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UNIVERSAL GELLING AGENT FOR THE CONTROL OF HAZARDOUS LIQUID SPILLS

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Summary

Under contract to the U S Environmental Protection Agency, Calspan Corporation developed methods to treat, control and monitor spilled hazardous materials One of the most successful spill countermeasures applied was a dry, finely-granulated blend which would, within seconds after contact with spilled liquids, begin their transformation into tough, immobile gels which could be easily controlled and removed This blend is a "universal gelling agent" in the sense that it can immobilize essentially all hazardous liquid spills without foreknowledge of the liquid composition The blend contains powdered polymeric components optimized separately for interaction with aqueous liquids, chlorinated organics, alcohols, and nonpolar hydrocarbons It also contains a fumed silica fluidizer, which provides ease of field application and imparts longer term stiffening of all gels formed The "universal gelling agent" has been demonstrated to be effective on a variety of medium scale (55-gallon drum) spills on both land and water For special uses, such as organophosphorus pesticide spill control, the blend can be reformulated to include de-toxifying (oxidizing, hydrolytic) ingredients as well

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Introduction

The extent of environmental damage produced by any spill is dependent on the nature and quantity of spilled material and the distribution of the spill within the environment Obvious advantages can be realized whenever it is possible to minimize the areal or volumetric extent of hazardous concentrations of spilled material either by interrupting the spill before containers are empty or by preventing the spread of material that has already spilled.

The ideal countermeasure to any spill is to terminate the spill as soon as possible by sealing leaking or split containers before they are empty. Once hazardous chemicals are on the ground, the most attractive secondary countermeasure would consist of immobilization of the chemical to minimize the affected land area, to prevent flow of hazardous liquids to surface water, and to minimize percolation of liquids to subterranean aquifers. For water spills, ecological damage can be reduced by minimizing the spread of floating liquids across the surface or by trapping water-immiscible liquids in streams and ditches, both without interrupting the flow of water. In all cases, additional advantages result if the immobilization procedure leaves the spilled material in a form which can be safely and quickly recovered and packaged for further treatment or shipment and disposal.

This paper describes methods we employed experimentally to accomplish these goals.

Four powdered polymers, each capable of congealing at least one class of hazardous liquid into an immobile mass, were selected and combined into what we have termed colloquially "the universal gelling agent" The combined gelling agent can be used to seal narrow splits in containers, to completely immobilize liquids on land, to prevent percolation into the soil, to reduce surface spreading on water, to improve the effectiveness of booms, and to permit the trapping of liquids floating on streams in small-mesh nets or screens. The resulting gel is easily shoveled into drums for subsequent treatment or shipment. In most cases, the immobilized chemical is available for recovery and reuse after simple separation processes, such as distillation.

Experimental rationale

One major class of chemicals shipped in huge volumes is the precursor organic chemicals which by polymerization, thickening, or other chemical techniques are turned into solid end-products. A simple example is the polymerization of the numerous organic monomers into the polymers which are the common plastics of everyday commerce. An apparent countermeasure for spills of this class of chemicals — to essentially polymerize them in place at the site of the spill — carries with it a secondary danger. most polymerization reactions are exothermic, giving off substantial heat as they proceed spontaneously, so that explosion dangers are inherent in the solidification of materials by allowing them to spontaneously solidify to their ultimate end product. A further environmental danger accompanies use of polymerization catalysts of the common type such as benzoyl peroxide or lauroyl peroxide. These catalysts cause polymerization by providing free radical moieties, and the catalysts themselves are both poisonous and explosive

Nonetheless, the plan to immobilize a hazardous liquid spill in place need not be abandoned. Rather, more innocuous thickening, solidifying or immobilizing techniques were sought.

