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Treatment of Hazardous Material Spills With Floating Mass Transfer Media

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TREATMENT OF HAZARDOUS MATERIAL SPILLS

WITH FLOATING MASS TRANSFER MEDIA

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ABSTRACT

An approach for the *in situ* treatment of spills of soluble hazardous polluting substances was developed and demonstrated on a field scale for a static body of water. Laboratory-scale experimentation showed that floating sorbents and ion exchange resins could be highly effective removal agents when applied as small particles beneath the surface of contaminated waters.

A lightweight commercial activated carbon was found to be particularly effective for removing organic substances such as phenol, aromatic hydrocarbons, and organophosphorus insecticides from water. The activated carbon can be pulverized to a small mesh size (100 x 325) which floats slowly to the surface of the water. The small mesh size enhances both the contact time and the sorption kinetics.

Floating ion exchange resins were also prepared for use on spills of acid (e.g., sulfuric and hydrochloric), alkalis (e.g., caustic soda) and toxic salts (e.g., sodium cyanide). Hollow glass microspheres are incorporated in the resin granules for buoyancy.

Delivery systems which show promise for field use include: (1) ice cakes containing floating media and gravel ballast; (2) clay cylinders; and (3) weighted plastic bottles.

Field demonstrations were conducted using carbon contained in weighted plastic gallon bottles. The carbon proved highly effective in removing an organophosphorus pesticide spilled in a large basin, and was easily collected through use of an oil containment boom. Ice encapsulated floating anion exchange resin beads were similarly employed to neutralize a spill of sulfuric acid.

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SECTION I

CONCLUSIONS

The removal of selected hazardous materials from water with floating mass transfer media was successfully demonstrated in laboratory and field tests, using floating activated carbon for organic removal and floating ion exchange resins for electrolyte removal. The following is a list of conclusions based on these studies.

GENERAL

- The technical feasibility of the concept of subsurface injection of floating mass transfer media for treatment of hazardous polluting substances has been established through field demonstration.

- This concept shows great promise as a spill response technique.

- Surface collection of spent floating media in a static body of water can be accomplished with existing oil spill cleanup equipment.

- The quantity of floating media required for a desired level of removal of spilled hazardous material will vary with the type and concentration of material being removed.

- The effectiveness of spill treatment decreases as the spilled hazardous material becomes more dilute. Thus, rapid response to a spill situation is of paramount importance. For example, 10 grams of activated carbon will remove 97 percent of the phenol from a one gram per liter solution of this material. Sixteen grams of carbon would be required to obtain the same level of removal if the one gram of phenol were dissolved in 10 liters of water.

- The use of weighted packages of floating media for treating hazardous material spills represents the most immediate possible response to these situations in remote areas. Where spill frequency is high (e.g., busy harbors) bulk application with infusion pumps is thought to be the preferred method of application.

FLOATING ACTIVATED CARBON

- Two commercially available activated carbons, Nuchar C-190 and Nuchar WA, can be applied at the bottom of a water column to effectively sorb organic matter as they float to the surface.

- Nuchar C-190 is the carbon of choice based upon superior sorptive ability and superior floatability.

- Fine carbon particles in the 100 x 325 mesh range are capable of approaching equilibrium sorption by floating once through the water column.

- Both dry and pre-wetted carbons are equally effective in removing organics from aqueous solution.

- Nuchar C-190 is highly effective in sorbing phenol, toluene, benzene, styrene, Diazinon, Malathion, and, to a lesser extent, acrylonitrile.

- A single pass of Nuchar C-190 through a water column removes approximately 80 percent of the Diazinon spilled in a ten million gallon water basin.

- The granular grades of Nuchar C-190 used in this study are no longer commercially available. A powdered grade, Nuchar C-190-N, is available but this material was not evaluated.

- An impact method of crushing the carbon produced a product superior to that obtained by ball milling.

- The floating activated carbon can easily be herded with the aid of a plastic containment boom and recovered from the treated water by pumping as a slurry from the surface of the water through a diaphragm pump.

FLOATING ION EXCHANGE RESINS

- The use of weakly acidic and weakly basic ion exchange resins for treating spills of acidic or basic electrolytes has two major advantages over the use of neutralizing chemicals. These are: (1) application of excess resin will not cause pH extremes and (2) the resins are effective for both neutralization and removal of dissolved matter. The principal disadvantage is the high cost of the resin (approximately $290 per cu. ft.)

- Floating ion exchange resins were synthesized by incorporating hollow glass microspheres in the resin matrix to provide the desired buoyancy.

- Bulk polymerization and suspension polymerization techniques were found to be successful for preparation of a floating weakly acidic carboxylic resin and a floating weakly basic epoxypolyamine resin, respectively.

- Suspension polymerization is the preferred production technique since it should be far more economical than bulk polymerization techniques. Both cationic and anionic resins can be produced by suspension polymerization; however, only the preparation of floating anion resin was successfully demonstrated by this method.

- The feasibility of commercial production of floating resins has been demonstrated by the production of several hundred pounds of floating epoxypolyamine anionic resin.

- A low removal level of sulfuric acid was observed in the field demonstration, but is not considered representative of the potential of floating ion exchange resins for treating spills of electrolytes. Rather, the low removal efficiency was the result of poor contact between the resin and the acid due to a bottom layering effect of the acid.

PACKAGING AND DELIVERY

- Ballast requirements to sink the floating media vary from 0.2 pounds of ballast per pound of wet media to 12 pounds of ballast per pound of dry media.

- The inclusion of water or ice in the interstices of the media significantly reduces the ballast requirement.

- Routine packaging techniques which show promise for field use include (1) ice cakes containing floating media and gravel ballast; (2) clay containers; and (3) weighted plastic bottles.

- Based on the work to date, the ice cake approach appears to be preferable because of lower ballast requirements and superior dispersion characteristics near the bottom of the water column.

- Ice cake packaging is the only identified technique with no potential for water quality impairment. This technique involves a large temperature drop near the ice cake but the average temperature change in the treatment area will be only 1 to 2 °F.

- The feasibility of packaging carbon and ballast in plastic containers and resin and ballast in ice cakes has been demonstrated in field tests.

- The feasibility of air drops of floating carbon packaged in plastic containers has been demonstrated on a large scale.

SECTION II

RECOMMENDATIONS

- As a result of the success of the laboratory studies and field demonstrations described in this report, efforts should proceed to further develop and implement the floating media concept for treatment of spills of hazardous polluting substances.

- A slurry injection system should be developed to allow routine use of floating sorbents in ports and areas with a history of high spill frequencies.

- Packaging techniques for air transport and delivery of floating media which were investigated in this program should be optimized.

- A program should be undertaken to extend the current work to flowing streams.

- Further studies should be initiated to establish the optimum media mesh size with respect to removal efficiency, cost, and in the case of the carbon, method of pulverization.

- Commercial production techniques for manufacture of floating ion exchange resins should be refined.

- Production techniques for suspension polymerization of floating cationic resins should be developed.

- Techniques for marking spills of various hazardous materials should be developed, permitting visual delineation of the spill area and greatly facilitating response activities.

- Consideration should be given to the development of a sinking sorption media which can be easily recovered from the bottom of a watercourse.

SECTION III

INTRODUCTION

Pollution resulting from the spillage of oil and hazardous materials has emerged as a major national problem. It is presently estimated that some fifteen thousand spills involving oil and hazardous materials occur annually in the navigable waters of the United States[1]. These spills range in size from small quantities to millions of gallons[2] and threaten many important waterways in the country.

Damage from such spills is often extensive. Massive spills can render waterways unfit for some or all major beneficial water uses and in some instances may eliminate large segments of the biota in the affected area. Recognition of the severe environmental threat represented by accidental spillage of hazardous polluting substances has led to legislative and administrative steps designed to minimize acute releases and provide for immediate response activities when necessary. Of particular importance is the development of methods for *in situ* treatment of spills. This report describes an EPA sponsored program aimed at the development of one such method of *in situ* treatment of hazardous materials spills.

Potential treatments which conceivably can be applied *in situ* to ameliorate the effects of hazardous polluting substances in the aquatic environment are almost as numerous as the substances themselves. Obviously, it would be impractical to attempt to develop a specific countermeasure for each individual hazardous polluting substance. Moreover, since the resources which can be invested in developing countermeasures against hazardous polluting substances in the aquatic environment are limited, efforts must be directed toward those areas which promise to produce the maximum return on this investment.

Battelle-Northwest used the following criteria to evaluate potential countermeasures.

- Countermeasures should be highly effective.
- Countermeasures should be applicable to a large number of substances.

- Countermeasures should be amenable to rapid, easy deployment. Equipment and/or chemicals which cannot be rapidly conveyed to the scene of an incident are undesirable.

- Countermeasures should be free from potentially harmful secondary effects in the aquatic environment, including noxious sludges.

- Countermeasures developed to combat spills of hazardous polluting substances should take advantage of existing technology, particularly that technology developed to combat oil spills, to the maximum possible extent.

- Countermeasures should provide for easy isolation and removal from water of substances added to extract or precipitate spilled materials.

Consideration of numerous potential methods for the *in situ* treatment of spills of hazardous polluting substances led to the following conclusions.

- *Chemical degradation* (transformation, oxidation-reduction, etc.) is generally unacceptable since in most cases the agents which must be added to effect reaction pose an equal or greater potential hazard to the aquatic environment than the original pollutant. The situation is further complicated by the nature of the spill environment which does not allow close control of operating conditions. Concentration changes resulting from natural dilution processes could cause excess chemical addition and so increase the damage to the aquatic environment.

