1A

Hazards from chemicals are identified, analyzed, and categorized prior to work being performed. A "hazard" is defined by DOE G 450.4-1A as a source of danger (i.e., material, energy source, or operation) with the potential to cause illness, injury, or death to personnel or damage to a facility or the environment (without regard to the likelihood or credibility of accident scenarios or consequence mitigation). OSHA's Hazard Communication Standard (29 CFR 1910.1200) defines a hazardous chemical as any chemical that poses a physical or health hazard. EPA defines hazardous wastes in 40 CFR 240-299 [(implementing regulations for the Resource Conservation and Recovery Act (RCRA)].

29 CFR 1910.1200, Hazard Communication

EPA RCRA

identifying site and facility hazards, including chemical hazards and the hazards associated with the disposal of the hazardous chemicals. Analysis can begin at these levels by assessing chemicals present in quantities greater than the threshold quantities (TQ) found in 29 CFR 1910.119 and 40 CFR 355. These materials are generally analyzed from the process safety perspective, i.e., potential for a catastrophic accident with immediate consequences.

Use of an integrated approach to hazard analysis will result in effectively

29 CFR 1910.119 40 CFR 355

Information from these hazard analyses can then be used as the basis for more detailed analysis at the activity or task level. At this level, hazards associated with a worker's exposure to chemicals, as a result of their daily activities, are assessed.

## 1.3 Develop and Implement Hazard Controls

Safety standards and requirements are identified and appropriate controls are developed using the information obtained from the hazard analysis and prior to work being performed.

The identification of standards, requirements, and work controls that are applicable to the entire life cycle of the work help ensure that the work is accomplished safely. This process is undertaken using the Standards/Requirements Identification Documents (S/RIDs), WSS, or a similar process to ascertain which standards, requirements, and work controls should be included in contracts.

S/RIDs Authorization Bases

Work Smart Standards (WSS)

**DEAR** 

For hazards that have been included in the site-wide analyses, Lists A and B at DEAR 48 CFR 970.5204-78(a) and (b) identify the applicable standards and requirements. List A consists of the required applicable Federal, State, and local laws and regulations (including DOE regulations), while List B contains the identified DOE directives appended to the contract. However, as a result of facility and activity level hazard analysis, new chemical hazards may be identified. These newly identified hazards may evoke standards not identified earlier in this process.

Based on the identified hazards and standards set, controls are developed to ensure safe operating conditions. The control of chemical hazards is, in general, no different than controlling other hazards, i.e., radiological hazards. An integrated process to identify and apply the hierarchy of controls (engineering, administrative, and personal protective equipment), including pollution prevention/waste minimization options, should be in place as part of the site's ISMS.

A multi-disciplinary hazard analysis team comprised of line management, health and safety professionals, and workers can effectively tailor the controls applied to the work at the facility and site level.

DOE-STD-3009-94 provides guidance for nuclear facilities on establishing documented safety limits, limiting control settings, and limiting conditions for operation, surveillance requirements, administrative controls, and design features

DOE-STD-3009-94

that result from a disciplined safety analysis. However, this standard does not address common industrial hazards that make up a large portion of basic OSHA regulatory compliance (DOE-STD-3009-94, Sections 3.3.1.1 and 3.3.2.3.3). Line managers need to ensure that this interface between the SAR hazard level and activity level is addressed. DOE O 440.1A and its associated guides can be used to assist in addressing activity level hazard analysis and controls.

**DOE O 440.1A** 

**EWP** 

For hazards not identified at a higher level analysis, unique activity-specific controls may be required. The Enhanced Work Planning (EWP) process relies on a work planning team to specify and tailor the controls for this level. At each level (site, facility, activity), these multi-disciplinary teams can address all relevant functional areas or disciplines of concern (e.g., quality assurance, fire protection, chemical safety, industrial safety, radiological protection, emergency preparedness, criticality safety, maintenance). Controls at the activity level may be developed from higher-level analysis or by using the results of activity hazard analysis. Emphasis, however, should be on designing the work and/or controls to reduce or eliminate the hazards and to prevent accidents, unplanned releases, and exposures (DEAR 970.5204-2(b)(6)).

#### 1.4 Perform Work within Controls

ISM Guide Vol 1 Vol 2 In addition to a discussion on authorization agreements, guidance for startup and restart of nuclear facilities is provided in the ISM guide, Chapter II, Section 5. While this process and guidance focus on Category 1 and 2 nuclear facilities, some concepts can be applied directly to chemical hazards at the activity level.

A process to confirm adequate preparation and application of controls prior to authorizing work at the activity level should be carried out by a qualified multi-disciplinary team. First line supervisors should team with employees and safety and health professionals to ensure the activity-level hazards and controls needed to establish a safe working environment. The hazard and complexity of work should determine the formality and rigor of the review process, documentation, and level of authority for agreement.

In general, the role of DOE and its contractors with respect to authorizing work and work changes at any level are defined in a properly implemented ISM system. This

agreement can become the binding contractual agreement between DOE and the contractor for predetermined hazardous facilities, tasks, or activities. However, because all activity-level hazards in general cannot be predetermined, activity-based hazards and controls (i.e., chemical hazards) will need to be continually identified.

Beryllium 10 CFR 850 The use of air monitoring data along with the appropriate statistical analysis can be useful in determining if the work is being performed within controls. Personal air monitoring for non-radiological chemical exposures is required by one DOE rule, 10 CFR Part 850, *Chronic Beryllium Disease Prevention Program*. If DOE O 440.1A is part of the contract's List B requirements, then application of the Order requires compliance with Title 29 of the CFR which contains substance-specific standards that also require air sampling. In addition, DOE O 440.1A requires exposure monitoring as appropriate for exposure assessments. In any case, good industrial hygiene practice calls for personal monitoring and/or medical surveillance for any unknown exposure. Applying appropriate statistical analysis to chemical sampling data will allow the industrial hygienist to determine potential employee exposures and the level of controls needed, as well as determine if the operation is in compliance with occupational exposure limits.

Chemical exposure data as part of the hazard analysis and air sampling should be communicated to the occupational medical organization. These data and information on hazards experienced may be used by the first line supervisor to improve the safety of future activities with the same type of exposures.

#### 1.5 Provide Feedback and Continuous Improvement

The expectation for continuous improvement in safety management systems is built into the ISM requirements. After a mission is translated into work and the set of requirements to safely accomplish the work is identified, the contractor and DOE should define the expectation for whether the safety management system is to meet or exceed requirements. This expectation can affect planning, prioritization of tasks, and resource allocation.

Sections (d) and (e) of DEAR, 48 CFR 970.5204.2, require contractors to develop safety performance objectives and measures, and commitments and measure ISMS effectiveness.

Several tool are available to assist managers and provide feedback on chemical management objectives:

CSTC Performance Measures

Occurrence Reports

Employee Concerns Program

- The set of performance measures developed by the Chemical Safety Topical Committee (CSTC), which are provided as examples of useful measures for a site's chemical management program;
- Occurrence Reports and corrective actions for ISMS improvement opportunities;
- Facility environment, safety, and health data and identification of environment, safety, and health issues to develop improvements required in the site ISMS;
- Worker or operator suggestions from the Employee Concerns Program and employee safety organizations;
- Review of DOE program and budget execution and guidance; and
- ES&H data collection and analysis systems that support the site's ISMS.

Chemical management should be an integral part of the ISM evaluation and annual reporting process. It may be appropriate to include the impact of effective chemical management in performance objectives and measures.

DOE sites and chemical industries with recognized world-class safety programs also use leading environment, safety, and health indicators, such as completed training, attendance at safety meetings, participation in daily or weekly walk-arounds, regulatory compliance, pollution prevention, and waste minimization, to assess the effectiveness of a chemical management system. DOE facilities that actively involve both employees and line management in hazard analyses and self-assessments can develop efficiencies, improve processes and controls, and empower employees to better manage the chemicals under their control.

Many commercial industries that produce or use large quantities of chemicals are committed to going beyond requirements to ensure safe and effective operations at their facilities. Safety performance records for these companies confirm that a commitment to exceeding safety and environmental requirements results in success. DOE sponsors or supports programs that can result in achieving excellent

ACC Responsible Care

DOE Voluntary Protection Program

ISO 14000

performance in management systems. Designed for chemical manufacturers, ACC's Responsible Care® Program elements may be adapted for use at DOE sites. The Department of Energy Voluntary Protection Program (DOE-VPP) results in safety management systems that compare to the best in industry. International Organization for Standardization (ISO) 14000 can be used to independently validate successful environmental management systems. Any or all of these programs are available to improve the safe management of chemicals at DOE sites.

Team Leaders Handbook

CSTC Lines of Inquiry In conclusion, the first measure of successful ISM implementation is the verification of the site's program. Guidelines for ISM verification can be found in the ISM Team Leaders Handbook (DOE-HDBK-3027-99). One step in the verification process is to develop Lines of Inquiry (LOI) for specific subject areas. The CSTC has developed a number of LOI (see Appendix A), which may be used by subject matter experts (SME) to evaluate a site's chemical management program.

## 2.0 Chemical Management Program

An effective chemical management program has a number of definable elements. First and foremost, the program is part of the site's overall ISMS. However, there are some elements familiar to any manager or safety and health professional that, while not unique to chemical management, should be addressed in terms of the hazards posed by chemical usage.

This chapter addresses ten elements, which can serve as the foundation of a comprehensive chemical management program. However, the breakdown of a chemical management program into any number of elements is an artificial process due to the considerable overlap between elements. By looking at chemical management in a broader sense, one can see that the management of chemicals is a continuum, which begins during the planning of work prior to purchase and continues through the final disposal of the chemical. For example, acquisition of chemicals usually does not consider the disposal of the chemical.