The "universal gelling agent" which we now proceed to describe works by the following active principle it selectively interacts with the chemicals themselves to create an immobile gel which is easily removed by mechanical means This is to be contrasted with other spill immobilization techniques, based upon simple absorption of the spilled liquid into a finely powdered mass

Materials required

The "universal gelling agent" is created by the mechanical blending of at least four, and preferably five or more, specific ingredients having the following purposes. The first ingredient is a material of the highly water-soluble polyelectrolyte-type, typified by polyacrylamide. This material could be substituted by any of a number of other polymers, including proteinaceous materials such as gelatin and casein. It is critical that this powder, and all the other components of the blend, be particle-size controlled within a precise range for speedy interaction with the target liquid, and for ease of deployment. It should also be so manufactured or admixed with a small surface-active additive that its speed of reaction and immobilization of its target class of liquids (in this case, aqueous liquids), is measured in seconds.

The second component of the blend is a loosely cross-linked copolymer, typified by polytertiary-butyl styrene copolymerized with divinyl-benzene. This material is selected to interact most strongly with liquids having almost no polarity and only poor solvent power (such as cyclohexane, gasoline fractions, and a variety of other inert spirits). A third component is a material of the polyacrylonitrile—butadiene copolymer class which is chosen to be especially effective against polar organic chemicals such as acrylonitrile, ethylene dichloride and other chlorinated or polar liquids. The fourth required component of the "universal gelling agent" blend is a material to cope with the most difficult of all hazardous liquids to thicken, solidify, and immobilize in place, typified by methyl alcohol and other chemicals of the alcoholic class. Materials suitable for this use include the polycarboxylmethylcellulose polymers or the polyethylene oxide materials These latter polymers can be replaced by one of the less expensive polysaccharide exudates produced by bacterial cultures, some of which grow preferentially on substrates as potent as that of wood alcohol. Our current embodiment of the above-described four-component blend uses the commercial products with the following trade names (1) Dow Chemical Corporation, Gelgard, to combat spills of aqueous liquids, (2) Dow Chemical Corporation, Imbiber Beads, to combat spills of the inert spirits-type liquids (typified by cyclohexane), (3) BF Goodrich Corporation, Hycar 1422, to combat the polar organic chemical spills including the chlorinated hydrocarbons; and (4) BF Goodrich Corporation, Carbopol, or Union Carbide, Polyox, to selectively thicken and control alcohol spills.

For ease of delivery of this four-polymer blend, it requires fluidization to ensure rapid, smooth egress from commercial spray equipment. A one-fifth by proportion addition of fumed silica components (such as that trade-named Cabosil, from the Cabot Corporation) has been used. It has been well-known in the paint and pigment industry, as well as in other chemical-based trades, that such finely powdered silicas are in fact thickeners for most organic vehicles. Unfortunately, the kinetics of such thickening action are far too slow to be useful in the manner envisaged here. Yet, the addition of Cabosil (to the four-component "universal gelling agent" blend described above) for the primary purpose of fluidizing that blend for ease of field deployment has a useful secondary benefit. It provides a much stiffer, resistant-to-hydrolysis gel of almost all hazardous liquids over the long-term than does the original "universal blend" itself Another significant advantage of the addition of the silica fluidizing agent is that it brings the overall coast of the blend down significantly since it is the least expensive component (judged by current market prices).

Cost factors

Consultation with manufacturers of the polymers mentioned in the preceding paragraphs and with others in competitive industries indicates that the final cost for the "universal gelling agent" can be brought to 50 ¢ per pound or less. It has been learned from laboratory experiments that approximately 10—25% of the "universal gelling agent" by weight, based upon the weight of the original spilled liquid, is required for complete immobilization. Field studies have shown, on the other hand, that — because of inefficiencies inherent in field deployment of the material and the poor mixing usually obtained — double this theoretical amount is regularly required.

Results of laboratory tests

Typical chemicals against which the "universal gelling agent" has been tested, with excellent results, are listed in Table I.