- *Complex formation and neutralization* suffer from difficulties similar to those of chemical degradation, in the lack of control of the reaction environment and the inherent threat to water quality of the necessary additives.

- *Precipitation techniques* at first appear to be an attractive solution; however, the ultimate reaction poses a new type of threat. Without an effective means for removing the precipitate, the watercourse is subjected to a concentrated buildup of fine particulate matter which could damage feeding and spawning grounds, with subsequent deleterious effects on aquatic life. The full

impact of this type of damage has never been satisfactorily explained, but presumably it could rival the damages of the original pollutant to water quality. Furthermore, the introduction of colloidal precipitates would threaten gilled species and would decidedly damage recreational and aesthetic water quality characteristics.

- Solvent extraction and foam separation processes have several intriguing characteristics. With proper choice of solvent, the product stream can be made to rise to the surface where collection with existing hardware should be possible. In addition, solvent extraction and foam separation processes are fairly broadbased, with a single component displaying applicability to many pollutant releases. Unfortunately, both processes require some control over the area to be treated, and treatment of any large body of water would necessitate use of several types of feed mechanisms. This implies high capital costs and storage facilities to stockpile such equipment regionally. Further, in the case of solvent extraction, the solubility of the solvent in water would cause a considerable pollution problem in itself due to the large quantity of solvent required.

- Skimming and booming are available techniques for oil spills. They could be applied to light insoluble materials as well as slightly soluble organics. Rapid response aimed at booming and skimming any undissolved portion of the contaminant could greatly reduce the severity of a spill.

- Flow augmentation can be applied only in certain circumstances. Mechanical mixers such as outboard motors can be used to aid diffusion. Flow augmentation may be utilized where stored water is available upstream. In any event, such a practice relies in part on good predictive models of the aquatic environment to determine the extent of contamination and expected duration of toxic concentrations. This information is available for a number of streams, as is time-of-travel data. Such data are not gathered in a single source nor properly referenced to allow for quick retrieval and application in a practical emergency, however.

- Burn-off techniques, because of safety and air quality considerations, are probably applicable only in very limited cases in which the material remains confined in a small isolated area. Many hazardous materials emit highly toxic vapors when heated to decomposition. Consequently, burning may intensify hazardous conditions and force evacuation of areas surrounding a spill site. The presence of heavy vapors which can travel along the ground and cause flash-backs further endangers safety when burn-off techniques are applied.

- Oxygen addition may be an attractive alternative for substances posing a BOD problem. The oxygen is added to the water to maintain dissolved oxygen levels while a spilled material is being dispersed and degraded aerobically. There has been recent interest in injecting air or pure oxygen into water courses to achieve this end in areas of chronic low dissolved oxygen. The required apparatus is simple enough to allow mobilization for transport to a spill site. The problems would involve supplying enough gas to accomplish the task and designing equipment capable of efficiently transferring the gas into a variety of potential stream or reservoir configurations.

- Biological degradation, while attractive in some respects, encounters several difficulties. In order to encourage degradation at a rapid rate it would be necessary to have on hand large quantities of acclimated cultures. The problems associated with stockpiling many such cultures, each specific to a particular substance, are obvious. Also, many hazardous materials are inherently resistant to biological degradation.

- Physical sorption and ion exchange processes can remove substances from solution within a period of a few minutes and hold the substances in a solid form for long periods of time. The use of ion exchange resins for acid, base, metal, or toxic salt spills and the use of activated carbon or sorption resins for organic matter could apply to a large number of hazardous polluting substances.

Based on the above considerations, it was concluded that physical sorption and ion exchange processes offer the greatest promise for treatment of acute spills in the aquatic environment.

The two major problems associated with the application of mass transfer media to counteract spills of hazardous polluting substances in a free water environment are:

1. the mechanics of introducing the active media into the water (a common problem with all treatment agents) and

2. the subsequent removal of the media from the water.

Traditionally, sorption and ion exchange processes have been largely restricted to operation within columns. This method of application is limited by some very real concerns: the cost of stockpiling mobile columns for spill treatment, the problem of rapid deployment of the large equipment involved, and the practicality of pumping free waters into a contained environment for treatment. Some studies have been conducted with powdered activated carbon in which the sorptive media was dispersed on the water and allowed to settle[3]. Although this approach may be satisfactory for selected impoundments, in flowing streams the aesthetic damage would be extensive and gilled species would be subjected to the problems inherent in an environment highly saturated with particulate and colloidal matter.

An alternative approach is the use of floating mass transfer media wherein the problems of posttreatment residual effects would be eliminated by collection of the spent media after use. Application problems would be reduced to those of subsurface injection and surface collection. Subsequent to these conclusions, a program was initiated by Battelle-Northwest under EPA sponsorship to develop and demonstrate the concept of floating physical sorbents and ion exchange resins for in situ treatment of spills of hazardous polluting substances. This report describes the results of the work accomplished in that program.

SECTION IV

THE CONCEPT

Sorption processes are highly effective for removing many different substances from water. Their principal advantages are: (1) treatment can be accomplished without the addition of chemical reagents to the water; (2) one sorbent can be used to remove a large number of different substances from water; and (3) the sorbent collects and holds a hazardous material in a less nocuous (undissolved) form for long periods of time. The term "sorption", as used in this report applies to both physical sorption (e.g., surface attraction as in activated carbon) and ion exchange.

Physical sorbents act like chemical sponges, soaking up dissolved pollutants without releasing undesirable materials in their place. Ion exchangers, on the other hand, replace a hazardous material in the aqueous phase with a less objectionable material. For acids and bases the H^+ and OH^- ions are neutralized to water and the anion or cation corresponding to the acid or base is sorbed by the exchanger. Therefore, the acid or base is essentially removed from the water and a corresponding amount of salt does not remain as would be the case if the acid or base were chemically neutralized. The treatment of a salt spill (e.g., $CuSO_4$) would most probably involve the replacement of the toxic ion(s) (e.g., Cu^{+2}) with ions (e.g., Na^+) that are more compatible with the aquatic environment.

Sorption may be accomplished either by batch treatment or by column treatment. Batch treatment is carried out by mixing the sorbent with the solution to be treated for a specified period of time after which the sorbent is separated from the solution for disposal or regeneration and reuse. This method is simple and may be carried out with relatively low-cost equipment. Column treatment is accomplished by percolating the solution through a bed of the sorbent until some level of the sorption capacity is utilized. The sorbent in the column is usually regenerated at this point and the loa ng cycle repeated. Column treatment is generally more efficient than batch treatment and lower effluent concentration values may be attained. However, in the case of a spill situation, column treatment would involve the transport of large

volumes of water to a treatment facility and then return of the treated water to the lake or stream. Another disadvantage of column treatment in the field is the substantial time period required to set up and operate the necessary equipment. Because response and treatment time must be rapid to minimize dispersal of the hazardous material from the site of the spill, batch treatment appears most feasible for field use.

Recovery of the sorbent after treatment is necessary to prevent slow desorption of highly toxic material and for aesthetic reasons. Most sorbents will sink when applied to water, which complicates their retrieval. Moreover, dredging may result in the removal of large quantities of benthic life and bottom materials with the media. Floating sorbents, however, can be recovered by oil skimming or similar well-established surface collection techniques.

It is anticipated that floating sorbents would be injected at the bottom of a watercourse and allowed to float to the surface through the zone of contamination. Because the sorbent must perform its function with only one pass to the surface, the kinetics of pollutant removal can pose a problem. Kinetic problems in columns are solved by adjustment of the throughput rate to achieve the residence time necessary to effect the desired degree of removal. However, kinetic problems are not so simply solved in a buoyant sorbent system.

The controlling parameters involved in a free-water mass-transfer system include temperature, concentration of solute, particle velocity, and particle surface area. Obviously, the first two parameters are functions of the location and nature of the spill and cannot be practically controlled in a free water environment. (Indeed, the purpose of applying a countermeasure is to reduce the concentration of the solute [hazardous polluting substance] to some acceptable level). However, particle velocity and particle surface area can be controlled through adjustment of the particle size.

Since mass transfer rates are proportional to surface area, the division of a large particle into several smaller ones increases the surface area and thus accelerates the mass transfer rates. Reduction in particle size also reduces the rate of rise of a floatable media since buoyancy is a function of r^3 while drag is a function of r^2. Reduction of the rate of rise increases the residence

time as the media rises to the surface. Thus, reduction of particle radius causes an increase in the rate of mass transfer to occur. Adjustment of media density can also be utilized to increase the contact time.

Effective use of floating media requires that (1) buoyant sorption media be deposited at the bottom of the water column so that it removes selected dissolved contaminants (i.e., toxic ions or organics) as it rises to the surface; (2) means be provided to uniformly distribute the media during the deposition step or as it rises to the surface; and (3) the application rate be properly proportioned to the amount of pollutant to be removed or neutralized per unit area of water surface.

Two general methods are envisioned for applying the mass transfer media to achieve such a distribution: (1) pumping bulk media as a slurry through a pipe which terminates near the bottom of the watercourse and which is installed on a boat or vessel propelled at a speed proportional to the application rate, and (2) dropping on the water surface packages or media capsules weighted with ballast, the packaging material of which disintegrates or opens upon exposure to water after sufficient time to allow the packages or capsules to reach the bottom.

The first method would involve the deployment of a specialized set of equipment on boats or vessels. In all likelihood, the equipment could be made air transportable. Nevertheless, some delay would result from the time required for equipment handling and setup and possibly for training local personnel to operate the equipment. On the other hand, the package or capsule "bombing" technique could employ aircraft as well as surface vessels. Moreover, the distribution of packages would be manually controlled and no special equipment would be required--eliminating the associated deployment delays.