The disposal of chemicals may not be considered part of the chemical management program, but rather is included in the site's environmental management program. However, if pollution prevention is integrated into analyses of chemical management operations, then operators can consider ways to minimize the generation of wastes and prevent pollution and releases for any operation. It is therefore important to ensure good coordination with the site's chemical management staff and the pollution prevention/waste minimization staff.

#### 2.1 Hazard Analysis

All chemicals have the potential to pose a hazard to human or environmental health and safety. Even essential chemicals, such as oxygen and water, may cause injury, fatality, or property damage given a specific set of conditions. It is the purpose of the hazard analysis to identify the conditions that can lead to these problems. In addition, the hazard analysis should address the severity of hazards, options for eliminating or substituting less toxic chemicals, assessing the feasibility of controlling the associated hazards, and assessing costs involved in the safe disposal of the chemicals. Ultimately the hazard analysis should lead to the identification of procedures in which chemical substances can be used in a safe, non-polluting manner.

Hazard analysis is a continuous process performed prior to the time a chemical is requested for purchase through final disposal. Early integration of exposure and hazard assessment with work planning activities will help ensure that potential exposures associated with the work are addressed in the work plan.

As part of a site's overall ISMS, hazard analyses are conducted at the site, facility, activity, and task levels utilizing a variety of resources. The need for an integrated approach is illustrated by reviewing DOE directives, and OSHA and EPA standards and regulations, many of which call for some type of hazard analysis. At the nuclear facility level, DOE-STD-3009-94, the preparation guide for SARs, requires hazard analysis in Chapter 3, "Hazard and Accident Analyses," and Chapter 8, Section 11, "Occupational Chemical Exposures." At the activity or worker level, DOE O 440.1A and its related guides (DOE G 440.1-1 and DOE G 440.1-3) requires the identification of workplace hazards and evaluation of risk, and calls out OSHA standards (i.e., 29 CFR 1910 and 29 CFR 1926).

DOE-STD-3009-94

DOE O 440.1A DOE G 440.1-1 DOE G 440.1-3

29 CFR 1910.119 1910.120 1910.1200 1910.1450 29 CFR 1926.64 1926.65 1926.59 Examples of the OSHA standards requiring hazard analyses, either directly or indirectly, include 29 CFR 1910.119 and 29 CFR 1926.64 [Process Safety Management], 29 CFR 1910.120 and 29 CFR 1926.65 [Hazardous Waste Operations and Emergency Response (HAZWOPER)], 29 CFR 1910.1200 and 29 CFR 1926.59 [Hazard Communication], 29 CFR 1910.1450 [Occupational

EPA 40 CFR 68.67 EPCRA Exposure to Hazardous Chemicals in Laboratories, or "Laboratory Standard"], and various substance specific standards in Subparts Z of 29 CFR 1910 and 29 CFR 1926. EPA also has requirements for performing hazard analyses, such as the Chemical Process Safety Standards (40 CFR 68.67). In addition, Section 313, Emergency Planning and Community Right-to-Know Act (EPCRA) contain hazard assessment requirements. Many of the hazard assessment components of these standards crosscut one another. Therefore, managers should evaluate and describe the relationship of these requirements to assure a coordinated approach which will greatly facilitate the hazard analysis process.

It is important to recognize that requirements flow down through the site, facility, operations, and task levels. The ability to communicate and exchange information regarding the various levels of hazards and risk analysis data is an important component of an ISMS. As a part of ISM, managers should be able to quickly understand the requirements, hazards, and controls of their chemical. The establishment of clear, direct lines of communication and exchange of information among those who conduct and use hazard analyses will provide results that support other needed analyses (engineering, operations, and work planning), help resolve conflicts, and eliminate duplication of efforts.

DOE-STD-1120-98

Table 1, "Hazard Analyses Required by Directives" (taken from DOE-STD-1120-98, "Integration of Environment, Safety, and Health into Facility Disposition Activities"), presents a model integrated approach to hazard analysis, which was piloted at Hanford. This table illustrates one example of the types of hazard analyses required by various directives.

Additional sources of information on hazard analysis and exposure assessment are listed in Appendix C, Program Resources.

Table 1. Hazard Analyses Required by Directives\*

Directive	Hazard Analysis Required	Documentation Required
29 CFR 1910.120 29 CFR 1926.65  Hazardous Waste Operations and Emergency Response	For decommissioning activities conducted under CERCLA, requires hazard analysis and control of change for all potential worker hazards.  (There are other OSHA regulations that require hazard assessments [e.g., lead and asbestos] that may be applicable to disposition activities.)	Health and Safety Plan     (Documentation of these other assessments as required by OSHA.)
DOE O 420.1  Facility Safety	Requires fire hazard analysis and natural phenomena analysis for all facilities. For Hazard Category 2 or 3 nuclear facilities only, requires a criticality safety evaluation.	Criticality Safety Analysis     Fire Hazard Analysis     Effects of natural phenomena hazards on facility systems, structures, or components (SSCs) included as part of safety analysis documented in the Safety Analysis Report (SAR), Basis for Interim Operation (BIO), or Auditable Safety Analysis (ASA).
DOE O 440.1  Worker Protection  Management for DOE  Federal and Contractor  Employees	Requires the identification, evaluation, and control of all workplace hazards.	Worker protection programs (including analysis of worker hazards, as needed) to implement applicable requirements.
DOE O 5480.23  Nuclear Safety Analysis Reports	For nuclear facilities only (Hazard Category 3 or above), requires preliminary and final hazard categorization and comprehensive hazard/safety analysis to support the conclusion that nuclear facility activities can be conducted without causing unacceptable health or safety impacts to workers, public, or environment.	<ul> <li>SAR prepared in accordance with DOE-STD-3009 or a BIO prepared in accordance with DOE-STD-3011.</li> <li>Annual updates to either SAR or BIO for those changes that affect the safety basis.</li> <li>Preliminary and final hazard categorization prepared in accordance with DOE-STD-1027.</li> </ul>
DOE O 151.1  Emergency Management	Identification of hazards and threats for emergency planning purposes.	Emergency Management Plan
DOE O 451.1A  National Environmental Policy Act (NEPA) Compliance Program	Consideration of potential environmental impact from proposed actions.	For proposed activities with potentially significant impacts, Environmental Impact Statement (EIS); or where significance of potential impact is unclear, Environmental Assessment (EA); unless the proposed action may be categorically excluded; or for the specific case of decommissioning, NEPA values may be integrated with CERCLA documentation.

\* Source: DOE-STD-1120-98/Vol. 1

#### 2.2 Acquisition

Acquisition includes approval, procurement, onsite makeup and mixtures of chemicals, individuals/organizations bringing chemicals onsite, and any other mechanism by which sites acquire chemicals. Acquisition management arranges for the procurement of needed chemicals after work planning, an approved hazard analysis, and life cycle analysis. In other words, effective acquisition management addresses options for eliminating or substituting less toxic chemicals, assessing the feasibility of controlling the associated hazards, and assessing the costs involved in the safe disposal of chemicals. Ultimately, acquisition management should lead to the identification of chemical substances that can be used in a safe, non-polluting manner.

Managers, scientists, and supervisors consider a number of factors during the work planning and acquisition of chemicals, including:

- Need for the chemical;
- Hazards of the chemical;
- Use of non-hazardous or less hazardous substitutes when appropriate;
- Justifiable quantities;
- Use of available excess chemicals in lieu of new purchases;
- Stability/shelf life/legacy hazards;
- Suitability of storage facilities;
- Availability of an appropriate safe and environmentally acceptable means for the final disposition of environmentally sensitive chemicals, products, and byproducts;
- Waste minimization and pollution prevention, e.g., use of micro scale vs. macro scale chemistry;
- Required safety documentation [e.g., material safety data sheet (MSDS)]; and
- Input of chemical information into the site chemical management tracking system.

Excess chemicals from within a site's inventory, as well from other sites, should be considered as the primary source of supply. Electronic procurement systems that

include a signoff of the site chemical coordinator before an order is filled have excellent control over the flow of chemicals onto the site.

DOE Materials Exchange

In addition to site-wide systems, DOE has established the Materials Exchange to help facilitate the exchange of chemicals and other materials. The Exchange web site is located at http://wastenot.er.doe.gov/doematex.

Chemical acquisition should be documented in a controlled process that addresses, as appropriate, the identification of: (1) roles and responsibilities of those individuals who are responsible for safely managing chemicals; (2) those individuals who are authorized to request, approve, and sign for receipt of chemicals; and (3) the individual (usually the requester) and group responsible for a chemical from time of its acquisition to final disposition.

**DOE O 440.1A** 

29 CFR 1910.120 29 CFR 1910.1450 Section 313 (EPCRA) The following DOE, OSHA, and EPA directives, regulations, and standards pertain to chemical acquisition. At the activity or worker level, DOE O 440.1A requires the identification of workplace hazards and evaluation of risk (440.1A.9). Many standards either directly or indirectly require acquisition management: 29 CFR 1910.120, HAZWOPER, 29 CFR 1910.1200, Hazard Communication, 29 CFR 1910.1450, Laboratory Standard, and Section 313 (EPCRA).

### 2.3 Inventory and Tracking

All chemicals brought on site should be tracked. In addition, secondary containers of chemicals which may already be on site should be accounted for. Examples of secondary containers include chemical process tanks, such as electroplating plants and chemical cleaning tanks, which can be the most prevalent source of chemical hazards.

Chemical inventory and tracking systems provide current information on the site's hazardous chemical and material inventories. A properly integrated inventory and tracking system can support other environment, safety, and health requirements (directives). This is a continuous process performed from acquisition, through storage and use, to final disposal.

Several inventory and tracking systems, often using bar code scanners and computer databases, are used throughout the complex. The databases typically include locations, amounts, uses, hazards, and custodians. Regardless of the inventory and tracking software used, it is important to integrate this software with other computerized environment, safety, and health systems, such as Hazard Communication, waste disposal, medical surveillance, and MSDS systems, at a particular site.

