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U.S. COAST GUARD RESEARCH AND DEVELOPMENT PROGRAM FOR HAZARDOUS CHEMICAL DISCHARGE RESPONSE*

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Summary

The U.S. Coast Guard's Office of Research and Development is presently conducting a program to develop equipment and methods for responding to discharges of hazardous chemicals into the waters of the United States. The program to ameliorate hazardous chemical discharges has been divided into six project areas. This paper will provide an overview of these six project areas as follows:

1. Prevention and Reduction: The development of techniques to prevent or reduce the discharge of a hazardous chemical.
2. Personnel Protection: The development of protective clothing, life support systems and personnel monitors for personnel responding to chemical discharges.
3. Detection, Identification, and Quantification: The development of techniques to allow response personnel to detect, identify and determine the concentration of hazardous chemical discharges.
4. Hazard Assessment Modeling: The development and refinement of mathematical models to predict the behavior of discharged hazardous chemicals.
5. Containment, Treatment, and Recovery: The development of hardware and methods to respond to a discharge and mitigate its environmental damage.
6. Disposal: The development of methods to dispose of chemicals which have been recovered.

When completed, each of these project areas should provide the Coast Guard with additional capability to respond to hazardous chemical discharges.

Introduction

Hazardous chemicals are being transported via marine and other modes in increasing amounts and variety. In spite of regulations and procedures which are designed to prevent hazardous chemical discharges, it is inevitable that such discharges will continue to occur.

To counter this threat, recent legislation such as the Federal Water Pollution Control Act Amendments of 1972 and the Clean Water Act of 1977 (as amended) has given the Coast Guard statutory authority to respond to any hazardous chemical discharge within the waters of the United States.

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The Coast Guard, however, is unable to respond satisfactorily at this time due to state-of-the-art limitations in response equipment and techniques.

In an effort to improve the state-of-the-art of chemical discharge response equipment and methods, the U.S. Coast Guard Office of Research and Development is conducting a program to provide a response capability for non-petroleum spills. Begun in 1974, the Coast Guard program is a comprehensive effort designed to provide response personnel with the knowledge, equipment, and protection to effectively respond to a long list of chemicals. The current program organization consists of the following six project areas:

1. Prevention and Reduction — the development of techniques to prevent or reduce the discharge of a hazardous chemical.
2. Personnel Protection — the development of protective clothing, life support systems, and personnel monitors for personnel responding to chemical discharges.
3. Sampling, Chemical Classification, and Quantification — the development of equipment and techniques to allow response personnel to detect, identify, and determine the concentration of hazardous chemical discharges.
4. Hazard Assessment Modeling — the development and refinement of mathematical models to predict the behavior of discharged hazardous chemicals.
5. Containment, Treatment, and Recovery — the development of equipment and methods to respond to a chemical discharge and mitigate its environmental damage.
6. Disposal — the development of equipment and methods to dispose of chemicals which have been recovered.

The primary users of any equipment or methods developed in these project areas will be Coast Guard response personnel, such as members of the National Strike Force and Marine Safety Offices. It is the intent of the Office of Research and Development to provide these response people with hardware and techniques which will enable them to respond safely and effectively to the discharge of a hazardous chemical.

Hazardous chemical discharge response projects

Prevention and reduction

The objective of this project is to develop equipment and methods to prevent the discharge of chemicals from a vessel or barge which is in distress, and to reduce the amount of chemical discharged from a vessel which is already leaking. The two principal methods used to reach these objectives are chemical lightering, and patching and plugging. These techniques were identified in a feasibility study [1] conducted to investigate promising prevention and reduction methods.

Chemical lightering

This technique consists of off-loading a vessel or barge which is in distress prior to the release of its chemical cargo. Early work concentrated on adaptation of a system developed for off-loading stricken oil tankers. A study was conducted to determine the applicability of this system (ADAPTS — Air Deliverable Anti-Pollution Transfer System) to off-load the pumpable CHRIS chemicals, and to identify modifications which would allow more chemicals to be pumped. A total of 461 chemicals which can be shipped in liquid bulk form were investigated. Of these, 60 could be pumped with the existing ADAPTS, 241 could be pumped if minor changes were made to seals and bearings, and 407 could be pumped with an all-stainless-steel pumping system. The minor modifications have been made to the ADAPTS which are in the Coast Guard inventory and a program to test commercially available stainless-steel pumping systems has been conducted.