Once the media has been applied and allowed to perform its function, relatively long periods can elapse before recovery of the spent media, because the potential pollutant will be sorbed or fixed on a material which is essentially insoluble. The physical recovery of the spent media can be achieved either manually or with mechanized equipment.

When treating a flowing stream, a simple but probably effective approach would call for positioning of floating baffles or booms at an angle across the stream and downstream of the spill treatment area. This would serve to direct the floating media to an accessible shore area.

Pickup of the media could then be achieved either manually or by using simple agricultural or earth moving equipment (e.g., drag lines, back hoes).

In the case of static waters such as lakes, ponds, reservoirs, bays, and harbors, a means would be needed for collecting or concentrating the media and then removing it from the water surface or from adjacent shore areas. This could be partially accomplished by techniques similar to those mentioned for a flowing stream. However, there is the added requirement for concentration and possible removal of the spent media from the static water surface. The techniques required for this are parallel to those necessary for recovering floating oil slicks. In fact, application of much of the technology developed for oil spill countermeasures to the recovery of spent sorption media appears feasible.

Use in saline waters will have differing effects. Sorption processes of materials less soluble in salt water than in fresh water will be aided by the presence of the salts, whereas sorption of organics more soluble in salt water will be hindered. Treatment of acid and base spills will be more efficient in salt water than in fresh, while treatment efficiency of toxic cations and anions will be reduced.

The economics of such a treatment scheme depend upon the mass transfer media selected. In commercial quantities activated carbon and common resins are relatively inexpensive. The opportunities for regeneration and possible salvage of the spilled contaminant may further improve the economics of this scheme.

The process is expected to be applicable to all types of impounded or flowing waters, fresh or saline (however, this work involved application to impounded waters only). A wide range of hazardous materials can thus be treated with a minimum of equipment and elapsed time. Stockpiling of materials could be reduced to one or two national centers. Oil collection equipment will in fact be used and thus should already be deployed through the National Contingency Plan. In many cases, the removal efficiency should be sufficient to return receiving waters to an acceptable water quality. In the remaining cases, treatment will substantially minimize the amount of dilution required to reduce the pollutant concentration below its damage threshold.

The simplicity of application and ultimate effectiveness of floating sorption media can best be illustrated with a hypothetical spill incident. Consider a barge which founders while carrying 50,000 gallons of benzene.

Assuming the nature and location of the spill is reported promptly and accurately, countermeasures could be taken to minimize the damage to marine fisheries in the area. Upon identification of the spilled material as an aromatic compound, transport aircraft would be loaded with packaged floating sorbents and dispatched to the release site.

Personnel at the spill site would maintain radio contact with the aircraft and direct their drops to cover the contaminant plume. If the aircraft arrived approximately six hours after the spill occurred and the stream had a one knot current and high diffusivities, the spill would have moved approximately 11,000 meters downstream and would be 580 meters long and the width of the stream. While making low passes over the stream, the aircraft would release a pattern of media packages over the affected area.

Individual packages would sink to the bottom, disintegrate, and release the floatable carbon. Particles of carbon would disperse with the eddy currents and slowly rise to the surface, sorbing benzene as it passed.

A screen skimmer or boom could be deployed downstream to guide the spent carbon to a surface pumping device. The collected media could then be stored for drying and subsequent disposal or regeneration and reuse. While retrieval is best accomplished as soon after deployment as possible, the carbon could be allowed to drift with the current for several days while skimming devices were located and put in place.

The sequential steps in treating a spill are illustrated in Figures 1-6.