DOE O 440.1A

29 CFR 1910.120 29 CFR 1910.1200 29 CFR 1910.1450 Section 313 (EPCRA)

EH-41 EPCRA Tutorial

40 CFR 355 40 CFR 302 The following DOE directives and OSHA and EPA standards pertain to inventory and tracking. At the activity or worker level, DOE O 440.1A requires the identification of workplace hazards and evaluation of risk (440.1A.9). This Order also calls out OSHA standards included in Title 29 of the CFR. Examples of OSHA and EPA standards which call for inventory and tracking include: 29 CFR 1910.120, HAZWOPER, 29 CFR 1910.1200, Hazard Communication, 29 CFR 1910.1450, Laboratory Standard, and Section 313 (EPCRA).

The DOE Office of Environmental Policy and Guidance maintains a web site (http://homer.ornl.gov/oepa/EPCRA) which provides a useful EPCRA tutorial. This tutorial includes a guide for identifying and tracking chemicals that are regulated under 40 CFR 355 (EPCRA) at DOE facilities, and Emergency Release Notification and reportable quantities (RQ) (40 CFR 302).

Inventory and Tracking Software

Examples of available inventory and tracking software can be found in Appendix C,

Program Resources.

#### 2.4 Transportation

The safe transportation of chemicals includes movement of materials from site to site, from storage to facility, and within a site. A major transportation concern is the potential health and environmental hazards associated with spills resulting from dropping or vehicle accidents.

DOT 49 CFR 172.329

29 CFR1910.120 1910.1200 1910.176 1910.178 Sites comply with Department of Transportation (DOT) requirements (49 CFR 172.329), as do the suppliers of the chemicals. In addition, transportation requirements are found in OSHA regulations (29 CFR 1910.120 (q), 1910.1200, 1910.176, 1910.178). However, it is good practice to have specific procedures for the internal transportation of materials, which avoid or minimize the potential for spills. These procedures should be properly documented. Transportation also is often tracked in the site chemical inventory systems.

Emergency Response Guide Book Roadside emergencies require quick action such as that found in the 2004 DOT Emergency Response Guide Book. For complete information, contact the shipper. Each shipment requires shipping papers that are placed in the cab of the truck. The shipping paper has an emergency contact phone number. Other emergency information can be found in the Chemical Transportation Emergency Center (CHEMTREC) system.

CHEMTREC

Transportation incidents that result in spills in excess of EPA reportable quantities (40 CFR 302.4) must be reported to the National Response Center. Spills must also be reported to state and local emergency response organizations as required by 40 CFR 355.40.

40 CFR 302.4

National Response Center

40 CFR 355.40

United Nations Placarding

49 CFR 172.329

Workers need to understand their roles and responsibilities in responding to a hazardous materials incident. Everyone involved in the transportation function should be familiar with DOT and United Nations placarding, as well as DOT rules for marking, packaging, and describing hazardous materials, and training (49 CFR 172). Those involved also need to know the special rules for loading, unloading, driving, and parking a truck with hazardous materials (including 49 CFR 172.329).

#### 2.5 Storage

Chemical storage includes bulk, tank, piping, cylinder, and container storage of solid, liquid, or gaseous chemicals. Storage regulations apply to new and unused chemicals stored in partially filled containers, chemicals stored in containers other than their original containers, and chemical residues left within tanks, piping, or containers.

The safe storage of hazardous chemicals includes, as appropriate, the following:

- Use of appropriate storage facilities (e.g., flammable storage cabinet for flammable solvents, appropriate distances between reactive chemicals, specialized cabinets for explosive chemicals, and gas cylinder storage sheds and racks);
- Records of quantities and types of chemicals at each storage location;
- Control and documentation of the addition or removal of chemicals from inventory at each location;
- Periodic physical confirmation and validation of inventory records;
- Documented maintenance and inspection programs that ensure facility integrity;
- Staying within facility storage limits;
- Awareness of chemical compatibility when storing chemicals; and
- Awareness of time sensitive chemicals and their associated hazards.

The documentation and periodic confirmation and validation of inventory records can be performed by the chemical inventory system mentioned in Section 2.3, Inventory and Tracking.

(Explosives)
29 CFR 1910.109
(Anhydrous
Ammonia)
1910.111
(Flammables)
1910.106
(Dip Tank Liq.)
1910.108
(Liquefied

1910.108
(Liquefied
Petroleum Gases)
1910.110
(Powered Industrial
Trucks)

1910.178

Section 2.3, Inventory and Tracking

#### 2.6 Control of Chemical Hazards

Control of chemical hazards should be carried out at all levels (i.e., site, facility, and activity) following the same hierarchy of controls as any other health and safety hazard, i.e., substitution, engineering, administrative, and personal protective equipment. The level and rigor to which chemical hazards are controlled will depend in part on regulatory or contract requirements, which may include WSS and S/RIDS. For example, if the quantity of chemicals on site exceeds TQs, the OSHA and/or EPA process safety standards would apply and a safety analysis may be appropriate. Conversely, for quantities less than the TQs, the OSHA Permissible Exposure Limits (PEL) or American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLV) would establish the allowable airborne concentrations to which workers may be exposed. In either case, a graded approach should be applied in establishing the controls.

OSHA PELs ACGIH

When controls for hazardous chemicals are established, they should be based on the hazard analysis, including any additive or synergistic effects. All controls should be evaluated using an integrated approach. Do not duplicate hazard analysis and overlay controls, i.e., if two types of hazard are present which use similar types of controls, the more protective control should be used.

To ensure control of chemical hazards, management should:

- Cooperate with workers or worker representatives to form chemical safety teams.
- Substitute less hazardous chemicals, when possible.
- Provide ventilation and/or enclosure, as needed.

 Ensure that all chemicals are in appropriate containers with labels and that MSDSs are readily accessible. Title 29 CFR 1910.1200, Hazard Communication, contains important sections about labels and MSDSs, and 29 CFR 1910.1450, Laboratory Standard, also contains a relevant section.

29 CFR 1910.1200

29 CFR 1910.1450

 Provide exposure monitoring, including medical surveillance. Management should establish procedures for monitoring of workers who handle hazardous chemicals. If worker exposure exceeds acceptable DOE or OSHA levels, an investigation should be conducted and corrective actions instituted promptly.

Based on the toxicology of the chemicals, exposed workers may need to undergo medical surveillance and periodic examinations.

- Conduct regular training programs, and provide workers with information and instruction on the use and storage of chemicals. Training supports procedural requirements by letting workers know why actions are needed that would otherwise be regarded as inconvenient or unnecessary.
- Inform personnel of the signs and symptoms of control failures.
- Provide and maintain personal protective equipment based on information contained in MSDSs and recommendations of safety and health professionals.
- Include housekeeping and work practices.

29 CFR 1910.120 HAZWOPER

Handbook

DOE-STD-5503-94

For hazardous waste sites, the mechanism for identifying work site chemical hazards and controls may be found in the site-specific Health and Safety Plan (HASP). Details of the HASP's requirements may be found in 29 CFR 1910.120, and guidance may be found in the "Handbook for Occupational Health and Safety During Hazardous Waste Activities" (DOE/EH-0535) and DOE-STD-5503-94, "EM Health and Safety Plan Guidelines."

#### 2.7 Pollution Prevention and Waste Minimization

Pollution prevention and waste minimization should be considered during planning, acquisition, use, consumption, excessing, recycling, and waste disposal. If the chemical management program does not cover waste management, some interface and coordination with the site waste management program should be in place.

Pollution prevention is the most responsible and preferred approach to minimizing DOE's impact on the environment and minimizing potential health effects on workers using toxic or hazardous substances or handling wastes, reducing compliance vulnerabilities, and saving money otherwise spent on waste management. Pollution prevention is one of the fundamental principles underlying Environmental Management Systems and, as such, should be part of each DOE site's ISMS. DOE and contractor pollution prevention coordinators should be consulted to assist with tailoring pollution prevention integration to meet program requirements and site needs.

Pollution Prevention Act The Pollution Prevention Act of 1990 established a hierarchy of preferred practices:

- Prevent or reduce at the source (source reduction);
- Recycle in an environmentally safe manner;
- Treat in an environmentally safe manner; and
- Employ disposal or other release into the environment only as a last resort and conduct in an environmentally safe manner.

November 12, 1999, Memo In a memorandum dated November 12, 1999, the Secretary of Energy announced a pollution prevention and energy efficiency leadership program with five environmental objectives, including:

- Design and operate DOE facilities using pollution prevention processes that lead to minimal waste generation and lowest life-cycle costs; and
- Diminish use of environmentally harmful materials, equipment, and processes to minimize releases of toxic chemicals, ozone-depleting substances, and greenhouse gases.

The Secretary also directed each Lead Program Secretarial Officer to implement programs to achieve fourteen Pollution Prevention and Energy Efficiency Leadership Goals, including waste and toxic chemical release reductions, as well as increased recycling. Pollution prevention opportunity assessments can be performed to identify the nature and amounts of waste, releases, and energy usage from processes and projects within a site's operations; identify the opportunities for pollution prevention and energy conservation; and evaluate those opportunities for feasible implementation. High return-on-investment projects can be conducted to reduce or eliminate the use of a toxic chemical or the generation of a waste stream.

EO 13148

On April 21, 2000, the President signed Executive Order 13148, "Greening the Government through Leadership in Environmental Management." This Executive Order calls for Federal agencies to set new goals for reductions in the release and offsite transfer for treatment and disposal of toxic chemicals and for reductions in the use of 15 chemicals, which will be identified in future guidance. It also requires that agencies review the feasibility of implementing centralized procurement and distribution systems that allow facilities to track the acquisition, management, distribution, and disposal of materials containing hazardous or toxic substances.

Finally, within the context of chemical management, pollution prevention is often associated with chemical substitution. However, the environmental benefits of pollution prevention should be carefully evaluated to ensure they never override worker safety and health considerations.