Interim storage

The Coast Guard is presently investigating two types of interim storage containers, rigid and flexible. The rigid container is a 5,000 gallon mild-steel intermodal container, being designed so that it may be transported on either flat-bed truck or railroad car, as well as being transportable by barge or boat. Foam flotation is presently being added to the container so that it may be transported by the Fast Surface Delivery Sled. This is a towable semi-submergible sled which sinks from under the payload, which may be an ADAPTS, or other pollution response equipment. Model testing for stability has been completed, and full scale tests will be conducted this summer. A feasibility study will be conducted to determine if the mild steel should be lined with Teflon to increase the range of chemicals the container is capable of storing.

Presently undergoing a feasibility study is the flexible container. This container is a large, towable bag, and has a capacity in the range of 25,000 gallons. Along with investigation of chemical compatibilities, the study will determine what flotation methods will be necessary due to density differences.

Patches and plugs

When a cargo tank has been holed due to a collision or grounding, it may be possible to reduce the amount of chemical discharged by using various types of patches or plugs. The feasibility study [1] identified a wide range of patching and plugging techniques, including magnetic patches, umbrella patches, bolt-on patches, and pipe wrappings. Based on this study, inflatable plugs and evacuated foam plugs were developed and are undergoing operational evaluation.

The Coast Guard, in conjunction with the Environmental Protection Agency, has developed an inflatable foam plug which, when inserted into a hole, swells and hardens to seal the leak [2]. Originally designed as a two-component, quick-hardening foam plug which could be inserted in a hole

above the waterline, recent improvements include the use of a single component foam and the capability to use the plug underwater. In conjunction with the use of patches and plugs below the waterline, an underwater TV system for conducting damage inspection has recently been acquired for evaluation.

Personnel protection

The objective of this project is to develop equipment and methods to protect Coast Guard response personnel from the hazards presented by the discharge of a hazardous chemical.

A response team could expect to encounter any or all of the following types of hazard:

- Toxicity hazards involving the toxic or irritating effects of hazardous chemicals through inhalation, ingestion or skin contact
- Fire
- Oxygen deficiency
- Explosion.

Although it appears unlikely that we will ever be able to protect an individual from explosions, the Coast Guard is working on systems to prevent injury in the other three areas.

Because of these hazards, each spill situation requires careful analysis to determine the approach to be used in clean-up. Among those factors which must be determined are:

- Identity of the chemical(s)
- Likely chemical reaction products
- Quantity spilled
- Environmental conditions
- Type(s) of hazard likely to be present.

These bits of information permit the on-scene co-ordinator to evaluate the consequences of either entering or not entering a contaminated area, and to set the level of protection needed if it is decided to enter a site.

The level of protection needed is specified for each of the CHRIS chemicals, and is divided into three levels:

(1) Level one affords the least protection, and consists of boots, gloves, hard hats, chemical resistant coveralls and vapor-tight goggles.
(2) Level two consists of boots, gloves, and a splash suit with a hood and a face shield.
(3) Level three consists of a fully encapsulated suit with a life support system to prevent any entrance of liquid, vapor, mist or dust.

The level of protection will probably change from initial response actions to final clean-up. Initially, a prudent approach would be to have the people in the highest level available, i.e., a totally encapsulated suit with a self-contained breathing apparatus (SCBA). As concentration, identity of chemical species present and hazard parameters become better defined, it may be possible to go to a lesser level such as a splash suit with an air purifying respirator.

A fully encapsulated suit to prevent any liquid, vapor, mist or dust entry is recommended for those chemicals which cause irreversible chronic, or acute

effects after short exposures. Known or suspected carcinogens are included in this level. Face and eye protection are provided either by the suit or by the full facepiece mask of the SCBA or both.

The ultimate goal of this effort is to provide Coast Guard response personnel with an integrated protective package which is compatible with a large number of chemicals, while providing sufficient monitoring capability to warn the wearer if he is in danger.

Since a survey study [3] indicated that there were a number of items of equipment available which would satisfy the requirements of the two lower levels, the Coast Guard has emphasized the development of a fully encapsulated, integrated suit.

As presently configured, this suit will consist of a fully enclosable suit with a 2.5 hour positive pressure rebreather, and a body cooling system. The body cooling system, which also cools the breathing air, is needed as the suit prevents dissipation of the heat generated by the wearer and the oxygen rebreather. The inhalation air is cooled to about 25°C for comfort and to prevent dehydration.

This package will also include a personnel monitor, presently under development at Argonne National Laboratory. This will enable the response personnel to assess the hazards of the environment outside the suit and to provide warning if the suit is compromised.