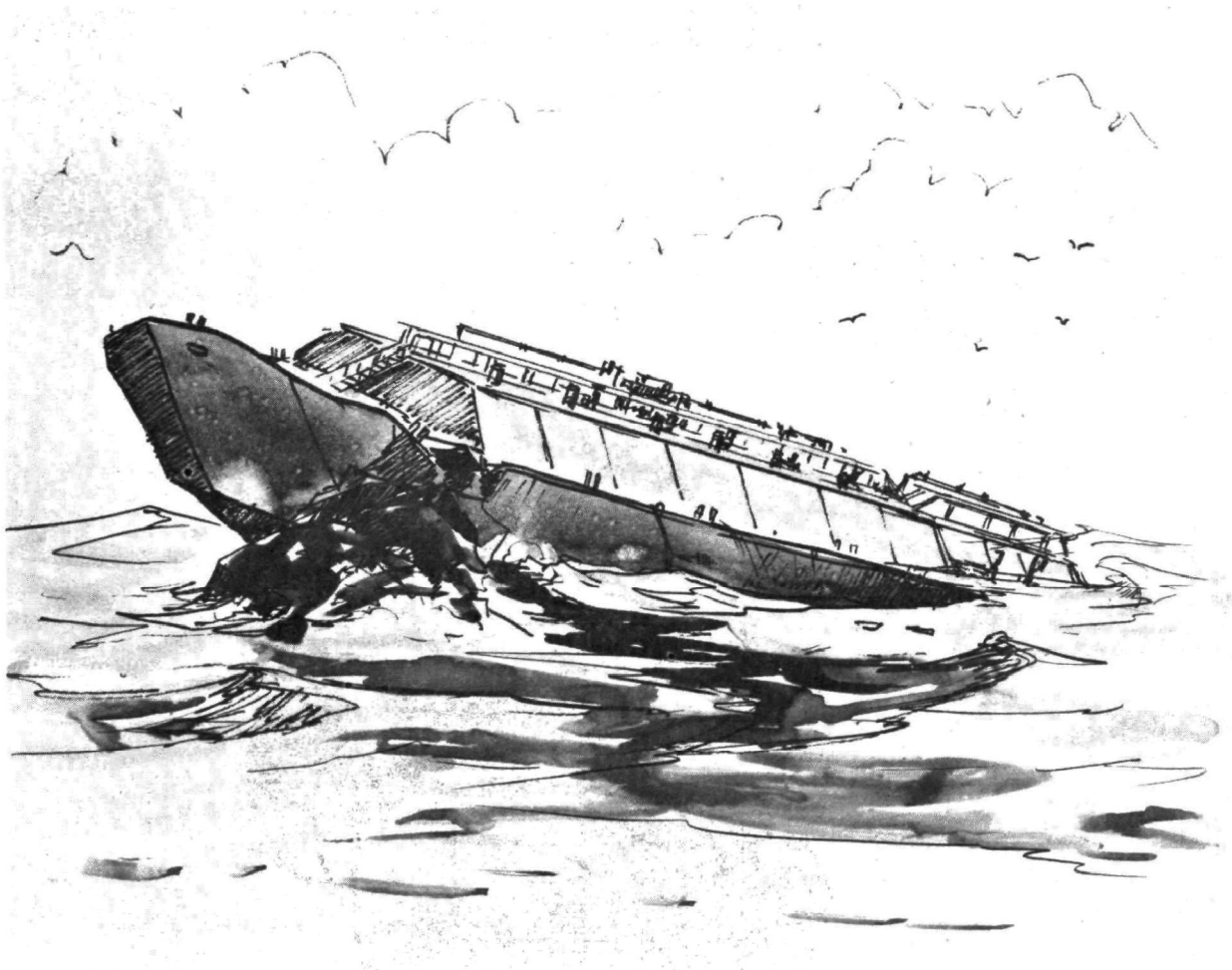


FIGURE 1

SPILL OF HAZARDOUS MATERIAL

FIGURE 2

OFFICIALS ARE NOTIFIED.
RESPONSE TEAM IS SET INTO ACTION

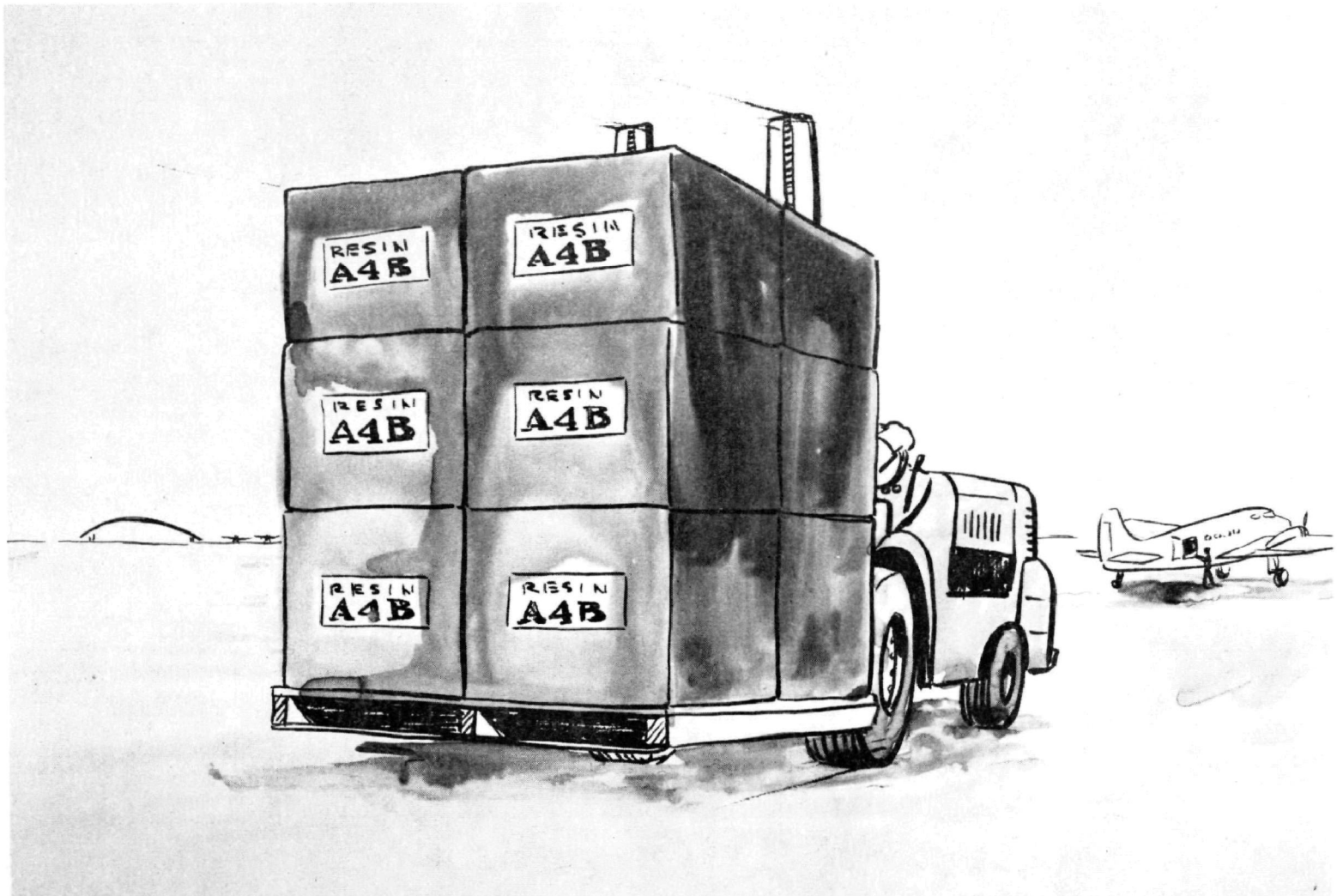


FIGURE 3

APPROPRIATE MEDIA TYPE IS SELECTED
AND LOADED ONTO DELIVERY PLANE

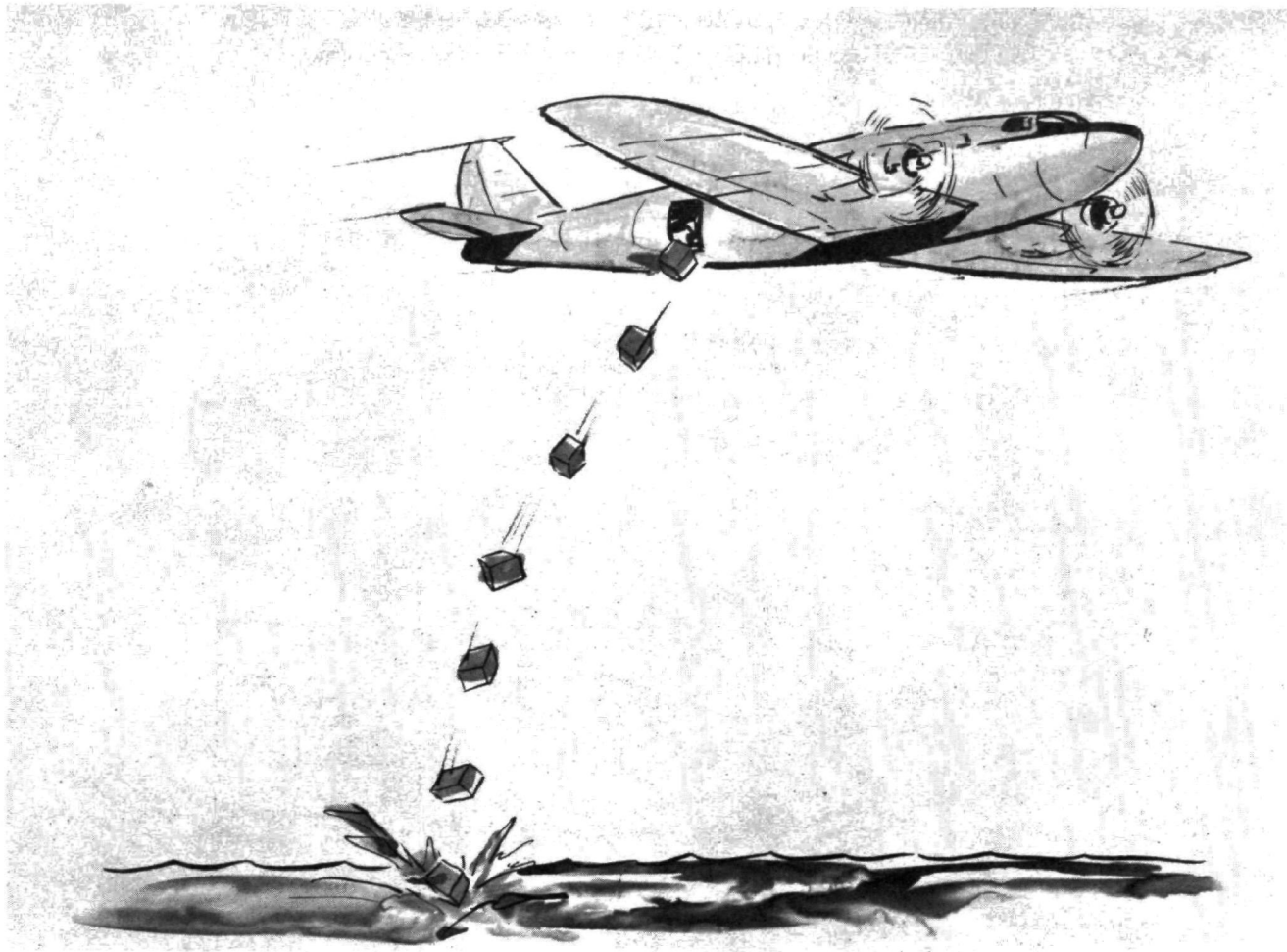


FIGURE 4

INDIVIDUAL MEDIA-PACKAGES ARE AIR DROPPED
INTO CONTAMINANT PLUME

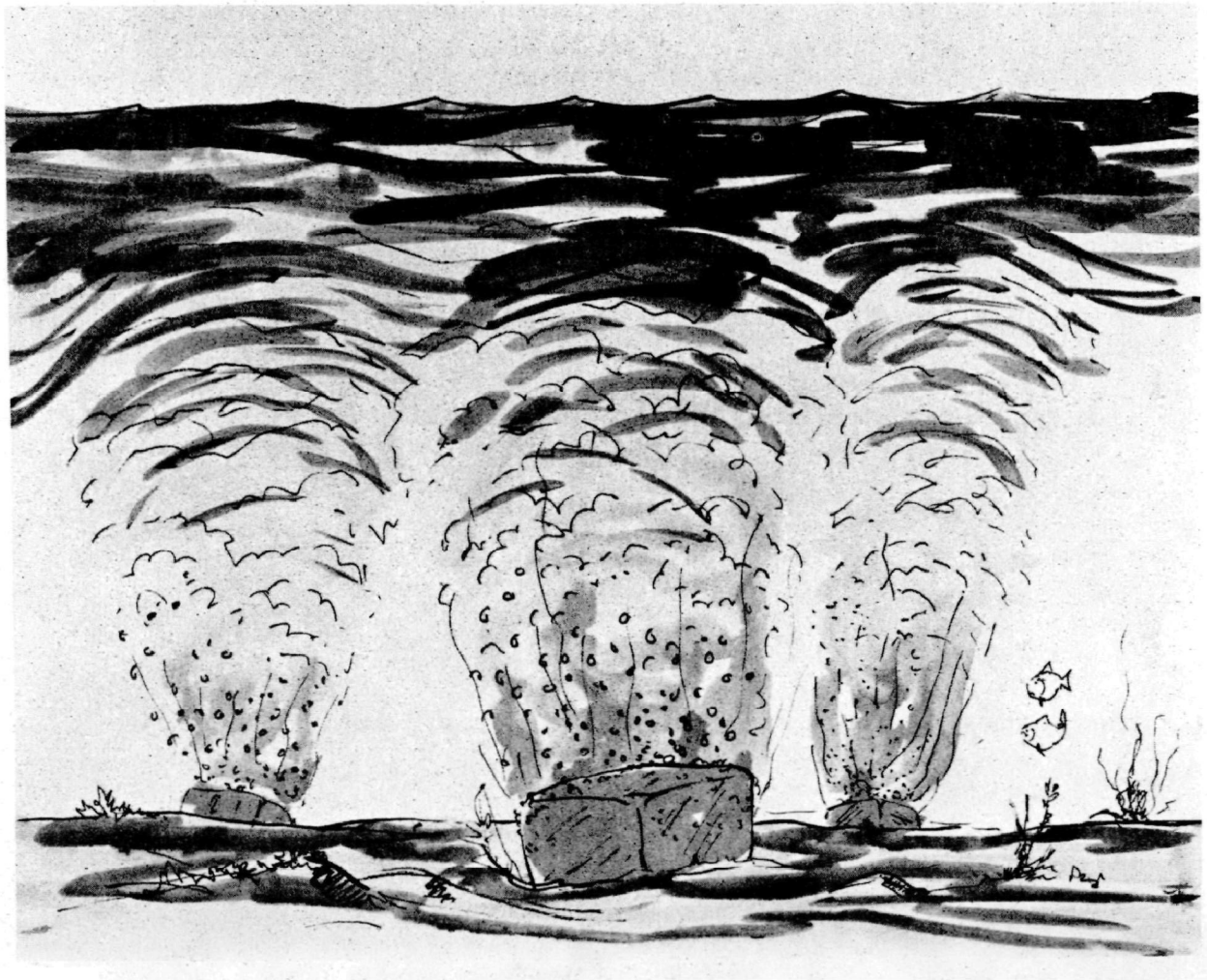


FIGURE 5

PACKAGES SINK AND BEGIN TO DECOMPOSE
MEDIA FLOATS TO SURFACE REMOVING CONTAMINANT

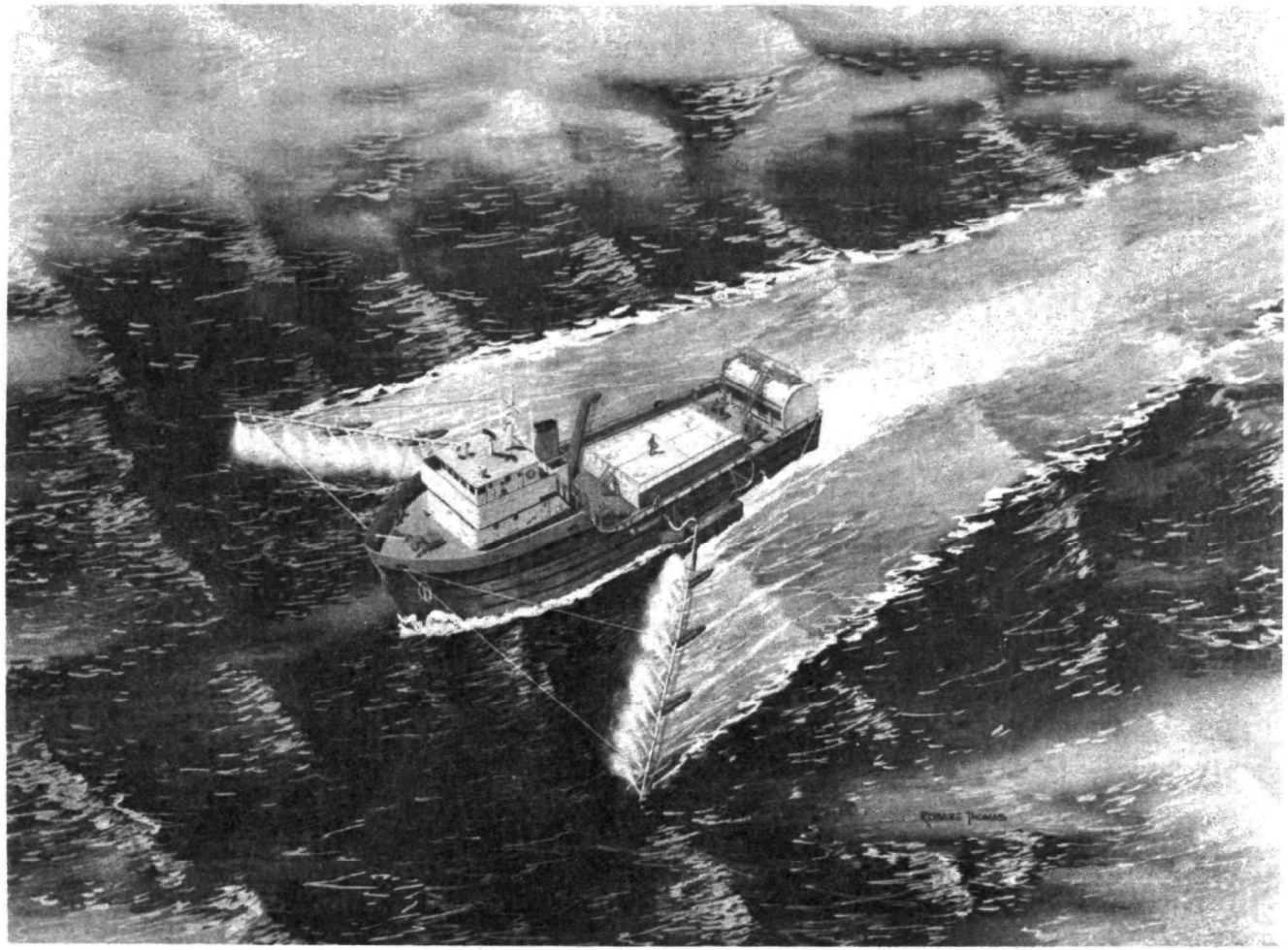


FIGURE 6

STANDARD OIL SKIMMERS ARE USED
TO RETRIEVE MEDIA

SECTION V

LABORATORY STUDIES

FLOATING CARBON SORBENTS

Physical sorption results from the attractive forces that are present at the interface of two phases. The surface of a solid will attract and hold molecules present in either gases or liquids. The amount held per unit area of the surface is relatively small but it becomes a significant fraction of the total mass of the solid phase when the surface area per unit of mass is very large. The surface area of a good activated carbon, for example, will be on the order of 1000 square meters or more per gram of carbon. Surface area values and iodine numbers are listed for several commercial grade carbons in Table 1. The iodine number gives a general indication of the efficiency of the carbon in adsorbing small molecules.

TABLE 1

Surface Areas and Iodine Numbers of Several Commercial Grade Carbons[4,5]

Carbon	Supplier	Surface Area (BET) m^2/g	Iodine Number, mg I_2/g Carbon
Darco	Atlas Chemical Industries	600-650	650
Filtrasorb 300	Calgon Corporation	950-1050	900
Filtrasorb 400	Calgon Corporation	1000-1200	1000
Nuchar WV-W	Westvaco Corporation	850	850
Nuchar WV-L	Westvaco Corporation	1000	950
Nuchar C-190	Westvaco Corporation	900	700-800

A number of physical sorbents are available for removing non-polar materials such as organic substances from water but the best known and most widely used is activated carbon. An investigation of available activated carbons with the desired floatability disclosed two commercial granular carbons which resist wetting and remain floating for long periods of time. These are Nuchar C-190 and Nuchar WA, both products of Westvaco.