#### 2.8 Emergency Management

DOE O 151.1B

EH-2 Emergency Management Evaluation Volume 1 Volume 2 DOE O 151.1B and its related guides establish requirements for Comprehensive Emergency Management Systems. In July 1998, the DOE Office of Independent Oversight found a number of weaknesses in both DOE and contractor Emergency Management programs. These findings indicate that this area should be closely examined in the evaluation of site chemical management programs.

Proper risk assessment, planning, and preparation followed by appropriate and timely response to emergencies is the most effective way to protect the worker, the public, and the environment in case of accidental releases of hazardous substances. Decisions regarding potential exposures should be addressed before an incident occurs. During an emergency, little time exists to resolve such issues or to practice and refine roles and responsibilities. Functions, authorities, and responsibilities for emergency management should be documented and all personnel properly trained. This goal is greatly enhanced by participation in an integrated planning process, including exercising and periodically revising the plan as needed.

DOE sites and facilities need to evaluate preparedness for hazardous materials incidents and plan accordingly, choosing the planning elements and processes most appropriate to their circumstances (i.e., geographic size, types of hazards, populations at risk, resources, and level of preparedness).

These elements should be incorporated in a single emergency preparedness and response plan that incorporates and integrates all of the various emergency requirements from DOE directives, as well as federal and state laws and regulations.

DOE O 5500.3A DOE O 5501.1 DOE O 5501.2 DOE O 5501.3

FEMA SLG 101 NRT-1

(EPA/FEMA/DOT) FEMA 141 Various explanations of the planning process can be found in the following documents: DOE Orders 5500.3A, 5501.1, .2 and .3; Guide for All-Hazard Emergency Operations Planning [Federal Emergency Management Agency (FEMA) State and Local Guide (SLG) 101]; Hazardous Materials Emergency Planning Guide (NRT-1); Technical Guidance for Hazards Analysis (EPA/FEMA/DOT); Handbook of Chemical Hazard Analysis Procedures

(FEMA/DOT/EPA); and Emergency Management Guide for Business & Industry (FEMA 141). These documents and planning approaches incorporate the generic functional requirements of planning, although the steps and procedures may be defined somewhat differently.

EPCRA RCRA Under EPA (EPCRA and RCRA), certain waste management facilities must comply with preparedness and prevention requirements (e.g., alarm/communications systems, fire control equipment, testing/maintenance of emergency systems, etc.); and must prepare a contingency plan designed to minimize hazards from fires, explosions, or any unplanned release of hazardous waste or constituents. These requirements as well as any additional state and local regulatory requirements and procedures should be integrated with the site's emergency preparedness program.

EH-41 EPCRA Tutorial The DOE Office of Environmental Policy and Guidance maintains a web site with an EPCRA tutorial (http://homer.ornl.gov/oepa/EPCRA) which is useful in identifying EPA requirements. Modules 2 and 3 cover Emergency Planning Notification and Emergency Releases.

# 2.9 Disposal

DOE Audit Report (Management of Unneeded Chemicals) Recycling and reuse are cost saving approaches to be considered prior to the disposal of excess chemicals and chemical materials. The cost saving comes from not having to pay for the disposal of the materials and in not having to purchase new chemicals for use in other projects. Savannah River Site (SRS) has realized a cost avoidance and cost savings of over \$3 million through reutilization, donations, and sales of excess chemicals (this is one of SRS's Chemical Management Program performance metrics.) Researchers at Pacific Northwest National Laboratory (PNNL) achieved a cost savings for a laboratory project when they utilized a chemical mixture no longer needed by other projects.

**PNNL Cost Savings** 

Chemicals no longer needed to support planned activities should be removed from the facility inventory in an expeditious manner that is documented and in compliance with all applicable regulations. For example, disposition of unneeded chemicals is handled through property management regulations. The final disposition of the chemicals should be recorded, and all applicable records should be transferred to the appropriate personnel.

Identifying a "waste"

A determination should be made as to whether a site's chemicals (materials) meet the regulatory definition of a "waste."

40 CFR 261.2

- A waste is any material that is discarded by being abandoned (i.e., disposed
  of, burned, or incinerated), recycled, or considered inherently waste-like
  [40 CFR 261.2].
- Certain materials that are "accumulated speculatively" (i.e., accumulated before being recycled) are designated as waste [40 CFR 261.2].
- It is important to recognize that certain materials in inventory (MIN) may
  meet the regulatory definition of a waste, and thus be subject to waste
  management requirements. If MIN chemicals are not reused or exchanged,
  they fall into the waste category and should be dispositioned [per the DOE
  Office of Environmental Management's (EM) MIN Initiative].

**EM MIN Initiative** 

Identifying a "hazardous waste"

The generator of a waste is responsible for determining whether waste is a "hazardous waste" subject to regulatory requirements.

- Procedures should ensure that a timely determination is made (by a qualified person).
- Procedures should be based on definitions in RCRA and applicable state law.
- To be classified as "hazardous," a chemical waste must exhibit one or more characteristics of hazardous waste (40 CFR 261.20-24), or be listed as a hazardous waste (40 CFR 261.30-33).
- Note that the listed hazardous wastes include pure and commercial grade formulations of certain *unused* chemicals [i.e., Pure (P) and Unused (U) listed wastes].

#### Some requirements for storage of hazardous waste

- Mark hazardous chemical waste accumulation tanks and containers with the date the waste was placed in the unit, as well as with the words "Hazardous Waste."
- Ensure that the wastes are accumulated in units that are in good condition, stored in areas with adequate ventilation and drainage, and kept closed except to add or remove waste.
- Certain chemical wastes can be accumulated in a "satellite accumulation area" (40 CFR 262.34(c)). Requirements are limited, but must be observed.
- Generators of hazardous waste are subject to specific quantity and time limits that restrict the amount of waste that may be stored on site at any one time (i.e., without a permit), and the length of time such storage is allowed.

#### Permitting

- Facilities that generate hazardous waste may be required to obtain a permit.
- Facilities that store hazardous waste for greater than 90 days require a permit.
- Facilities that treat or dispose of hazardous waste generally require a permit.

Hazardous Waste

40 CFR 261.20, 261.21, 261.22, 261.23, 261.24

40 CFR 261.30, 261.31, 261.32,

261.33

40 CFR 262.34

# Requirements for disposal

- Hazardous waste must be treated in accordance with the land disposal restriction (LDR) requirements before being disposed.
- LDR treatment standards are established as either constituent concentration levels or specified treatment technologies.

This brief overview cannot identify all regulatory requirements which may apply to a site's waste. However, it is the responsibility of the site to do so.

# 2.10 Training

29 CFR 1910.132
29 CFR 1926.95
29 CFR 1910.134
29 CFR 1926.103
29 CFR 1910,
Subpart Z substance specific standards
29 CFR 1926,
Subpart Z substance specific standards
29 CFR 1926,
Subpart Z substance specific standards
29 CFR 1910.1200
29 CFR 1910.1450
EO 13148

A comprehensive integrated environmental, heath and safety training program is a key element in providing a cost-effective means to meet the training requirements for personnel who handle chemicals. The training program must cover all applicable OSHA and DOE requirements for personnel at DOE sites handling chemicals, including workers, supervisors, managers, and visitors. The content and rigor of training should be commensurate with the potential hazards, exposures, worker roles and responsibilities, and requirements. All personnel who may be potentially exposed to hazardous chemicals require hazard communications training.

Training is particularly important for new workers. All workers should be retrained regularly or whenever there is a change in processes or procedures.

Instruction at a minimum should enable employees to:

- MSDS
- Identify resources for chemical information.
- Explain information contained on the MSDS and label.
- Locate the MSDS in their area.
- Name hazardous substances in their area.
- Describe the proper handling and storage of chemicals.
- Demonstrate actions necessary to handle chemical spills.
- Describe the proper disposal of chemicals.
- Demonstrate proper use and care of protective equipment.
- Explain emergency and first aid measures.
- Understand pollution prevention requirements.

RCRA

Note: RCRA regulations and permits may require specific training in identifying and handling hazardous waste.

# References

- Emergency Planning and Community Right-to-Know Act (EPCRA), 1986
- Pollution Prevention Act of 1990, November 1990
- Resource Conservation and Recovery Act (RCRA), Pub. L. 94-580, 1976
- Executive Order 13148, "Greening the Government through Leadership in Environmental Management," April 21, 2000
- U.S. Department of Energy, 10 CFR 850, "Chronic Beryllium Disease Prevention Program"
- U.S. Department of Labor, 29 CFR 1910, "Occupational Safety and Health Standards"
- U.S. Department of Labor, 29 CFR 1926, "Safety and Health Regulations for Construction"
- U.S. Environmental Protection Agency, 40 CFR 68, "Chemical Accident Prevention Provisions"
- U.S. Environmental Protection Agency, 40 CFR 261, "Identification and Listing of Hazardous Waste"
- U.S. Environmental Protection Agency, 40 CFR 262, "Standards Applicable to Generators of Hazardous Waste"
- U.S. Environmental Protection Agency, 40 CFR 302, "Designation, Reportable Quantities, and Notification"
- U.S. Environmental Protection Agency, 40 CFR 355, "Emergency Planning and Notification"
- U.S. Department of Energy Acquisition Regulation (DEAR), 48 CFR, Chapter 9
- U.S. Department of Transportation, 49 CFR 172, "Hazardous Materials Table, Special Provisions, Hazardous Materials Communications, Emergency Response Information, and Training Requirements"
- U.S. Department of Energy, DOE O 151.1, "Comprehensive Emergency Management," 8-21-96
- U.S. Department of Energy, DOE O 440.1A, "Worker Protection Management for DOE Federal and Contractor Employees," 3-27-98
- U.S. Department of Energy, DOE G 440.1-1, "Worker Protection Management for DOE Federal and Contractor Employees Guide for use with DOE O 440.1," 7-10-97
- U.S. Department of Energy, DOE G 440.1-3, "Implementation Guide for use with DOE O 440.1, Occupational Exposure Assessment," 3-30-98