Sampling, chemical classification, and quantification

The objective of this project is to develop equipment and methods for use by Coast Guard response personnel to sample, classify, and quantify discharges of hazardous chemicals with sufficient accuracy to make initial response decisions and to monitor the progress of mitigation efforts. To obtain a better understanding of the state-of-the-art of techniques to perform these tasks, a feasibility study [4] was conducted to identify promising techniques.

Based on that study, a number of analytical techniques have been and will continue to be evaluated for application as spill response tools. These techniques include molecular spectroscopy, atomic spectroscopy, chromatography, electrochemistry, wet chemistry, and mass spectrometry. Each of these techniques can vary in its precision and accuracy based on its level of sophistication and its remoteness from a central laboratory. The modes of response may be classified roughly in terms of increasing time to obtain an answer as follows:

(a) Remote sensing apparatus
(b) On-site continuous direct reading instrumentation
(c) Towed or on-site sensors or systems
(d) Field test kits
(e) Pumped water being passed through stationary or shipboard system
(f) Marine Safety Offices (MSO)/Captain of the Port (COTP) facilities
(g) Mobile laboratories
(h) Central research laboratory.

In order to achieve the desired capability for sampling, classification, and quantification of hazardous chemical discharges, a four-tiered system is visualized (portable field systems, MSO/COTP laboratories, mobile laboratory, and central laboratory), with each tier representing a higher level of analytical capability. The MSO/COTP laboratories and the mobile laboratory will be linked to the central laboratory via computer terminals to allow rapid data transmission.

Hazard assessment modeling (CHRIS/HACS)

It was recognized that it was necessary to provide Coast Guard response personnel with as complete a system of chemical specific and chemical related response information as possible. To meet this requirement, the Office of Research and Development produced the Chemical Hazards Response Information System (CHRIS). CHRIS is a system of chemical and chemical-hazard-related information, both quantitative and qualitative, developed originally for use by field personnel in responding to emergency spill situations. Use of the system within the Coast Guard has now evolved to encompass contingency planning, vulnerability modeling, and risk analysis.

The Chemical Hazards Response Information System is composed of six basic elements: four manuals (three containing chemical data and one containing hazard assessment computations), data bases for regional contingency planning, and a computerized hazard assessment model. It is designed to support two basic modes of response to hazardous chemical discharges. The first encompasses the initial stages of involvement by Coast Guard personnel. These early stages of response, lasting from a few minutes to several hours, will be limited primarily to precautionary measures, rescue, first-aid, observation, and reporting. At this time, the first manual (A Condensed Guide to Chemical Hazards) is most useful. The second response mode involves concerted efforts by Coast Guard personnel to minimize the threat and to take direct action to eliminate or correct the chemical discharge situation. These actions demand the involvement of technically trained personnel and detailed information on chemicals, their hazards, vulnerable resources, and response methods. This information is contained in the three remaining publications in the series, the Hazardous Chemical Data manual, the Hazard Assessment Handbook, and the Response Methods Handbook, and also in the Regional Contingency Plan Data Bases.

The processes of dispersion, evaporation, combustion, and the like, which are associated with the chemicals of concern are quite complex and depend on many variables, not the least of which is the nature of the chemical itself. The Hazard Assessment Computer System (HACS) offers a systematic and convenient approach to estimate the type and extent of hazards. Hazard assessments are given in terms of distance and time over which a toxic or flammable concentration of a given chemical may exist in water and in air, and the minimum safe distance between the spill site and people or combustible materials should a fire ensue. HACS presently contains all necessary physical

and chemical property data to allow hazard assessments to be performed for 900 commonly shipped chemicals included in the CHRIS Data Manual. It consists of eighteen analytical models whose purpose is to delineate the behavior of the chemicals when spilled on water and to calculate the hazard presented by the spills.

Future work in this project will include the addition of more chemicals to the Chemical Hazards Response Information System, the filling of data gaps, and refinement and verification of the eighteen models in the Hazard Assessment Computer System.

Containment, treatment, and recovery

The objective of this project is to develop equipment and methods to contain, treat, and recover discharges of hazardous chemicals into the waters of the United States. The basic technical approach for this project consisted of a series of feasibility studies to identify potential techniques for responding to hazardous chemical spills, and several test programs to evaluate off-the-shelf or easily-modified containment and recovery devices, chemical agents, and sorbents. An initial study [5] was conducted to identify potential techniques for each of four behavioral groups. The chemicals of interest were divided into groups which are based on their behavior when released into water, i.e., they float, sink, vaporize, or dissolve. These categories are not mutually exclusive and a single chemical may exhibit several of these behaviors. Subsequent work in this project has been broken down in accordance with these groups.