Early in the program, some qualitative observations on the floatability of various mesh sizes of Nuchar C-190 were made. Samples of this carbon were slurried in water and shaken for various time intervals. After shaking, the samples were allowed to stand for five minutes and visual observations were used to estimate the quantity which remained floating. Table 2 summarizes the observations, which show that the finer mesh sizes are more susceptible to wetting and sinking than the larger. Due to the vigorous mixing in these tests, the percentage of floating carbon is probably lower than that which would normally be anticipated in actual spill cleanup operations.

TABLE 2

Approximate Floatability of Various Mesh Sizes of Nuchar C-190

Shaking Time (hours)	1	2	4	6	24
Mesh Size	Approximate Percent Floating				
>20	100	100	95	95	85
20-30	95	95	95	90	85
30-50	95	95	95	90	85
50-100	95	90	90	90	85
100-200	90	90	85	80	80
200-325	80	80	75	70	70

Batch contact experiments were conducted to determine the sorption isotherms for phenol using Nuchar C-190 activated carbon. The procedure involved mixing various quantities of carbon with a standard solution of phenol (183 mg/l) buffered at pH 6.5[6]. Phenol is more strongly sorbed below pH 7 and buffering is required to prevent a significant change in pH. Samples of 100 x 325 mesh carbon were mixed with the phenol solution for 16 hours (to assure equilibrium conditions) after which the solution was filtered and analyzed for total organic carbon. Reagent blanks with and without carbon but containing no phenol were run simultaneously to correct for very small amounts of extraneous organic matter or carbon which may have penetrated the filter. The quantity of phenol sorbed by the carbon was determined by the difference in phenol concentration before and after contact with the carbon. The results of the experiments are illustrated as a sorption isotherm in Figure 7. The sorption isotherm compares favorably with data reported in the literature.

The relationship between mesh size and rise time was investigated using a two inch diameter glass column and a water depth of four feet. Carbon was placed on the water surface and the column was inverted. The time required for the bulk (~95 percent) of the carbon to rise through the water column to the surface was recorded. The results of these experiments are presented in Table 3.

TABLE 3

Rise Time for Nuchar C-190 in Four Feet of Water

Mesh Size	Time for ~95 Percent of Carbon to Surface (minutes)
30-50	5
50-100	10
100-200	15
200-300	15

Various mesh sizes of Nuchar C-190 and Nuchar WA in both wetted and dry form were evaluated for their uptake of phenol by floating the carbons through a five foot column of phenol solution (185 mg/l) buffered at pH