TABLE I

Typical compounds immobilized by "universal gelling agent"

Acetone	Ethylene glycol
Acetone cyanohydrin	Formaldehyde
Acrylonitrile	Gasoline
Ammonium hydroxide	Isoprene
Aniline	Isopropyl alcohol
Benzaldehyde	Kerosene
Benzene	Methanol
Butanol	Methyl Ethyl ketone
Carbon disulfide	Octane (2, 2, 4 trimethyl pentane)
Carbon tetrachloride	Petroleum ether
Chlorine water (saturated)	Phenol (89%)
Chloroform	Pyridine
Cyclohexane	Sulfuric acid
Cyclohexanone	Tetrahydrofuran
o-Dichlorobenzene	Trichloroethylene
Ethanol	Water
Ethylacetate	Xylene
Ethylene dichloride	

Field tests

Site used

These experiments were performed on a half-square-mile tract of abandoned farmland owned by Calspan Corporation near Bethany, New York. After a series of soil tests showed that the possibility of significant percolation of purposely-spilled chemicals into subterranean aquifers or surface drainage into nearby streams was negligible, the experimental facilities depicted schematically in Fig.1 were constructed.

Two sets of ditches, 2 ft. wide by 2 ft. deep and 100 ft. long, were constructed to determine the effectiveness of immobilization procedures against surface flow of spilled materials. At the foot of each set of ditches, a large excavation was constructed to house two, 12-ft.-diameter, 3-ft.-deep, plastic-lined swimming pools intended to capture all spilled material before escaping to the natural environment. The basic experimental concept used in most

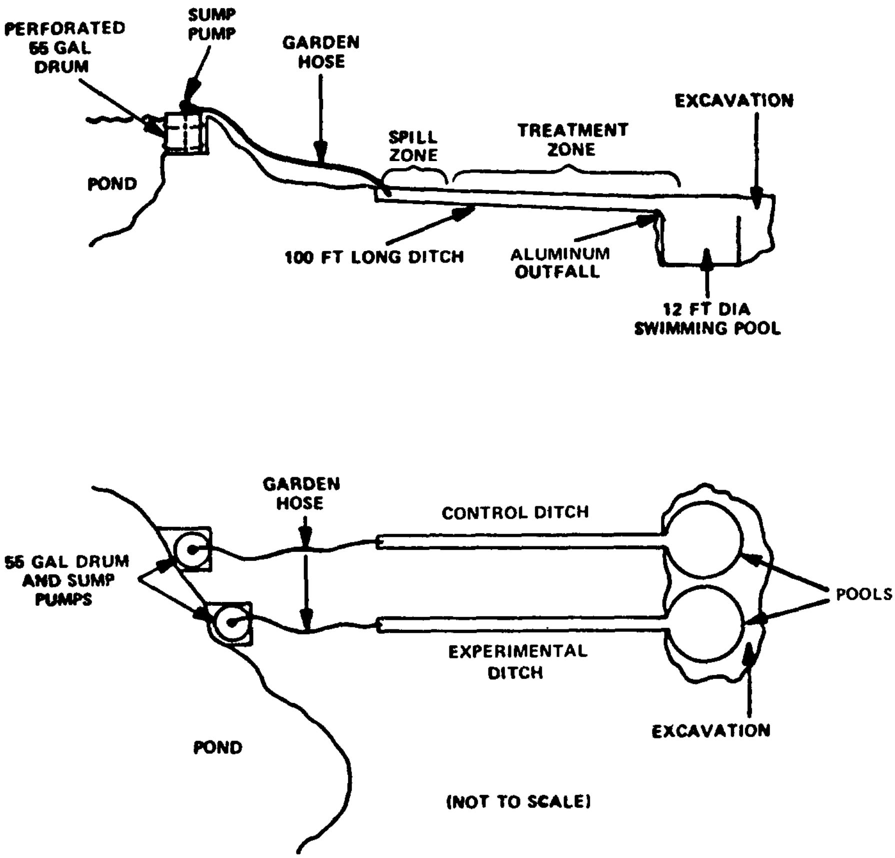


Fig 1 Experimental facility at Bethany test site

experiments was to simulate two spills in each test. One spill was treated experimentally in an effort to immobilize the chemical and the second was used as a control i e , to establish a baseline against which the behavior of the treated spill could be compared.