- U.S. Department of Energy, DOE P 450.4, "Safety Management System Policy," 10-15-96
- U.S. Department of Energy, DOE G 450.3-3, "Tailoring for Integrated Safety Management Applications," 2-1-97
- U.S. Department of Energy, DOE G 450.4-1A, "Integrated Safety Management System Guide," 5-27-99
- U.S. Department of Energy, DOE-STD-1120-98, "Integration of Environment, Safety, and Health into Facility Disposition Activities," Volume 1 of 2
- U.S. Department of Energy, DOE-STD-3009-94, "Preparation Guide for U.S. Department of Energy Nonreactor Nuclear Facility Safety Analysis Reports"
- U.S. Department of Energy, DOE-STD-5503-94, "EM Health and Safety Plan Guidelines"
- U.S. Department of Energy, DOE-HDBK-3027-99, "Integrated Safety Management Systems (ISMS) Verification Team Leader's Handbook"
- U.S. Department of Energy, DOE/EH-0535, "Handbook for Occupational Health and Safety During Hazardous Waste Activities"

# Appendix A

During the 1999 joint DOE/Energy Facility Contractors Group Chemical Safety Workshop, a subgroup was formed to better integrate Chemical Management into the Department's ISM policy. The team, representing both DOE and contractor representatives from across the complex, developed the following sample Lines of Inquiry.

# REVIEW CRITERIA AND SAMPLE LINES OF INQUIRY FOR CHEMICAL MANAGEMENT FOCUSING ON CHEMICAL HAZARDS MANAGEMENT

The following provides a collection of lines of inquiry that could be used in an assessment of the chemical management functional area. The lines of inquiry are grouped according to the general criteria for a subject matter expert (SME) evaluation recommended in the Integrated Safety Management System (ISMS) Team Leader's Handbook. These lines of inquiry are suitable for use by a chemical management SME within a broader ISMS review or in a "stand-alone" review of a chemical management program.

The lines of inquiry may be used in reviewing requirements' documentation, interviewing personnel, or observing activities. A robust set of lines of inquiry would enable determination that the given criteria are met.

Members of the Chemical Safety Topical Committee and others with experience in reviews and verifications in this functional area are invited to add to these suggested lines of inquiry, so this collection continues to grow as a valuable resource.

#### **OBJECTIVE**

Within the Chemical Management area, the planning of work includes an integrated identification and analysis of hazards, and development and specification of necessary controls. There is an adequate process for the authorization and control of work, and a process for identifying opportunities for feedback and continuous improvement. Within the Chemical Management area, line managers are responsible for safety; clear roles and responsibilities have been established; and there is a satisfactory level of competence.

# **CRITERIA AND LINES OF INQUIRY**

# Criterion 1

Procedures and/or mechanisms for activities involving chemicals require adequate planning of individual work items to ensure that <u>hazards</u> are identified and analyzed, and that appropriate controls are identified and selected for subsequent implementation.

- What is the process used to identify potentially hazardous chemicals that are used or stored in the facility? What hazard analyses are conducted for such chemicals and for chemical processes in the facility? What is the "driver" for these hazard analyses?
- What are the qualifications of personnel performing chemical hazard analysis? Are "hands-on" employees involved in all chemical hazard analyses conducted by SMEs? Do environment, safety and health (ES&H) professionals conduct walk-downs of facilities in which chemicals are to be used or stored, prior to completing the hazard analysis?
- Do the work packages reflect a well-developed planning process that incorporates potential chemical safety concerns?
- Has the facility adequately implemented a job hazard analysis procedure for work planning? Is chemical safety integrated into this process? Is identification (and reduction) of waste generation integrated into this process?
- Are there procedures or instructions in place to specify when review and approval are needed on project documentation to ensure that any chemical hazards management concerns are addressed?
- Does a facility-specific procedure exist to implement a comprehensive chemical hazard management program? Does it reflect site-wide requirements and all applicable standards?
- Are waste types, quantities, and their associated hazards identified in the job hazard analysis and work planning process?

- Are hazards of legacy chemicals (e.g., abandoned, residual chemicals in tanks and pipes with inadequate controls) properly identified and addressed? Have their potentially degraded storage conditions been considered? Have these chemicals been sampled and characterized? Are there adequate controls to prevent and mitigate adverse consequences? Are the containers of these chemicals periodically inspected and maintained? Are the hazards of these chemicals appropriately and sufficiently addressed in the facility's safety basis?
- What is the regulatory status of the legacy chemicals in the facility? Has the regulatory status of the legacy chemicals as hazardous waste been appropriately determined?
- Has pollution prevention (substitution with a non-hazardous material or reduction in quantity used) been considered, when applicable, as a way to prevent or mitigate chemical hazards?
- Are adequate and appropriate controls for chemical hazards identified through the hazard analysis? Are adequate controls identified for all chemical hazards? Are engineered controls preferred over administrative controls? Are administrative controls preferred over personal protective equipment? Are passive controls preferred over active controls?
- Are hazard assessments essential to emergency response established and maintained?

#### Criterion 2

Procedures and/or mechanisms for the acquisition, storage, use, and disposal of chemicals contain clear roles and <u>responsibilities</u>. Chemical management is effectively integrated with line support managers to ensure that line managers are responsible for chemical management.

- Are the responsibilities of line management for chemical safety and chemical management clearly defined, documented, and understood?
- Are the roles and responsibilities of support staff and other personnel associated with the facility's chemical management program/system clearly defined, documented, and understood? Have the primary and secondary points of contacts been identified?

- Are the roles and responsibilities of personnel providing chemical safety expertise and support properly integrated with the line management's responsibilities relative to operations?
- Who is responsible for controlling the hazards arising from chemical storage and use in the workplace? How are they held accountable?
- What processes are in place to ensure adequate input by ES&H and other appropriate professionals in the designation of controls for chemical hazards, and in how they are implemented?
- Are the resources needed for providing an adequate level of chemical safety and management support being communicated to the line management? Is management responsive to the resource needs and concerns identified by ES&H and other appropriate professionals?

#### Criterion 3

Procedures and/or mechanisms for the acquisition, storage, use, and disposal of chemicals require selected <u>controls</u> to be implemented, that those controls are effectively integrated, and that their readiness is confirmed prior to the performance of work.

- Do facility and warehouse control procedures properly implement chemical management procedures to ensure safe handling and storage of chemicals?
- Is prevention and source reduction of hazardous materials supported by appropriate procurement and inventory practices?
- Is the chemical inventory at a given storage location being properly updated as the inventory changes? Is the inventory inspection and surveillance conducted at an appropriate frequency? Do all chemical storage areas receive adequate coverage through periodic surveillance?
- Is a database or hardcopy file maintained of Material Safety Data Sheets (MSDS) for chemicals used and stored at the work-site and at the facility? How is access to MSDS information provided to workers?

- Is there a procedure that ensures that chemicals stored in a given location are compatible? Is it adequately implemented?
- What criteria are used to select appropriate standards and requirements (e.g., Work Smart Standards, Standards/Requirements Identification Documents, or others, as applicable) to address all chemical hazards? What are the qualifications of individuals performing standards selection?
- What processes are in place to ensure adequate input by ES&H professionals in the implementation of controls for chemical hazards?
- What is the process for authorizing a chemical to be used on the site? What pollution prevention practices are conducted at the site? Is there a list of restricted chemicals? How is chemical storage and use policed? How are excess or waste chemicals disposed of? What processes are in place to assure chemicals are not abandoned when work on a project ceases?
- What means are employed to ensure that the identified controls are implemented, and are operable and functioning so long as a chemical hazard is present?
- Is personal protective equipment required to be used for any activity involving hazardous chemicals? Has substitution of a less hazardous chemical been considered? Are engineering controls in place or planned for these operations? What other controls or measures are in place for these operations?
- When and how is a decision made to evaluate employee exposure to a chemical hazard? What is management's role in assuring that chemical exposures are evaluated and properly addressed?
- How does your occupational medicine group become aware of chemical usage and employee exposure to specific chemicals? What are their roles and responsibilities once an employee's exposure has been demonstrated?
- Are changes to mission, operations, and conditions analyzed for needed changes to requirements? How are ES&H personnel involved in this process?

## Criterion 4

Procedures and/or mechanisms for acquisition, storage, use, and disposal of chemicals require that personnel who are assigned to the subject area have a satisfactory level of competence.

- What training is provided to employees on the hazards of chemicals and chemical processes they work with, and on the controls that are most appropriate for those hazards? How frequently is this training provided? Is this training kept current? What is the frequency of refresher training provided for affected employees? Is training effectiveness measured? If so, how?
- What training is provided to supervisors and managers on management of hazards arising from chemical storage and use?
- Are requests for assistance and documents for information or review distributed to appropriately qualified and knowledgeable staff?
- Are chemical safety support staff sufficiently familiar with facility operations? Do they participate in routine inspections, assessments, and audits; in training; and in the categorization, analysis and development of corrective actions for occurrences?
  Do they participate in overseeing the implementation of selected controls and in followup inspections of those controls?
- Are the managers, supervisors, and support staff sufficiently knowledgeable about pollution prevention and waste minimization (prevention and source reduction of hazardous materials), such that these are incorporated into their chemical hazard prevention and mitigation activities?
- Does the organization (internal or subcontractor) responsible for providing chemical safety support use a training implementation plan to manage staff training and qualifications?
- Do position descriptions for points-of-contact or coordinators responsible for chemical hazards management appropriately reflect their duties and responsibilities relative to chemical safety, as well as their training and subject matter competency?