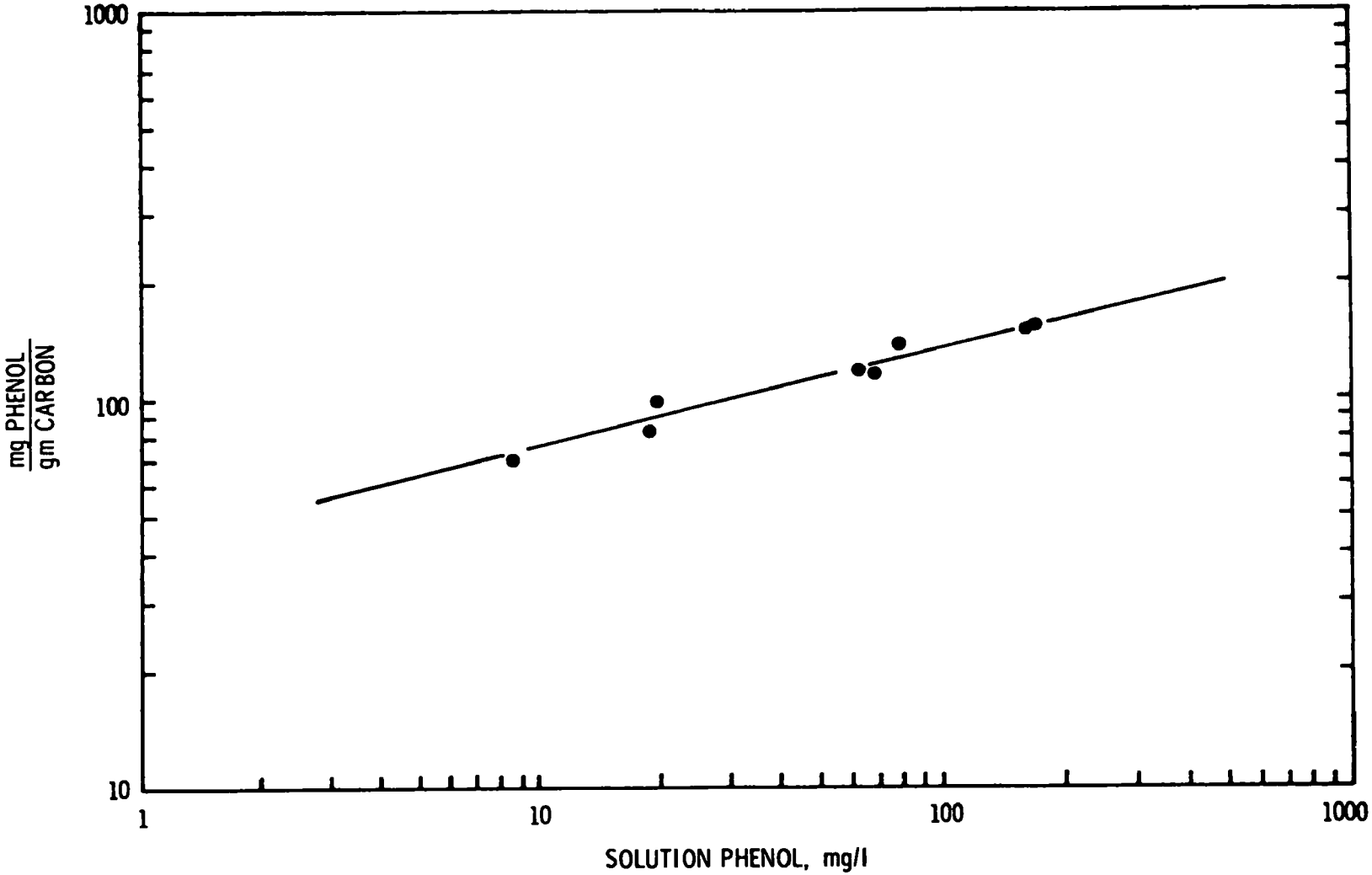


FIGURE 7

SORPTION ISOTHERM FOR PHENOL AND NUCHAR C-190

6.5. The carbon was released from a bottle at the bottom of the column at an application ratio of 2000 mg of carbon per liter of solution. The results of these experiments are illustrated in Figure 8. The dry carbon was prepared by oven drying at 100°C for 16 hours and the wet carbon was contacted with water for two hours and then filtered to remove interstitial water before use. The time required to float approximately 95 percent of the carbon through the five foot column varied from 3 to 12 minutes for the dry and wet 30 x 50 mesh carbon, respectively to 20 to 25 minutes for the dry and wet 200 x 325 mesh carbon, respectively. Nuchar C-190 was selected for further study on the basis of its superior sorptive ability and floatability. The Nuchar C-190 was found to contain a smaller percentage of sinking granules than the Nuchar WA. A mesh size of 100 x 325 was selected for further study because phenol removal is near maximum with carbon particles in this size range.

In order to assess the effectiveness of Nuchar C-190 in sorbing other hazardous organic materials, a set of batch removal experiments was conducted. Toluene, benzene, styrene and acrylonitrile were selected for study. Samples containing 50 microliters of each of these materials in 200 ml of water were contacted with 400 mg of 100 x 325 mesh carbon and were shaken vigorously for one hour. Each sample was allowed to stand overnight in a closed container and the aqueous phase was then analyzed for TOC with the results given in Table 4.

TABLE 4

Removal Effectiveness for Nuchar C-190 for Various Organic Materials

Material	Initial TOC (mg/l)	Final TOC (mg/l)	Removal Percent
Toluene	184	8	96
Benzene	198	12	94
Styrene	174	8.5	96
Acrylonitrile	146	90	38

Nuchar C-190 Dose = 1000 mg/l

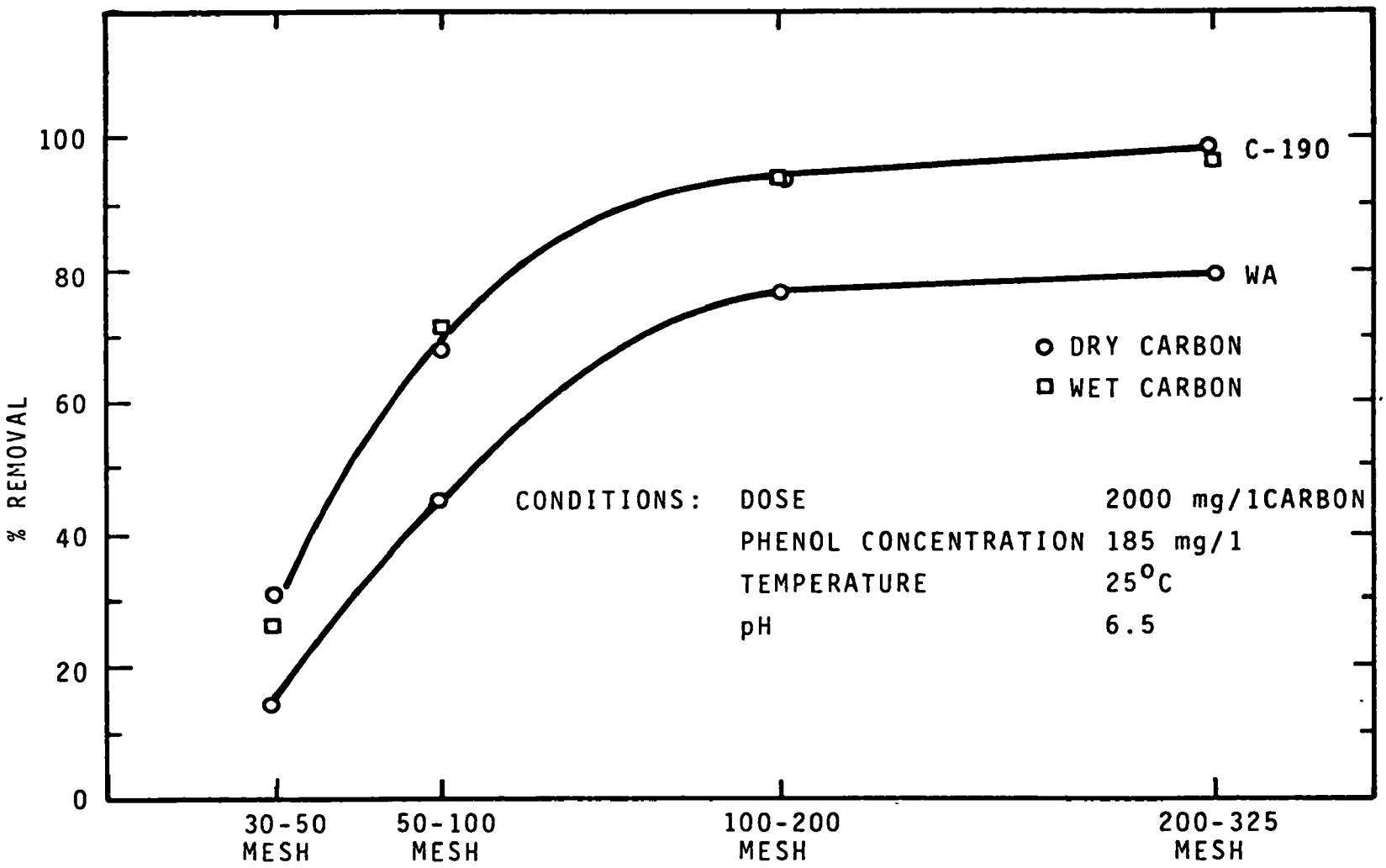


FIGURE 8

COMPARISON OF C-190 WITH WA FOR REMOVAL OF PHENOL

Two organophosphorus pesticides were similarly examined with the results shown in Table 5. In addition to TOC measurements, phosphate analyses were conducted using the perchloric acid digestion technique for total phosphate as described in Standard Methods[7].

TABLE 5

Removal Effectiveness of Nuchar C-190 for Organophosphorus Pesticides

Material	Carbon Dose (g/l)	TOC Concentration (mg/l)	TOC Removal Percent	Total PO_4 (mg/l)	PO_4 Removal Percent
Diazinon	0	114	---	21.4	---
	1	8	93.5	2.8	87.0
	2	6	94.5	1.4	93.0
Malathion	0	120	---	20.0	---
	1	8	93.0	0.6	97.0
	2	9	92.5	1.0	95.0

Diazinon

Active Ingredients

0,0 diethyl 0-(2-isopropyl-4 methyl-6-pyrimidinyl) phosphorothioate 16.75%

Aromatic Petroleum Derivative Solvents 68.875%

Inert Ingredients 14.375%

Malathion

Active Ingredients

0,0-dimethyl dithiophosphate of diethyl mercaptosuccinate 57%

Aromatic Petroleum Derivative Solvents 33%

Inert Ingredients 10%

Larger scale experiments were conducted in a six inch diameter, six foot deep column of tap water containing 200 mg/l of (1) phenol, (2) an oil emulsion of Malathion, and (3) an oil emulsion of Diazinon. Removals of 86 percent, 82 percent, and 86 percent, respectively, were obtained by floating 1000 mg/l of 100 x 325 mesh carbon through the water. The percent removal of phenol and pesticide did not vary significantly at various depths through the column after flotation of the carbon (see Table 6). Carbon containing sorbed phenol was observed to remain floating for at least two days following application.

