

A perspective on the application of chemistry to oil spill response*

F. R. Engelhardt

ENOVA Research Applications, Orleans, ON, K1C 7A9, Canada

It might seem incongruous that a research focused organisation such as the International Union for Pure and Applied Chemistry would pay attention to an issue as pragmatic as oil spills. After all, an oil spill tends to be viewed as a very practical matter, its issues characterised by loss of a valuable commercial product, damage to the environment, high costs of clean up, high legal liabilities, and very much media attention. Oil spills are not generally considered a pure or even applied chemistry issue. However, this would be a very short-sighted interpretation. Effectively every element of an oil spill, whether environmental, physical, operational or legal, is related to the complex chemistry of the oil and its breakdown products released to the environment. Indeed, it would be safe to say that if petroleum were a simple chemical product, the difficulties inherent in clean up of an oil spill would be much reduced, no matter what the origin or cause of the spill.

The chemical nature of oil is directly related to the fate and environmental impacts of spilled oil, whether on water or on land, and to the effectiveness of the diversity of countermeasures which might be deployed. While evaluation of the effects of spilled oil on the environment receives much attention in forums with a biological or toxicological focus, which often do take into consideration chemical factors, the complex topic of the chemistry of oil spills in direct relation to countermeasures is examined more rarely. The various chapters in this document discuss a diversity of oil spill countermeasures, and target the chemical and consequently physical behaviour of oil which determines its characteristics at the time of the spill. While oil spills occur in fresh and salt waters, and on land, marine oil spills remain the larger issue—there tends to be more oil spilled, environmental problems are more complex, and countermeasures are more difficult to implement.

The following papers generally reflect and review the current state of knowledge in their topic area, and are representative of the most recent surge in research and development activities, stimulated particularly by the *Exxon Valdez* spill in Prince William Sound, Alaska in 1989. It appears that oil spill research undergoes cycles of interest, activity and funding, linked to key oil spills. Previously, the *Torrey Canyon* spill in the English Channel off Land's End, in the United Kingdom in 1967 provided general incentive for research and development, as did the *Amoco Cadiz* spill off the coast of Brittany, France in 1978. Other oil spills, such as the 1968 Santa Barbara Channel, California spill, or the *Braer* spill off the Shetlands in 1993, have also stimulated specific areas of research and development on the basis of issues that arose in their particular spill scenario.

The articles in this publication have been contributed by recognised international experts in the spill response field, and have received the benefit of peer review. The articles are representative of the major categories of oil spill response research, spanning a wide range of technologies, supportive knowledge and experience, to include reviews of:

- oil fate and physico-chemical behaviour;
- mechanical countermeasure developments;
- remote sensing for surveillance of spills and as a support tool in response actions separation of recovered oil and water in relation to response and disposal;
- oil spill dispersants from an operational and environmental perspective;

**Pure Appl. Chem.* 71(1) (1999). An issue of special reports reviewing oil spill countermeasures.

- burning of spilled oil as a response measure;
- the use and issues surrounding a diversity of chemical countermeasures other than dispersants;
- the contribution of mineral fines and colloids;
- occupational health aspects in response;
- consideration of the net ecological effectiveness of countermeasures and response actions;
- the broad topic of bioremediation;
- ice-covered waters as a special response environment, and
- Orimulsion, as a special case for response.

This collection of review articles concludes with an evaluation of oil spill response technologies for developing nations, appropriately so since that is where much of the oil development and production currently occurs in the world.

One area which has seen much recent expansion is that of the essential linkage between detailed understanding of spilled oil physical/chemical properties and the effectiveness of response countermeasures. Crude oils and oil products are known to differ greatly in physical and chemical properties and these tend to change significantly over the time course of spilled oil recovery operations. Such changes have long been recognised to have a major influence on the effectiveness of response methods and equipment, which increases the time and cost of operations and risk of resource damage. All countermeasures are influenced, whether sorbents, booms, skimmers, dispersants, burning of oil and so forth. The incentive is for a rapid and accurate method of predicting changes in oil properties following spill notification, which could be used in both the planning and early phases of spill response, including an initial specific selection of an effective countermeasure. In later stages of the response, more accurate planning for clean up method and equipment deployment would shorten response time and reduce costs. An additional benefit would be more effective planning for recall of equipment not needed, as well as potentially decreasing the risk of natural resource damage and costs due to more effective spilled oil recovery. The concept of 'Windows of Opportunity' for oil spill response measures has been derived from multiple investigations in industry and government research organisations.

Although dispersants have been used to date in almost one hundred large spills world-wide, government approval for dispersant use has long been inhibited by a lack of understanding of the factors determining the operational effectiveness of dispersants, and the environmental trade-offs which might need to be made to protect sensitive areas from spilled oil. Recent advances in chemical dispersant development, formulation of low toxicity dispersants with broader application, and better understanding of dispersant fate and effects have combined to a more ready acceptance of this countermeasure by many, although not yet all, regulatory authorities throughout the world.