Chemicals used

The chemicals used for experimental spills in the field were selected to represent classes of materials that pose serious hazards in the real world Water was used to simulate aqueous solutions. Cyclohexane was selected as a serious real threat which is representative of chemicals with specific gravity smaller than unity and which are immiscible with water Ethylene dichloride, again a prime threat, was selected to represent immiscible chemicals that are more dense than water

To minimize cost and, more importantly, the clean-up problem after experiments, specific gelling agents were used in all large-scale field experiments. Confirmatory tests with the complete "universal" blend were carried out on the laboratory scale, only. To develop safe and effective treatment procedures before proceeding to the use of hazardous chemicals, ten preliminary experiments were performed on 55-gallon water spills in the 1% and 2% ditches

Results of preliminary outdoor experiments

Treatment procedure

In these field tests, dosages ranging from 2 to 6 lb. of dry powder were used to immobilize (but not completely gel) 1—5-minute-long 55-gal spills in distances ranging from 25 to 75 ft in the ditches. This quantity of powder represented an overtreatment which was required to compensate for inefficient distribution of the agent on the spill Much of the gelling agent fell on already congealed water. Extra agent was also used for creating a stiff gel to break the momentum of water at the head of the flow and create a dam capable of retaining the pressure of as-yet-untreated water. Since ditches were always saturated with water before experiments, the control spills of water always resulted in 55 gal flowing over the outfall 100 ft. downstream In the course of these preliminary tests, we developed the following procedure for evaluating the field performance of gelling agent countermeasures.

To minimize the area affected by the spill, it is necessary to inhibit flow as soon as possible. In our experience, it was particularly important to treat the head of the flow first. Not only does this create a dam to interrupt the flow, but this region of maximum turbulence produces excellent mixing of the agent with the liquid to promote efficient treatment Typically, the first dam of congealed material builds to a depth of ½—1 in. before overflow begins It is most effective then to move downstream to form a second dam. With the flow inhibited by the first dam, the second is more easily formed and, by continued treatment, it can be built to depths exceeding 2 in before overflow begins By progressive treatment in this way the final dam usually exceeds 4 in. in depth with a 55-gal spill before flow is terminated in the ditch. Once this is accomplished, it is a simple matter to move upstream and treat the liquid trapped behind the dams that were formed earlier. For containment purposes, the peripheral dams are adequate without further treatment of the major volume of the spill.

Methods of application evaluated

A variety of dispersal methods were tested. It was apparent that broadcasting the agent with shovels would constitute a simple and effective procedure for spills with minimum dimension of 4 or 5 ft. Much of the material was lost in our narrow ditches with this procedure When attempts were made to sprinkle the material from shovels, the distribution of the agent across the surface was usually uneven and as water flowed around the thicker regions, an impenetrable gel formed at the surface, producing a large clump with dry, unused agent at its center.