TABLE 6

Percentage Removal of Phenol, Malathion, and Diazinon at Various Depths in the Treatment Column After Flotation of the Carbon

Depth, ft.	Phenol Removal, Percent	Malathion Removal, Percent	Diazinon Removal, Percent
1	82	79	90
2	86	76	84
3	88	82	--
4	87	82	--
Composite Sample	86	82	86

Column experiments were also conducted with a more concentrated Diazinon mixture (48 percent in xylene) added to the six inch diameter column containing 28 liters of tap water. In the first experiment, 4 ml of 48 percent Diazinon oil emulsion were rapidly mixed with 8 ml of tap water to form a stable emulsion. The emulsion was then added to the column followed by the introduction of a weighted bottle containing 40 g of 40 x 325 mesh Nuchar C-190 which floated through the diluted emulsion. Diazinon removal in this first experiment was 89 percent as determined on a total phosphate basis. A second experiment was conducted wherein

both the Diazinon and carbon were reduced to 25 percent of that used in the first experiment. The Diazinon removal in the second experiment was 85 percent which illustrates the higher removal efficiency obtained at higher concentrations by the same proportion of carbon.

Final laboratory work was aimed at identifying the best means of producing large quantities of floating carbon in the appropriate mesh sizes. A comparison was made between a sample of ball-milled Nuchar C-190 and a sample of Nuchar C-190 that had been hand crushed on a 100 mesh screen. When floated through a two inch diameter, four foot deep column of 200 mg/l phenol solution, the hand crushed carbon removed 62 percent of the phenol compared to 57 percent removal by the ball-milled carbon. Both carbons were applied at the 1000 mg/l level. The ball-milled carbon appeared to flocculate to a greater degree than the hand crushed carbon when released from the bottle at the bottom of the column of phenol solution. The greater degree of flocculation would tend to reduce contact of the carbon with the phenol solution and thereby reduce the amount of phenol sorbed from solution.

Two mesh sizes of Nuchar C-190 were commercially available: (1) +30 mesh which is essentially 12 x 30 mesh, and (2) "unground" material which is largely 14 x 325 mesh. In view of the lower uptake of phenol by ball-milled carbon it was decided to employ an impact method of crushing a large quantity of Nuchar C-190 for use in a field demonstration. A jet pulverizer, marketed by Majac, Inc., Pittsburgh, Pennsylvania, was initially considered for crushing the carbon. This device pulverizes granular material by impacting the particles in opposing jet streams. The +30 mesh Nuchar C-190 was selected for crushing on the basis that the narrow mesh size range would provide a higher anticipated yield of a 100 x 325 mesh size using the jet pulverizer. On the basis of prior performance with similar materials, a yield of about 50 percent was anticipated.

A 4000 pound order of +30 mesh Nuchar C-190 was shipped to a pilot plant facility for crushing. Subsequent testing with a jet pulverizer showed a yield of only 20 percent in the 100 x 325 mesh range. Further testing indicated that a similar mesh range could be obtained at a higher processing rate and lower cost with an air impact pulverizer. The bulk of the 4000 pounds of carbon was then subjected to the impact pulverizer and air classified to give 2387 pounds of +325 mesh material which was reported to contain 38 percent of the desired 100 x 325

mesh size. Subsequent analysis of a sample of the +325 mesh fraction showed only 17 percent 100 x 325 mesh carbon. The mesh size used for the field demonstration was therefore broadened to 40 x 325 mesh to give a maximum recovery of 49 percent of the +325 mesh fraction or 29 percent of the total carbon that was pulverized. The actual recovery was 23 percent of the total prior to breakdown of the sieving apparatus, which was used to classify the carbon. A total of 675 pounds of 40 x 325 mesh carbon was obtained which was supplemented with 170 pounds of 12 x 325 mesh carbon for the field demonstration. As a result of the low yield of the desired mesh size from processing +30 mesh Nuchar C-190, it is believed that the "unground" Nuchar C-190 may have been a more desirable starting material. Alternate sources of floating activated carbon will have to be investigated for future work because neither the unground nor +30 mesh Nuchar C-190 are commercially available any longer. Since the completion of these studies, Westvaco has discontinued sales of unground and +30 mesh Nuchar C-190 and will soon discontinue sales of the same grades of Nuchar WA. Westvaco is continuing to market a powdered grade of Nuchar C-190 which has a significant fraction of the carbon particles in the +325 mesh size. This and other potential sources of floating activated carbon are discussed in the Appendix.

FLOATING ION EXCHANGE RESINS

Ion exchange resins are effective for removing and/or neutralizing a broad spectrum of hazardous ionic substances from water. These substances include acids, bases, and toxic salts where either the cation or the anion or both are toxic to some degree.

The degree of sorption for a particular ion under equilibrium conditions is largely a function of: (1) the concentration of that ion; (2) the concentration and types of competing ions; and (3) temperature. A number of different types of ion exchange resins are available under the categories of cation exchangers or anion exchangers. The cation exchangers can be divided into different types depending on the acid strength of the groups. Strong acid groups such as $-SO_3^-$ remain ionized even at low pH and can function in acid solutions.

In contrast, weak acid groups such as $-COO^-$ are ionized only at high pH. At low pH they combine with H^+ to form undissociated -COOH and no longer act as fixed charges

where an exchange of ions can take place. For example, a weakly acidic cation exchange resin would not be effective for removing ammonium ion from a solution at pH 3 because of the resin's strong affinity for hydrogen ion. Under neutral to basic conditions, as in the case of an ammonia spill, a weakly acidic cation exchange resin could be effective for both neutralizing the basicity and sorbing the ammonia. The titration curve of a weakly acidic resin is illustrated in Figure 9 along with that of a strongly acidic resin. Using a weakly acidic ion exchanger for treating a caustic spill would have an advantage in that an overdose would not cause an overreaction which would produce acidic instead of neutral conditions. Anion exchangers which vary in base strength and act in a manner similar to cation exchangers are also available.

Boyd, et al[8] note that for organic zeolites in the 60 to 70 mesh range, up to 90 percent of the theoretical capacity can be achieved within 30 seconds. Kressman and Kitchener[9] found phenolsulphonic resins reach 90 percent of capacity in two to nine minutes with simple cations. Helfferich[10] makes similar observations for strong acid and base exchanges. At the beginning of this program it was postulated that adjusting the rise rate of the selected media to provide the several minutes required for utilizing the major portion of the media's capacity should be possible.

The first attempts to produce floating ion exchange beads employed suspension polymerization techniques. Preliminary experimentation centered around the inclusion of hollow glass microspheres (Eccospheres® manufactured by Emerson and Cumming Inc., Canton, Massachusetts) in the resin matrix. Standard styrene-divinylbenzene ion exchange resin beads are generally prepared by polymerizing a mixture of styrene and divinylbenzene in a stirred aqueous suspension containing a suspension stabilizer (e.g., starch, gelatin, polyvinyl alcohol). The size of the resin beads produced is determined by the stirring rate. Polymerization usually requires several hours after the addition of a catalyst (e.g., 1 percent benzoyl peroxide). Ion exchange groups are normally inserted into the resin matrix after preparation of the beads.

Initial attempts to include the hollow microspheres in the monomer phase during aqueous-suspension polymerization with styrene-divinylbenzene mixtures were not successful. Though mixed with the monomer phase prior to suspension, the glass microspheres quickly transferred

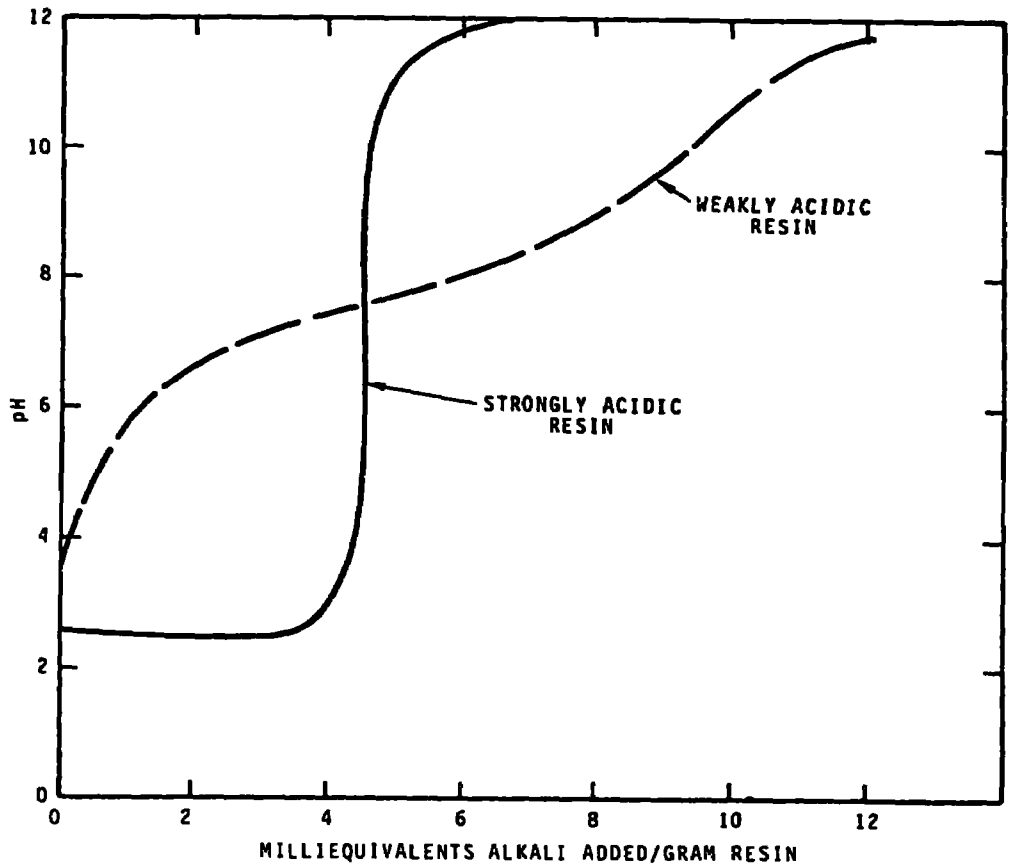


FIGURE 9

TITRATION CURVES FOR A STRONGLY ACIDIC CATION EXCHANGE RESIN AND A WEAKLY ACIDIC CATION EXCHANGE RESIN (Titration in 0.01 M KCl[8])

to the aqueous phase when the phases were mixed. This can be attributed to hydrophilic characteristics on the surfaces of the microspheres. Treatment of the beads with silicone formulations failed to alter the hydrophilic characteristics sufficiently to favor the organic phase.