## Criterion 5

Procedures and/or mechanisms require that <u>feedback</u> and continuous improvement occur with regard to chemical management, chemical safety, and pollution prevention.

- Has the facility performed an assessment and gap analysis to identify significant gaps and deficiencies in its program? Does the facility maintain its corrective action plan up-to-date? Are the action items prioritized? Have the corrective actions completed been properly closed? Are open items being pursued according to their priority?
- Do post-job critiques and reviews reveal that chemical safety concerns were adequately handled, or if identified, they were adequately pursued and resolved? Is there evidence showing that lessons learned are properly used to improve work conditions or performance?
- Are assessment results communicated to senior management for their use in making informed determinations? Do managers routinely use feedback tools, such as performance indicators, reviews, debriefs, and lessons learned?
- Are occurrence reports evaluated for applicability and communicated to the right individuals?
- Are suggestions of employees and other professionals used to improve performance?

# Appendix B

# LESSONS LEARNED

The following lessons learned are extracted from DOE Operating Experience (OE) Weekly Summary and Occurrence Reporting and Processing System (ORPS) reports and are included in this Appendix as potential learning and training tools for the reader.

# Safe storage of chemicals.

• Students discovered a cylinder containing hydrogen fluoride (HF) that had ruptured inside a storage room next to a laboratory. Following the cylinder failure, investigators learned of a letter DuPont Fluoroproducts sent to its customers two and a half years earlier about the potential over-pressure hazard associated with the long-term storage of Anhydrous HF in carbon steel cylinders. The cylinder was a lecture bottle that had been stored at the university for 22 years. (OE Weekly Summary 99-25)

- Three reactor auxiliary operators were exposed to trimethylamine above the short-term (15-minute) exposure limit while recharging an ion exchange resin in a demineralizer tank. Investigators believe that the excessive off-gassing of trimethylamine resulted from the drums of resin being stored at a higher temperature than that recommended on the MSDS. (ORPS Report ID--LITC-ATR-1998-0014)
- Facility chemists found five sealed containers of lithium metal stored inside a nitrogen glove box instead of an adjacent argon glove box. Lithium reacts with nitrogen and can result in highly exothermic reactions when exposed to water or oxygen. (ORPS Report ID--LITC-ERATOWNFAC-1998)
- A cleaning subcontractor employee became nauseous and vomited while spraying a chemical cleaner
  in a restroom in the administration building. Investigators determined that the spray bottle was
  mislabeled "Crew," which is a chemical manufactured for cleaning toilet bowls and sinks. The label
  did bear the manufacturer's warnings, but the bottle actually contained nearly full strength Lysol
  liquid cleaner. (ORPS Report ORO--MK-WSSRAP-1998-0040)
- A maintenance crew discovered a small vial labeled "picric acid" in a crawl space while they were performing a pre-job walk-down for maintenance on some steam lines. Picric acid is normally used as an aqueous solution and an explosive mixture results when the solution crystallizes. Eight similar occurrences involving picric acid were found dating back to 1990. In these events, explosive safety specialists removed the acid and either chemically neutralized it or detonated it in a safe area. (OE Weekly Summary 98-05)

# Inadequate control of chemical hazards.

• The Type A investigation of a sodium potassium (NaK) accident that occurred at the Y-12 plant on December 8, 1999, identified a lack of understanding of the hazard from NaK and its reactive byproducts as one of the root causes of the accident. The investigation found that personnel involved in planning the task, the safety documentation for the facility, the procedure for the task, and the procedures supporting hazard identification and analysis did not address the complete NaK hazard. The investigation also determined that detailed hazard identification data supported by accident analysis and appropriate control information was readily available.

*Training.* These events underscore the importance for chemical worker training to include hazard information and lessons learned from accidents, previous studies, and similar events involving the same chemicals and chemical work practices

- A chemical tank explosion caused significant localized damage to a facility. Personnel failed to recognize the phenomenon that was being created inside the tank. Concentration by evaporation of a dilute solution of hydroxylamine nitrate and nitric acid occurred to the point where an autocatalytic reaction created a rapid gas evolution that over-pressurized the tank beyond its physical design limitations. Similar hazards were identified as early as 1970, and reports of various accidents were available to the facility. However, these hazards were not included in training and qualification programs to heighten awareness of the chemical hazards. (ORPS Report RL--PHMC-PFP-1997-0023, Final Report 05-17-99)
- An explosion occurred when a chemical operator performing lithium hydride recovery operations submerged a high-efficiency particulate air (HEPA) filter embedded with lithium hydride residue into a salvage vat containing demineralized water. Lithium hydride reacts exothermically with water to form caustic lithium hydroxide and flammable hydrogen gas. The exothermic reaction produced enough heat to begin burning the filter's wood framing, even though the filter was submerged. Investigators believe that oxygen from air trapped in the filter combined with the hydrogen generated from the reaction caused the explosion. Investigators also determined that it had once been a skill-of-the-craft practice to perforate a filter with holes before cleaning to more efficiently liberate entrapped air and hydrogen during the reaction. This past practice had been lost over time, owing to the attrition of experienced operators, and had not been captured in the procedure for cleaning the filters. (ORPS Report ORO--LMES-Y12NUCLEAR-1999-0031)
- A high-pressure carbon dioxide (CO2) fire suppression system unexpectedly actuated, resulting in one fatality, several life-threatening injuries, and significant risk to the safety of the initial rescuers. Investigators determined the inadvertent operation of electric control heads released CO2 into the occupied space without a discharge warning alarm. In addition, the CO2 system was not physically locked out as was required. The procedure that required this barrier had not been updated or used for this work. The requirement to train workers in the hazards of emergency response to CO2 discharges had not been incorporated into training programs. A contributing cause for the accident was the failure to take corrective actions and apply lessons learned from previous accident investigations, particularly in work planning and control. (ORPS Report ID--LITC-TRA-1998-0010)

- A subcontractor employee was sprayed with acid when he inserted a hydrochloric acid pump into a
  drum of sulfuric acid. When the two acids mixed, a violent chemical reaction caused acid to be
  sprayed from the drum approximately 10 feet to the ceiling and onto the employee. (ORPS Report
  ORO--MK-WSSRAP-1999-0004)
- A technician working in a laboratory discovered a ruptured 1-liter polyethylene bottle of acid on the
  floor of a chemical hood. Laboratory personnel had heated it to approximately 140 degrees, capped
  it, and placed it in the hood to cool down. Chemists believe that off-gassing of the acid mixture at an
  elevated temperature built up sufficient pressure to rupture the bottle. (ORPS Report SR--WSRCFSD-1998-0004)
- Hazardous waste workers discovered a ruptured 1-liter glass bottle labeled "Used Nitric Acid" in a
  waste room. Investigators determined that the unvented bottle had accumulated pressure over time,
  causing it to burst. (ORPS Report CH-BH-BNL-NSLS-1996-0002)
- A building was evacuated due to fumes generated by mixing a solution of nitric acid, hydrogen fluoride, and acetic acid with a solution of ethanol, hydrofluoric acid, and water. Investigators determined that the fumes resulted from a reaction between incompatible materials being mixed for waste disposal by a technician. (ORPS Report SAN--LLNL-LLNL-1997-0037)
- A researcher was adding methanol to two vials containing sodium permanganate and polychlorinated biphenyls when an unexpected energetic reaction caused the mixture to spray from the vials and onto the researcher's gloves. Investigators determined that there was an inadequate evaluation of chemical compatibility. (ORPS Report ORO--ORNL-X10ENVIOSC-1996-0001)
- Personnel who responded to a chemical spill of methyl acrylate were never briefed by facility personnel. As a result, they did not assume command of the event, even though facility procedures require the command to be transferred to Emergency Management and Response (EM&R) if the facility does not have adequate resources to handle an event. The fact that the facility called for the hazardous materials (HAZMAT) team and used the services of occupational medicine was a sign that it did not have the necessary personnel to deal with the event, so EM&R should have assumed the role of incident commander. Furthermore, no one was concerned about the flammability of the chemical. No one called the fire department to respond as a precautionary measure. If the methyl

acrylate had ignited, a fire could have quickly spread through the rest of the lab. Also, if a fire had occurred when the spill response team entered the room, they could have been severely burned. (ORPS Report ALO-LA-LANL-TA55-1999-0032)

- During a chlorine leak, the emergency response team was not totally familiar with the facility systems. Plant operators had to tell them how to isolate chlorine cylinders and how to reset alarms to determine if they were still detecting chlorine. (ORPS Report RL--PHMC-S&W-1999- 0002)
- A researcher did not immediately notify his manager or emergency response personnel after a vessel ruptured and expelled a mixture of 130 degrees centigrade trichloroethylene and hydrogen peroxide from the face of a fume hood. (ORPS Report RL--PHMC-PNNLBOPER-1998- 0022)
- Facility personnel waited approximately 30 minutes before reporting a 2-gallon spill of radioactive phosphoric acid. Also, personnel in the spill area did not observe restrictions on eating, drinking, and smoking, and some workers assisted emergency operations personnel without wearing personal protective equipment. (ORPS Report RFO--KHLL-LIQWASTE-1998-0002)

# **Appendix C**

#### PROGRAM RESOURCES

The following list of program resources is not intended to be a comprehensive list (no list can be), however it does provide useful references most of which can be accessed via the internet. This list will be updated and additional resources will be added to the electronic version of this document available on EH-5's Chemical Management Web Site (http://www.eh.doe.gov/web/chem\_safety/).