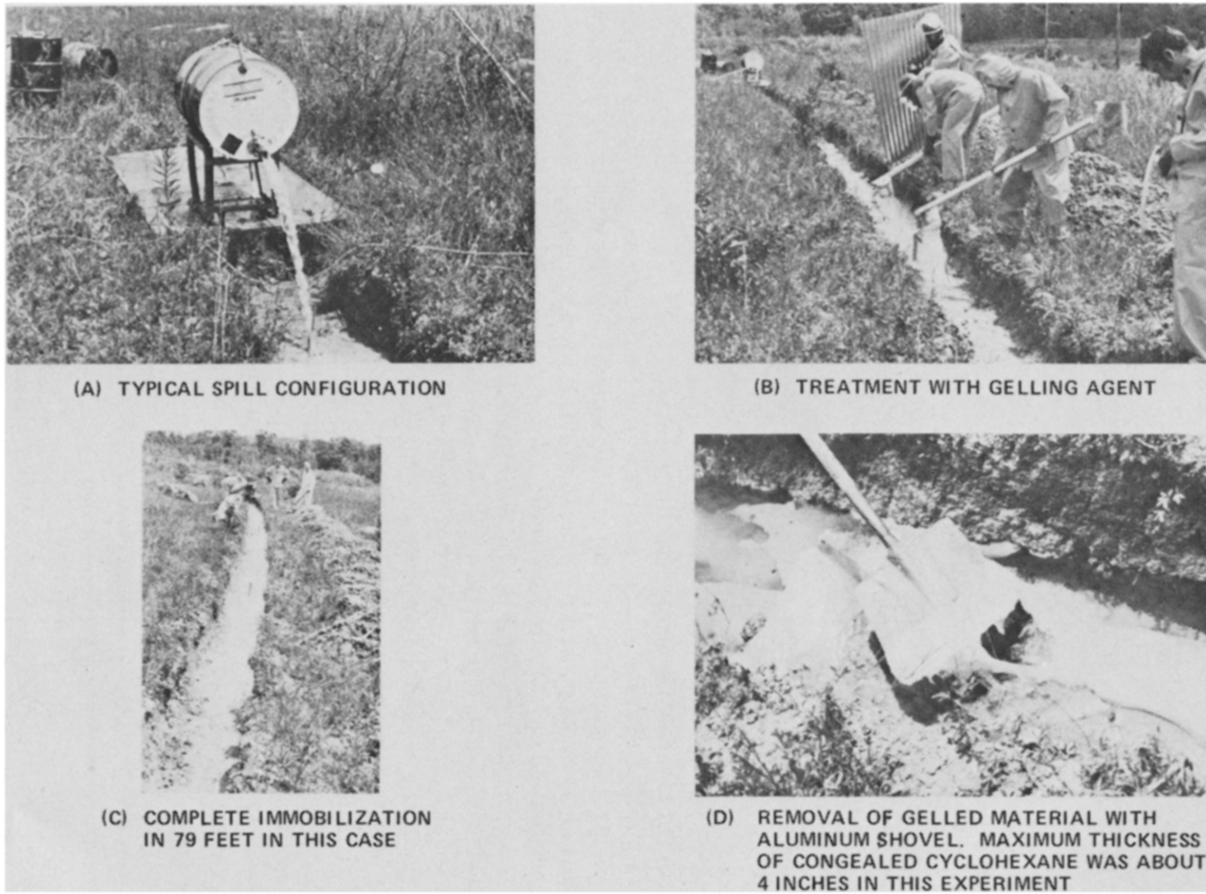
More uniform distribution was achieved with sprinklers constructed from 3-lb. cans to which 6-ft.-long handles were attached. These proved to be very effective for treating in narrow confinements.

Hand pump dusters normally used for insecticide application could not deliver the agent fast enough to stop a 1/2-gal-per-second flow in the 2-ft -wide ditches. Larger hand-powered dusters intended for agricultural use delivered material at an adequate rate but were so tiring for operating personnel that continuous operation could not be maintained. This type of duster could be equipped with battery-powered explosion-proof motors to produce effective portable equipment for treatment of spills that have reached remote areas (*e g* , where the spilled material flows into heavily wooded areas through gulleys or small streams)

Dry chemical fire extinguishers produced an airborne plume of agent that was too wide to treat spills in confined areas. Since fire extinguishers cannot hold a sufficient mass of agent for treating large spills, they do not seem practical for use against material that is already on the surface. With a different nozzle design, they could be made into very effective portable devices for sealing splits in containers, however. High-pressure dispersal devices appear to be suitable for immobilizing large spills that require large amounts of gelling agent where the use of compressor-operated equipment is appropriate. Paint sprayers proved effective but could not deliver the agent at a sufficient rate to treat large spills. In our experiments, sand blasters, delivering 5—10 lb. of agent per minute, provided an appropriate distribution for large spills, even though some of the agent was always blown out of the simulated spill area by the wind

Final recovery and clean-up procedures

Removal of the bulk of gelled material was readily accomplished mechanically by shoveling the material into 55-gal drums. Heavy earth-moving equipment would be useful for large spills of nonflammable materials, but should



(A) TYPICAL SPILL CONFIGURATION

(B) TREATMENT WITH GELLING AGENT

(C) COMPLETE IMMOBILIZATION IN 79 FEET IN THIS CASE

(D) REMOVAL OF GELLED MATERIAL WITH ALUMINUM SHOVEL. MAXIMUM THICKNESS OF CONGEALED CYCLOHEXANE WAS ABOUT 4 INCHES IN THIS EXPERIMENT

Fig 2 Immobilization of hazardous chemicals on land with gelling agents

be avoided where a fire hazard exists. The consistency of most gelled chemicals makes pumping inappropriate.