In addition to the category of dispersants, chemical countermeasures include many diverse agents, such as beach cleaners, demulsifiers, elasticity modifiers and bird cleaning agents, each with a unique and specialised role in clean up activities. However, the concerns for the use of these 'alternative chemicals' relate to the interpretation and application of toxico-ecological data to the decision process. If in the future the ecological issues concerning chemical treating agents can be further successfully resolved, the oil spill response community will have an increased range of options for response. However, extensive laboratory and field testing is required in many instances for new chemical dispersant materials and demulsifiers to improve the effectiveness of these materials on weathered oils and water in oil emulsions.

The acceptance of *in situ* (i.e. 'on site') burning of spilled oil has been limited by valid operational concerns about the integrity of fireproof booms, the limited weather window for burning due to the rapid emulsification of oils, the need to develop methods for the ignition of emulsified and weathered oils, and public concerns about the toxicity of the smoke generated during burning. However, burning provides an option, another tool in the tool-box, for the responder called in to combat an oil spill. Burning decreases the amount of oil that must be collected mechanically, thus reducing cleanup costs, storage, transportation, and oily waste disposal requirements. It also would decrease contact with sensitive marine and coastal environments and consequently reduce the potential for associated damage costs.

Laboratory and field studies over the last 10 years have addressed essential information requirements for feasibility, techniques, and effectiveness, as well as health and safety. The promising results of research *in situ* burning have led to its acceptance in a number coastal jurisdictions throughout the world, prompting the response industry to purchase and position *in situ* burning equipment and train its operators to use this alternative technology in approved regions.

Although not a direct recovery measure in itself, the application of remote sensing to oil spill response assists in slick identification, tracking, and prediction, which in many instances is an early requirement for effective response. An inadequate ability to see spilled oil seriously reduces effectiveness of oil spill response operations. Conversely, good capability to detect spilled oil, especially areas of thick oil, at night and other conditions of reduced visibility could more than double response effectiveness and greatly enhance control of the spill to minimise damage, especially to sensitive shorelines. Advances have been made in both airborne and satellite remote sensing. It has become possible to move from large and expensive to operate airborne systems to small aircraft, more widely available and practical for spill response operators. Also, the limitations in delayed data processing and information communication are being overcome by development of systems operating in functional real-time, which is essential for enhanced response capacity. Spill detection using satellites has also advanced markedly since 1989, with the ongoing intention to provide coverage of oil spill areas as early warning, or when flying by aircraft is not possible. An early useful application was an ERS-1 satellite program for detection of oil slicks, launched in 1992. More recently, spill detection capability has been developed for the Canadian Radarsat satellites, ERS-2 and a few other satellite programs.

The topic of bioremediation of spilled oil, that is, to use microbes to assist in clean up, is a corollary to the deployment of traditional countermeasures. It had not seen much operational or regulatory support until the *Exxon Valdez* spill, where it was initiated as a spill mitigation method, establishing bioremediation as a major oil spill R&D area. Bioremediation of oil spills was defined as being one of three different approaches: enhancement of local existing microbial fauna by the addition of nutrients to stimulate their growth; 'seeding' the oil impacted environment with microbes occurring naturally in that environment; and, inoculating the oil impacted environment with microbes not normally found there, including genetically engineered bacterial populations. Research emphasis and regulatory countenance has been predominantly on the first approach. Evaluation of operational utility of is continuing to identify conditions under which bioremediation can be used in an environmentally sound and effective manner, and to make recommendations to responders for the implementation of this technology.

The issue of hydrocarbon toxicity has been examined in petroleum refinery and petrochemical workers for more than a decade, and experimentally in test animals for a much longer period. However, there has been little specific information available on the effects of oil spills on human health, neither for oil spill response workers nor for incidentally exposed individuals. More recently, as reviewed in an article on human health effects in this publication, some reports have been published of skin irritation and dermatitis from exposure of skin to oil during cleanup, as well as nausea from inhalation of volatile fractions. Although there are to date no epidemiological studies of exposure by oil spill workers to petroleum hydrocarbons, the matter is drawing increasing attention.

One of the more important issues surrounding the choice and extent of application of oil spill countermeasures is knowledge about the ecological effectiveness of such response, that is, the balance point between continuation of clean up activities and letting the environment take care of its own eventual recovery. It is the last point which has driven much of the discussions and research associated with the concept of 'how clean is clean', or, how much cleanup is enough or too much. The results of such diverse research efforts are being used increasingly and successfully to link spilled oil chemistry to countermeasures practices and equipment. The advances are being integrated into more effective response management models and response command systems.

In summary, applied chemical research and development has actively contributed to an enhancement in oil spill response capability. Nonetheless, it seems that the pace of oil spill research and countermeasures development is slowing. The decrease is at least temporally associated with a decline in the frequency and magnitude of oil spills in recent years. Spill statistics gathered by organisations such as the publishers of the Oil Spill Intelligence Report, show that world-wide oil spill incidence and volume

have continued to decline since the time of the *Exxon Valdez* spill event (see the Oil Spill Intelligence Report publication *International Oil Spill Statistics: 1998*, Cutter Information Corp.). It is probably not coincidental that the amount of funding available for oil spill research and development, from both government and private industry sources, has declined similarly. In that context, the following articles are more a statement of currently accepted knowledge and practice, rather than being a 'snapshot in time' of intense ongoing research activities. The articles serve to capture the applied chemistry knowledge and experience of practitioners in a complex field, application of which remains essential for the development of improved oil spill countermeasures, and their effective use in real spill situations.