Floaters

It was recognized that many of the devices designed to contain and recover oil spills could be used for floating hazardous chemicals. A study [6] was undertaken to determine the material compatibility of existing devices with a group of representative chemicals. It was determined that devices which did not contain polyvinyl chloride components could be used unmodified and those that did contain PVC could be used if PVC was replaced by superior materials (e.g., Buna-N, neoprene, or other elastomers). A series of tests [7] was conducted in conjunction with the Environmental Protection Agency to determine the ability of these devices to contain and recover chemicals and confirmed that the chemicals behave like oils with similar physical properties.

A secondary problem which is encountered while responding to a floating chemical is the hazard posed by toxic and/or flammable vapors emanating from the slick. A study [8] was conducted to evaluate the feasibility of using flammability reduction techniques, vapor concentration reduction techniques, and vaporization rate reduction techniques. Techniques which were examined include the application of fire-fighting foams, surfactant foams, sorbents, water aerosols, and encapsulation. Future work in this area is expected to emphasize the use of foams and aerosols.

Sinkers

Dredging, burial, and techniques such as sorption and chemical treatment were examined for their application to hazardous chemicals that sink [9]. These chemicals were divided for examination according to their physical state as normally shipped and according to their chemical composition (inorganics, halogenated organics, and non-halogenated organics). By considering both the nature of the chemical spilled and its interaction with the sediments it was possible to develop recommended response procedures. In the majority of incidents which involve these chemicals, the high degree of hazard associated with these materials will require removal through dredging. Some burial methods and other techniques such as chemical treatment and sorption also showed some promise, although a higher environmental risk is involved. Future efforts are expected to focus on improving dredging capabilities in the areas of minimizing sediment resuspension and improving the accuracy of the dredging operation.

Vapors

The study [10] which addressed hazardous chemical vapors examined the feasibility of fogging, forced dispersion, containment, electrostatic dispersion, and other high-potential techniques for chemicals that produce a toxic or flammable vapor at atmospheric pressure and ambient temperature. This group of chemicals also included those which react with water to produce a vapor and those which would sink if spilled on water but which may frequently be spilled on land. Response techniques which hold the most promise for future development include the use of helicopters for forced dispersal of non-flammable vapors, and the use of water sprays (fogging) to divert or "knock down" hazardous vapors.

Mixers

Possible techniques which could be used to ameliorate discharges of hazardous chemicals that mix with water (dissolve) include neutralization, solvent extraction, precipitation, and chelation [11]. Neutralization, using sodium bicarbonate for acids and sodium dihydrogen phosphate for bases, appears to be a feasible and practical technique. With proper deployment, these chemicals can be expected to greatly ameliorate the effects of the spilled chemical without additional adverse effects on the environment. Solvent extraction processes are feasible but suffer from more practical limitations than neutralization. Only 20% of the organic chemicals studied are extractable with vegetable oil, the most environmentally-safe solvent. Future efforts will concentrate on the development of neutralization techniques, including a field test to be conducted on a deliberate anhydrous ammonia spill.

Disposal

The objective of this project is to develop equipment and methods to dispose of oils and hazardous chemicals which are recovered from spills. The

chemical nature of the oils and chemicals of concern indicate that two basic categories should be investigated: oils and organic chemicals, and inorganic chemicals. Disposal of oil has been included in this project since many of the techniques which can be used for oil disposal can be extended for use with hazardous chemicals. The techniques which can be useful for oil and hazardous chemical disposal include incineration, landfilling, landfarming, and biological treatment. The principal techniques of interest for the disposal of inorganic chemicals are chemical treatment and engineered storage.

Another aspect of the disposal problem is the concept of interim storage and transportation of spill material and debris between the spill site and the ultimate disposal site. This problem was addressed in a study [12] which recommended ten disposal equipment systems for further investigation. This study will be the basis of the development of Coast Guard disposal equipment. The first effort was the test and evaluation of a portable oily waste incinerator which was developed under contract to the Canadian government.

Conclusion

This paper has presented a brief look at each of the six projects which comprise the Coast Guard's research program concerning response to hazardous chemical discharges. It is felt that these projects cover all of the important aspects of chemical discharge response. Although it is recognized that the Coast Guard will never have the capability to respond to every chemical which is transported, the successful completion of these six projects will provide the Coast Guard with an increased ability to respond safely and effectively to a vast majority of hazardous chemical discharges.

The opinions or assertions contained herein are those of the authors and are not to be construed as official or reflecting the views of the Commandant or the Coast Guard at large.

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