Typically, 75—85% of the spilled material was recovered in gelled form during our experiments. Our experience was that some material was always inaccessible to shovels after gelling chemicals on land, but the amount was a small fraction of the mass lost by a combination of evaporation and percolation into the soil.

In some cases, depending on the toxicity of the spill, further recovery would be required. In all cases in which polymeric gelling agents are used on highways or city streets, thorough washdown will be required to eliminate the hazard posed by the excellent lubricating effect of dilute mixtures of these polymers and water. Most polyelectrolytes produce a nearly friction-free environment that could be extremely hazardous to pedestrian and automotive traffic.

Gelling of large spills of hazardous liquids

In addition to the experiments with water, experiments were also performed in the ditches to test immobilization and gelling procedures against cyclohexane and ethylene dichloride. In both cases, the 2% ditches were presaturated with water but no standing water was present. Seventy-five pounds of dry powder was used to completely gel (not just immobilize) a 55-gal cyclohexane spill within 80 ft. of the spill point. Forty-one and one-half pounds of dry powder arrested and completely gelled 55-gal of ethylene dichloride in slightly less than 70 ft. After the treatment was completed in each case, water was pumped into the spill zone to determine if the gelled material could be dislodged. As water seeped under the gelled cyclohexane, buoyancy dislodged approximately 50% of the material in 30 minutes, but none flowed down the ditch. The gelled ethylene dichloride was unaffected. A surge flow of water, produced by releasing 55 gal at the head of the ditch in 2 minutes, washed approximately 75% of the gelled cyclohexane into the pool. The consistency of the floating material was such that it could easily have been trapped with a small-mesh net or screen. Again, the gelled ethylene dichloride was unaffected. In both cases, a total of 75% of the spilled material was recovered in gelled form by shoveling and 75% of the respective control spills was flowed into drums placed at the outfall 100 ft. downstream. The sequence of four photographs in Fig.2 illustrates the results of these experiments.

The use of gelling agents on water spills

Limited small-scale experiments using gelling agents to immobilize hazardous liquids floating on water showed that the fraction of liquid that had not gone into solution could be readily congealed Tests with benzene, cyclohexane and gasoline showed that the congealed material continued to float indefinitely. Treated acrylonitrile, on the other hand, floated for approximately 48 hours in the beaker experiments and then gradually sank to the bottom. Bioassay tests with both benzene and acrylonitrile showed that fathead minnows mistook small floating particles of gelled material for food and died within a few hours. The ease with which the gelled material could be very quickly removed from the water surface suggested, however, that the procedure could be quite useful and that larger-scale tests were warranted. Ungelled organic chemicals in control bioassays did, of course, prove to be toxic

Several large-scale laboratory experiments were performed in 12-ft.-diameter swimming pools to determine the effectiveness of gelling procedures for immobilizing spills of material that is both immiscible with water and less dense than water. Cyclohexane was used as the test material.

In a variety of experiments in which cyclohexane was spilled both from beneath the water surface and poured onto the surface, the spontaneous spreading was prevented by treatment with gelling agent. As spillage and treatment continued, the gelled material reached thicknesses up to approximately a half centimeter as it gradually drifted outward from the spill center. Light breezes caused noticeable drift of rafts of the congealed material. No tendencies to sink were observed.