## **Hazard Analysis**

DOE G 440.1-3, "Occupational Exposure Assessment"

http://www.directives.doe.gov:1776/pdfs/doe/doetext/neword/440/g4401-3.pdf

EPA Guidelines for Exposure Assessment (Federal Register Vol. 57. No 104. May 29, 1992) http://www.epa.gov/ncea/exposure.htm

American Industrial Hygiene Association White Paper On A Generic Exposure Assessment Standard

http://www.aiha.org/papers/exposure.html

National Institutes of Health National Institute of Environmental Health Sciences Chemical Health & Safety Data

http://ntp-server.niehs.nih.gov/Main\_Pages/Chem-HS.html

National Institute for Occupational Safety and Health (NIOSH) Databases offer online chemicalspecific safety, emergency response, and medical surveillance information

http://www.cdc.gov/niosh/database.html

# Acquisition

Bechtel Hanford Incorporated (BHI), BHI-01248, Chemical Management Plan

Savannah River Site (SRS) Chemical Management Program, AID-AMS-99-0052, September 3, 1999

## **Inventory and Tracking**

The following are a sampling of computerized inventory and tracking systems across the complex:

- Sandia National Laboratory (SNL) Cradle-to-Grave Tracking and Information System (CGTIS)
- Brookhaven National Laboratory (BNL) Standards-Based Management System (SBMS)
- Pacific Northwest National Laboratory (PNNL) SBMS
- Los Alamos National Laboratory Automated Chemical Inventory System (ACIS)
- National Renewable Energy Laboratory Chemical Inventory System (modified from PNNL)
- Oak Ridge Hazardous Materials Information System (HMIS)

## **Transportation**

DOT Emergency Response Guidebook (ERG2000)

http://hazmat.dot.gov/gydebook.htm

#### Storage

ES&H Bulletin EH-91-2, "Safe Chemical Storage"

http://www.eh.doe.gov/docs/bull/bull0062.html

National Oceanic and Atmospheric Administration – "The Chemical Reactivity Worksheet"

http://response.restoration.noaa.gov/chemaids/react.html

Texas A&M College of Science "Safe Storage of Laboratory Chemicals"

http://www.science.tamu.edu/safety/chemstorage.html

## Control

DOE-STD-5503-94, "EM Health and Safety Plan Guidelines

http://www.eh.doe.gov/techstds/standard/est5503/est5503.pdf

Handbook for Occupational Health and Safety During Hazardous Waste Activities

http://www.eh.doe.gov/docs/haz\_waste\_activity\_handbook/hwa\_handbook.html

#### **Pollution Prevention and Waste Minimization**

Applicable pollution prevention regulations/policies and other useful information may be found at DOE's Pollution Prevention Clearinghouse at

http://epic.er.doe.gov/epic/

DOE Pollution Prevention Team (EM-22)

http://twilight.saic.com/wastemin/default.asp

ChemAlliance Pollution Prevention

http://www.chemalliance.org

Project list for the U.S. EPA - Office of Research and Development

http://www.pprc.org/pprc/rpd/fedfund/epa/epastd/

**EPA Waste Minimization National Plan** 

http://www.epa.gov/epaoswer/hazwaste/minimize/

**EPA Waste Minimization Documents** 

http://www.epa.gov/epaoswer/hazwaste/minimize/

Pacific Northwest Pollution Prevention Resource Center

http://www.pprc.org

#### **Emergency Management**

EH-2 Emergency Management Evaluation Vols. 1 and 2

http://www.eh.doe.gov/iopa/reports/emevals/9808eval/em-vol1.pdf

http://www.eh.doe.gov/iopa/reports/emevals/9808eval/em-vol2.pdf

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The Federal Emergency Management Information System (FEMIS©), developed at PNNL, provides planning, coordination, response, and exercise support for emergency management.

http://www.pnl.gov/femis/

National Atmospheric Release Advisory Center Modeling System developed at Nevada Test Site is an emergency response system.

http://narac.llnl.gov

National Safety Council (NSC) Emergency Management Resources

http://www.crossroads.nsc.org/emerg manag.cfm

Computer-Aided Management of Emergency Operations (CAMEO®) helps emergency managers plan for and mitigate chemical accidents and comply with requirements under the Superfund Amendments and Reauthorization Act (SARA) Title III.

http://www.nsc.org/ehc/cameo.htm

Mapping Applications for Response and Planning of Local Operational Tasks (MARPLOT®) allows users to search and display roadways, street addresses, waterways, railroads, census blocks, and other political boundaries.

http://www.nrt.org/nrt/hazmat2000/hazmat2000.nsf/pages/625.html

Agency for Toxic Substances and Disease Registry's (ATSDR) Hazardous Substance Release/Health Effects Database provides access to information on the release of hazardous substances from Superfund sites or from emergency events and on the effects of hazardous substances on the health of human populations.

http://www.atsdr.cdc.gov/hazdat.html

CHEMTREC is a source for hazardous materials/dangerous goods information and communication.

http://www.chemtrec.org/Chemtrec

NSC Environmental Health Center provides emergency response information on specific chemicals as well as additional links.

http://www.nsc.org/ehc/chemical.htm

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Risk Management Plans (RMP) from Right to Know Environmental Databases - Under the Clean Air Act Amendments of 1990, certain chemical facilities must report RMPs to prevent and respond to chemical accidents in the United States.

http://www.rtk.net/aboutrmp.html

RMP\*InfoTM - displays Risk Management Plans submitted by facilities under Section 112(r) of the Clean Air Act that include information about Risk Management Programs implemented to prevent and prepare for chemical accidents.

http://www.epa.gov:9966/srmpdcd/owa/overview\$.startup

# **Disposal**

RCRA Orientation for Facility Managers (Computer Automated Guidance), Version 1.0, September 1998. (See "Training")

http://www.eh.doe.gov/oepa

Definitions of Solid and Hazardous Wastes (Computer Automated Guidance), Version 1.0, April 1997. (See "Tools")

http://www.eh.doe.gov/oepa

RCRA Guidance Manuals (See "Policy & Guidance")

http://www.eh.doe.gov/oepa

RCRA and Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Information Office of Environmental Policy and Guidance Publications List - RCRA/CERCLA Division (EH-413)

http://www.eh.doe.gov/oepa/guidance

**EPA Office of Solid Waste Materials** 

http://www.epa.gov/epaoswer/osw/publicat.htm

Identifying Your Waste: The Starting Point, EPA530-F-97-029, September 1997.

http://www.epa.gov/epaoswer/osw/mbodyi.htm

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RCRA Orientation Manual, EPA530-R-98-004, May 1998.

http://www.epa.gov/ncepihom/Catalog/EPA530R98004.html

# **Training**

OSHA 2254, "Training Requirements in OSHA Standards and Training Guidelines" (revised 1998)

http://www.osha-slc.gov/Publications/osha2254.pdf

Addendum

http://www.osha-slc.gov/Publications/2254addendum.pdf

Voluntary Training Guidelines; Issuance of Revised Training Guidelines - 49:30290 http://www.osha-slc.gov/FedReg\_osha\_data/FED19840727.html

Training Requirements in OSHA Construction Industry Standards and Training Guidelines http://www.osha-slc.gov/doc/outreachtraining/htmlfiles/osha2254.html

DOE National Environmental Training Office (NETO) Training on Pollution Prevention Opportunity Assessment

http://www.em.doe.gov/neto/index.html

# APPENDIX D

#### LIFE CYCLE MANAGEMENT OF SHOCK SENSITIVE CHEMICALS

## **Introduction and Scope:**

The purpose of this appendix to the DOE Chemical Management Handbook Volume 1 is to heighten complex wide awareness and concern for the safe lifecycle management of shock sensitive chemicals. It provides an overview of this subject. For specific information on the management of shock sensitive chemicals, consult the listed publications at the end of this appendix and qualified professionals.

## **Background:**

Shock sensitive chemicals are those chemicals that may explode with impact, movement or handling, friction or heat. These chemicals have the potential to undergo a rapid, uncontrolled reaction that may be violent enough to produce an explosion.

There are two types of shock sensitive chemicals. Some chemicals are inherently shock sensitive. These materials have known hazards, predictable properties and may be governed by various codes and standards. The other group of shock sensitive materials is those compounds that initially are not shock sensitive but become so due to chemical changes, such as those from improper or prolonged storage. Properties of these materials are unknown, unpredictable and these additional hazards may or may not be identified on the Material Safety Data Sheet (MSDS) of the parent chemical. Mechanisms causing chemicals to become shock sensitive upon chemical changes from improper or prolonged storage include, but are not limited to drying, decomposition, and slow reactions with oxygen, nitrogen, or the container.

#### **Incidences and Causes:**

The following are examples of the numerous reports of incidents involving shock sensitive chemicals. Note that both of these incidents involved chemicals that became shock sensitive upon prolonged storage.

A technician used a pair of channel lock pliers to twist the rusty lid off a small, dark green bottle to characterize the unknown chemicals inside. There was an immediate explosion and glass shards embedded in a nearby chair. Analysis showed that over time the picric acid in the bottle combined with the metal lid to form shock sensitive metal picrates that lodged in the threads in the neck of the bottle.

A technician was remotely handling an old, opened, metal can of anesthesia grade ethyl ether to add more ethyl alcohol as an inhibitor. Enough inhibitor was thought to be present, so the ether was not considered hazardous. The liquid level in the can was low so the technician had to tilt the can to pipette out an aliquot for the peroxide test strip. As the technician turned the can

upright, an explosion occurred and a fireball filled the fume hood. The slight handling of the can was enough of a mechanical shock to cause peroxide crystals in the top portion of the can to explode.

## **EXAMPLES OF SHOCK SENSITIVE CHEMICALS**

The following are only examples. Not all members of the above classes may be or may become shock sensitive. Likewise, some chemicals in classes not listed above may be or may become shock sensitive. Currently there is no available methodology that would allow DOE to create a thorough definition or an exhaustive list of shock sensitive or potentially shock sensitive chemicals. Additional lists of chemicals or chemical classes of shock sensitive chemicals have been published (2, 4, 5, 12, 15, 23).