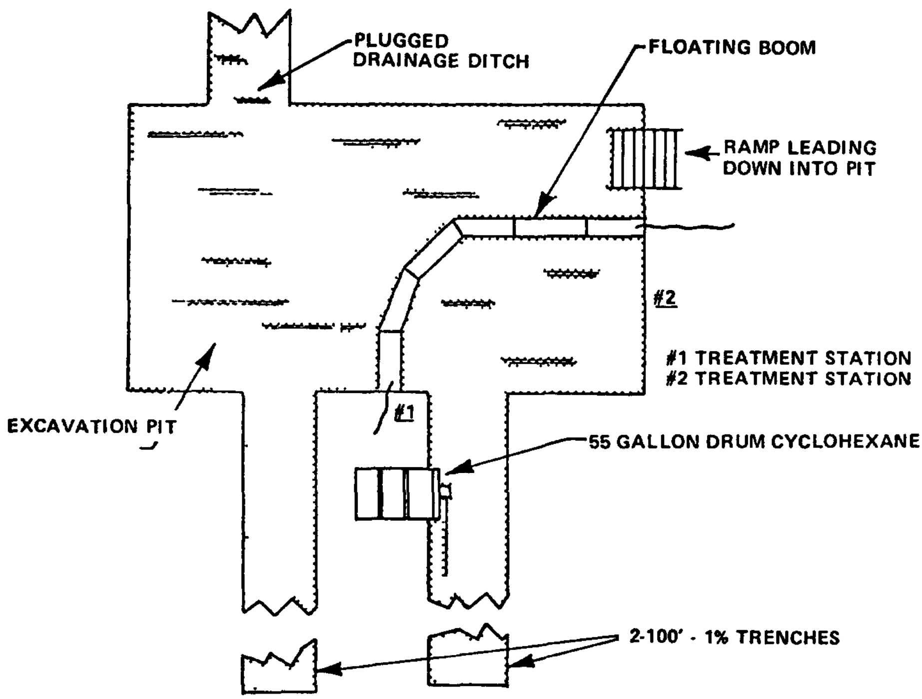
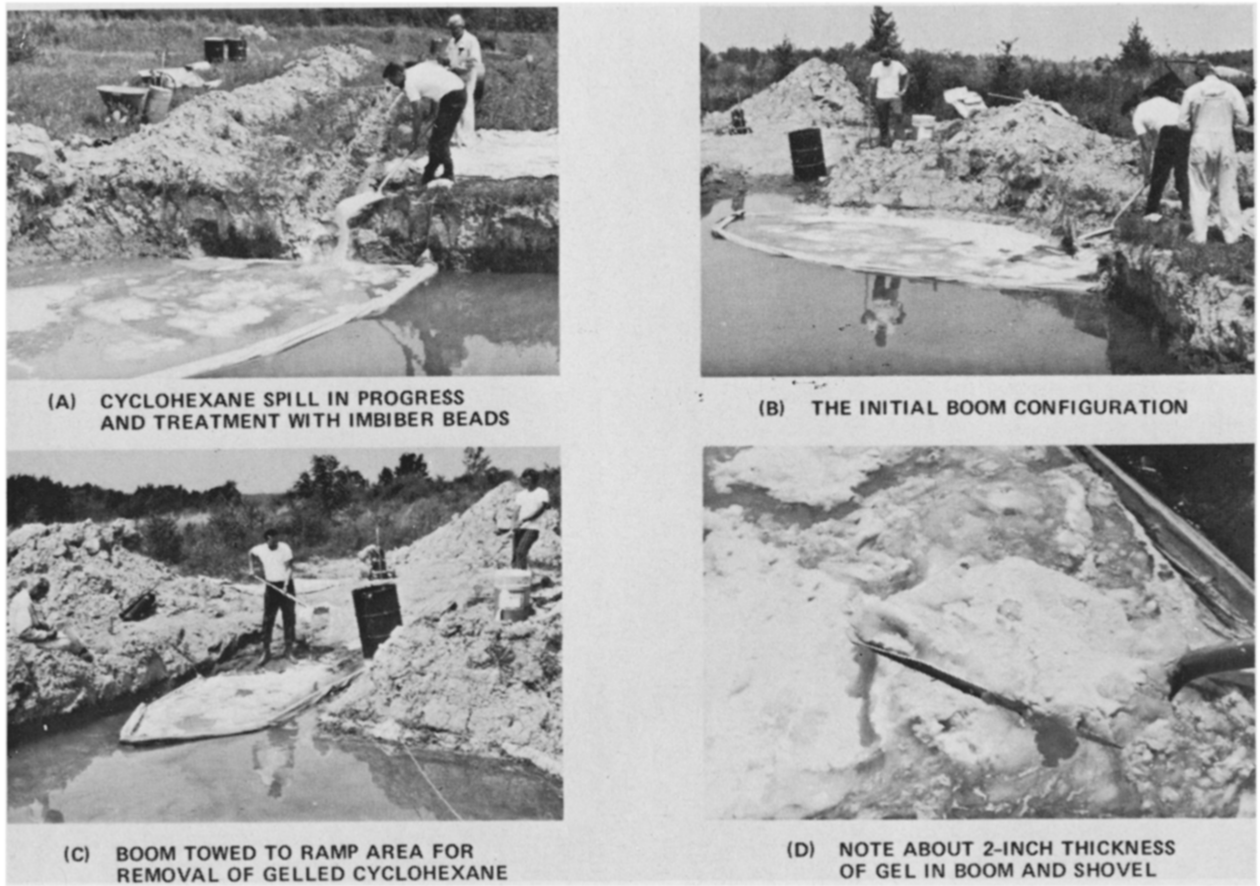