# Classes of Inherently Shock Sensitive Chemicals:

```
Azides:
       Silver azide,
       Organic azides,
       Metal azides.
       Nonmetal azides
               (-N_3 \text{ or } N_3)
Acetylides of heavy metals:
       Copper, silver, and mercury salts
       (-CCH)
Amine oxide:
       (=N^{+}-O^{-})
Chlorite Salts:
       Silver chlorite
               (Cl0_2)
Diazo:
       Diazomethane,
       (-N=N-) Diazonium salts (when dry),
       benzene diazonium chloride
       (-N_2^+)
Fulminates:
       Fulminating Silver
       (ONC^{-})
Haloamines:
       Chloro benzyl amine
        (-NHX)
```

```
Hydroperoxide:
       Cumene Hydroperoxide
       (-OOH)
Hypohalite:
       Iodoform
       (OX^{-})
Nitrate salts or esters:
       Ammonium nitrate,
       Guanidine nitrate
       (NO_3^- \text{ or } -ONO_2)
Nitrite salts or esters:
       (NO_2 \text{ or } -ONO)
Nitro compounds:
       nitrocellulose
       (-NO_2)
Nitroso;
        Dinitrosylnickel
       (-NO)
Oxidizers:
       Ammonium perchlorate,
       Ammonium permanganate
Organic Peroxides:
       Benzoyl peroxide (over 98%),
       t-Butyl hydroperoxide (over 90%),
       di-isopropyl peroxydicarbonate (100%)
Ozonide:
       trans-2-Butene ozonide
       (-O_3^-)
Peracid:
       Performic acid
       R-CO<sub>3</sub>H
Perchlorates:
       Potassium perchlorate
       -ClO<sub>4</sub>
Polynitroaromatics:
       Picric acid,
       TNT
```

Metal Picrate:

Copper picrate,

Transition and heavy metal picrates such as nickel, lead, mercury, zinc

# Classes of Chemicals that may become Shock Sensitive:

Acrylates or Methacrylates:

Methyl methacrylate

Aldehydes:

Acetaldehyde

Alkanes and Cylcoalkanes with tertiary Hydrogen:

Cyclohexene

Alkenes with alyllic Hydrogen:

2-ethyl-1-pentene

Alkylalkyenes with alpha Hydrogen:

Isopropyl benzene,

Alkylalkyenes with tertiary alpha Hydrogen:

Ethylcyclohexane

Dienes:

Butadiene,

Chloroprene

Ethers and Acetals with an alpha Hydrogen:

Diethyl ether,

Di-isopropyl ether,

Dioxane,

Tetrahydrofuran

Fluoro or Chloroalkenes:

tetrafluoroethylene

Ketones with alpha Hydrogen:

dilsopropyl ketone

Secondary Alcohols:

DiPhenylmethanol

Ureas, amides and lactams with alpha Hydrogen on a carbon attached to nitrogen:

N-ethylacetamide,

N-isopropylacetamide

Vinyl halides, esters or ethers:

Vinylidene chloride,

Vinyl chloride,

Vinyl acetate)

Vinylalkynes with alpha Hydrogen: diAcytylene, Vinylacetylene

Note: Some chemicals such as secondary alcohols will form explosive peroxides, but these products need to be evaporated to dryness before the explosion hazard manifests itself. A critical part of managing the life cycle of shock sensitive chemicals involves the identification of those chemicals (see below).

# **Handling and Use:**

# Respect the chemicals and the dangers they present

If you find chemicals that are or have the potential of becoming shock sensitive and they are outdated (expired shelf life), suspect, or show signs of degradation, immediately contact your supervisor and your organization's environment, safety and health (ES&H) or hazardous materials department.

#### DO NOT TOUCH OR MOVE SUSPECT CHEMICALS!

## When working with shock sensitive chemicals

Make sure that you have access to the MSDS, the chemical is labeled as required by your facility, and the container is entered into your facility's hazardous chemical management program. Study the chemical's MSDS and label. Look for information about the chemical's reactivity, stability and hazards. If there is a National Fire Protection Association (NFPA) diamond or a Hazard Material Information System (HMIS) label, look for a 2, 3, or 4 in the yellow "Instability" (formerly Reactivity) section or a \(\psi\) (water reactive) in the white "Special Hazards" section.

Closely follow approved work procedures and hazard controls. Review information from other chemical safety resources. Check with your facility's chemical safety personnel. Use appropriate personal protective equipment (PPE). Protect the chemical from shock, friction or heating.

#### **Standards and Codes:**

29CFR1910.1200 – *Hazard Communication*Reactive hazards must be noted on the MSDS.

29CFR1910.1450 – *Occupational Exposure to Hazardous Chemicals in Laboratories* The chemical hygiene plan should address shock-sensitive hazards.

NFPA 45 - Standard on Fire Protection for Laboratories Using Chemicals

NFPA 432 - Code for the Storage of Organic Peroxide Formulations

NFPA 430 – Code for Storage of Liquid and Solid Oxidizers

NFPA 704 - Standard System for the Identification of the Hazards of Materials for Emergency Response

See the DOE Handbook on *Chemical Management* (Volume 3 of 3) *Consolidated Chemical User Safety and Health Requirements* for a detailed compilation of all requirements.

http://www.eh.doe.gov/techstds/standard/hdbk1139/hdbk11392003vol3.pdf

# **Chemical Lifecycle Management:**

# **Management Support**

Management needs to understand liabilities associated with shock sensitive chemicals and support those programs necessary for the management of these chemicals. Management also should develop clear roles responsibilities and authorities so that various aspects of chemical management are never in question.

# **Training and Qualifications**

Management should ensure that employees who handle, store, or use shock sensitive chemicals understand the hazards and recognize when a potentially shock sensitive chemical has become a risk.

When shock sensitive, unstable compounds are found they should only be handled by trained, qualified specialists as identified by management.

Such qualified specialists could be persons (1) who, because of education, training, or experience, or a combination of these factors, is capable of understanding the health and environmental risks associated with the chemical substance which is handled under his or her supervision, (2) who is responsible for enforcing appropriate methods of handling, treating and disposing of chemicals to minimize risks, and (3) who is responsible for the safety assessments and clearances related to the procurement, storage, use, and disposal of the chemical substance as may be appropriate or required.

# **Identification of Shock Sensitive and Potentially Shock Sensitive Chemicals**

The most important element of a shock sensitive chemical management program is to determine how shock sensitive and potentially shock sensitive chemicals will be identified and managed. Since there is no definitive answer as to what should or should not be defined as being shock sensitive, written guidance should be developed at the local level. This guidance should take into account the type of work being performed, the nature of the chemical in question, storage conditions, other safety systems present, relevant references, etc., and should be implemented by a qualified person designated by management. It should also be made available to all employees

and the employees should be encouraged to question any determinations that do not appear to be valid

# **Acquisition Control**

Experiments and processes should be planned appropriately so that necessary quantities can be procured. With "Just-In-Time" contracting, shock sensitive chemicals can be obtained within a short period. This could be used to meet the needs of chemical workers while keeping inventories of shock sensitive chemicals to a minimum. Using "Just-In-Time" contracting essentially causes the chemical supplier to become the storage facility for one's shock sensitive chemicals.

Just-In-Time contracts usually consist of agreements with suppliers that provide for a firm delivery time. This time, coupled with internal delivery time, allows the worker to plan ordering lead-time in order to have the chemicals arrive just prior to needing them. These materials are usually ordered with slight excess and any left over materials should be disposed of to reduce the potential for aging inventories (leftover reagent) in storage.

Consider purchasing peroxide formers with inhibitors if possible.

# **Tracking of Shock Sensitive Chemicals**

Once a chemical is determined to be shock sensitive or have the potential of becoming shock sensitive over time, it should be tracked. Availability of this information within a data system will support tracking and proper management of shock sensitive chemicals. Data elements should include each container's contents, container owner, amount, location, date received, date opened, and last date inspected and/or next inspection date. If this information is not available, then the container cannot be found and inspected at the required time and properly managed.

# **Defining Storage Conditions**

Different chemicals have different storage needs and these needs should be clearly defined. The first reason for this is to prevent incorrect storage conditions that could result in hazardous situations. Some conditions such as exposure to heat, light, air, and humidity can aid reactions that cause chemicals to become shock sensitive. Other conditions such as refrigeration can cause the inhibitor to become ineffective and allow peroxide formation.

A second reason to define storage conditions is to articulate policy concerning the storage of shock sensitive and potentially shock sensitive chemicals.

# **Defining Inspection Period**

Because all chemicals are not the same, inspection periods need to be adjusted for each chemical. Storage conditions should also be included in determining the inspection frequency. An important part of managing time-sensitive chemicals is to determine appropriate inspection periods for each chemical in the program. Inspection periods for each chemical should be

defined as a part of the organization's chemical management program. NFPA 45 requires the inspection of these types of chemicals in a laboratory every 6 months. However, some peroxide formers, such as disopropyl ether, may require more frequent inspections.

Do not assume that a new, recently purchased, unopened chemical is safe. Testing before initial use is recommended.

# Defining "Unsafe"

As chemicals are inspected, there needs to be a definition by the facility as to what constitutes an unacceptable risk (or "unsafe" is not defined, then one cannot determine when a container fails inspection. If needed, review commercial industry practices for reported safe storage times before chemical disposition occurs. DOE sites could also determine what other DOE sites are doing.

It is important to note that some measurements such as peroxide determinations can be inherently low. To prevent dangerous levels of peroxide, a routine monitoring program should be put in place to watch the trend of peroxide concentrations. Once peroxide formation has started it will tend to accelerate at a nonlinear rate and the container should be disposed as waste immediately

# Managing "Unsafe" Chemicals

Once a chemical or waste stream has become unsafe due to dehydration, solvent evaporation, or the formation of hazardous products, processes used to manage the material must be clearly defined in the chemical management program. Employees need to know if they call the professional expert designated by management, if they are to call the bomb squad or emergency response, etc.

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# **CONCLUDING MATERIAL**

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