Fig 3 Plan view of "lake" cyclohexane spill treatment test



(A) CYCLOHEXANE SPILL IN PROGRESS AND TREATMENT WITH IMBIBER BEADS

(B) THE INITIAL BOOM CONFIGURATION

(C) BOOM TOWED TO RAMP AREA FOR REMOVAL OF GELLED CYCLOHEXANE

(D) NOTE ABOUT 2-INCH THICKNESS OF GEL IN BOOM AND SHOVEL

Fig 4 Increasing the effectiveness of booms by congealing the trapped liquid

The gelled cyclohexane could be readily confined and immobilization completed with booms constructed of short lengths of lumber to which screen wire had been attached. These booms completely confined the gelled material and permitted it to be compressed to thicknesses of four inches

One field experiment was performed with the same materials at our Bethany site. The 15 × 30-ft. excavation at the foot of the 1% ditches was filled with water to simulate a lake. A 24-ft. boom constructed of wood 4 × 4's with screen and an 8-in. plastic skirt was placed around the outfall in such a way as to confine the spilled material to about one quarter of the excavation surface. Fifty-five gallons of cyclohexane were spilled 15 ft. upstream from the outfall of a ditch in which a continuous water flow was also maintained. The experimental configuration is illustrated in Fig.3 Sixty pounds of gelling agent were broadcast onto the spill from shovels as the cyclohexane entered the excavation. As with the pool experiments, the treatment was highly effective The cyclohexane was congealed into a floating mass with an average thickness of approximately ¼ in. that was completely contained within the boom. The boom was used to drag the treated material to the ramp area of the pond (see Fig.3) and to compress the gell to thicknesses up to 2 in. without loss Aluminum shovels were then used to skim the 1—2-in. layer of stacked gelled material from the water into 55-gal drums. Approximately 75% of the original spill volume was collected from the ramp area. Losses occurred in the ditch by evaporation and by adhesion to the walls of the excavation. These results are illustrated in the four photographs presented as Fig 4

After removal of the bulk of the gel, the surface of the pond was swept with a piston film of sorbitan monooleate to complete treatment [1]. Bulk water contained 3.8 ppm of residual cyclohexane at the conclusion of the test.

Conclusions

This study was performed as only one project in a larger EPA-sponsored program on "Methods to Treat, Control and Monitor Spilled Hazardous Materials"[2]. The results obtained allow the optimistic conclusion that a "universal gelling agent" consisting of a dry, cost-effective blend of common polymeric and inorganic materials can be added to the increasing list of available countermeasures for hazardous liquid spills. The material can be stored at a number of centralized sites and used immediately without requiring prior knowledge of the spill's composition. In this sense, the "universal" quality of the material represents a significant logistical advantage which offsets the increased cost of manufacturing the blend. The lack of chemical reaction between the blend and the chemicals immobilized allows the possibility of secondary recovery of the spilled liquids

In an active current program to "optimize universal gelling agent and develop means of applying to spilled hazardous materials"[3] the generic specifications of the most effective blends are being written, the cost factors evaluated, and methods for efficient dissemination — including tests of commercial equipment — field-tested.

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