Parallel efforts were directed to formulation of resins via bulk polymerization techniques. Here, the glass microspheres are stirred into the catalyzed monomer as it begins to set, resulting in the formation of a solid mass of resin with individual microspheres trapped throughout the resin matrix. The resin mass is then fractured and sieved to obtain the mesh size desired. This technique showed promise with soft aqueous gels of weak acid acrylic polymer resins, but did not produce satisfactory yields of small mesh sizes with hard resin masses. Excessive shattering of the glass microspheres occurred when crushing the hard resin masses to produce small grain sizes.

An initial attempt was made to produce a resin with acrylamide crosslinked with N, N'-methylenebisacrylamide. These two organic monomers are water soluble and can be readily polymerized at room temperature. A floating ion exchange resin was prepared by mixing hollow glass microspheres in the monomers prior to polymerization. (Hydrolysis converts the amide group in the resin structure to carboxyl groups with ion exchange capability). Unfortunately, the product beads were found to be structurally weak and consequently unsatisfactory.

Two types of resin were successfully prepared and selected for further study in preparation and evaluation of floating ion exchangers. These were (1) a weak acidic carboxylic resin prepared from acrylic acid and a suitable crosslinking agent using bulk polymerization techniques which included a soft gel intermediate, and (2) a weakly basic epoxypolyamine resin prepared from epichlorohydrin and polyethyleneimine using suspension polymerization.

The acrylic resin granules were produced in a modified bulk polymerization technique from acrylic acid crosslinked with ten percent ethylene glycol dimethyacrylate. The hollow glass microspheres were incorporated into the resin matrix by trapping an aqueous mixture of the monomers and microspheres in the interstices of a packed bed of small glass beads or other granular material (e.g., gypsum) prior to polymerization. After the monomers polymerized,

the solid mass of resin was crushed and the usable resin granules separated by filtration with water. The grain size and shape of the bed material dictates the size of the resin granule produced. An alternative method of preparation was used which employed a soluble salt (e.g., NaCl) rather than insoluble granules to trap resin monomers and hollow microspheres together for polymerization. This method is more adaptable to production of small resin particles. The salt can be removed to a large degree by dissolution, thus avoiding excessive crushing which tends to fracture the glass microspheres. Some crushing, however, is still required which increases the number of hollow microspheres required. Microspheres constitute the greatest single cost for production of floating resins.

Weak acid acrylic ion exchange resins have very high exchange capacities due to the relatively large number of carboxylic (-COOH) groups on the resin matrix. An example of the resin structure of polymerized methacrylic acid crosslinked with divinylbenzene is illustrated in Figure 10. The H^+ on a COOH group is exchangeable to a large degree with other cations providing that the solution pH does not fall below a minimum level (5-7). This ability to act as a buffer is desirable since an excess of the resin applied to counteract a caustic spill will not result in "salt splitting" to produce acids which may cause as much difficulty as the spilled caustic. For example, a carboxylic exchanger has a high affinity for hydrogen ion with the result that this resin displaces sodium ion from a solution of sodium chloride with great difficulty due to the formation of a strong acid, HCl, as one of the reaction products. Thus, the equilibrium is shifted far to the left as illustrated by the following reaction:

$$RCOOH + NaCl \rightleftharpoons RCOONa + HCl$$

For the case of reaction with sodium hydroxide, the equilibrium shifts far to the right since water is the reaction product rather than acid:

$$RCOOH + NaOH \rightleftharpoons RCOONa + H_2O$$

The resin illustrated in Figure 10 is the standard weak-acid acrylic resin of commerce (Amberlite IRC-50), which is made from methacrylic ester and divinylbenzene by the aqueous suspension polymerization process. This resin has an ultimate exchange capacity (at high pH) of 10 milli-equivalents per gram of dry resin. At pH 7, the capacity is about eight milliequivalents per gram of dry resin.

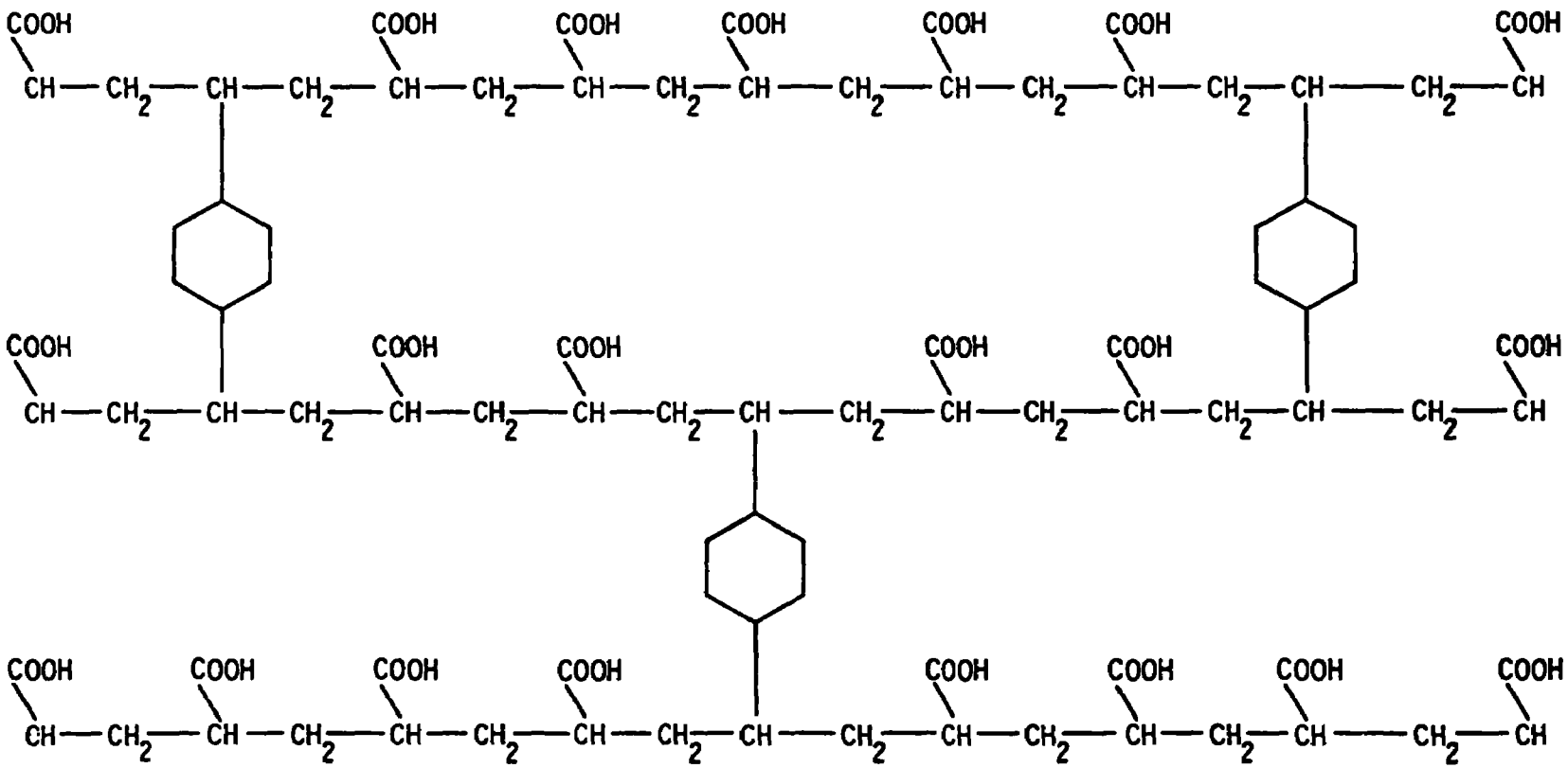


FIGURE 10

POLYMERIZED ACRYLIC ACID CROSSLINKED WITH DIVINYLBENZENE

The ultimate exchange capacity of the floating acrylic resin, prepared in the laboratory from acrylic acid crosslinked with 10 percent ethylene glycol dimethacrylate was found to be eight milliequivalents per dry gram (including the weight of the hollow microspheres). The structure of this resin is illustrated in Figure 11. Two different batches of floating resin, 20 x 50 mesh and 25 x 70 mesh, were used to determine the uptake of alkali from a 200 mg/l solution of NaOH in distilled water. Six grams of resin of each mesh size were released at the bottom of a four foot by two inch column of 200 mg/l NaOH solution; the uptake of alkali by the 25 x 70 mesh resin was determined to be 82 percent as compared to 66 percent removal by the coarser 20 x 50 mesh resin. The 82 percent removal represents about 25 percent utilization of the ultimate exchange capacity of the resin. Uptake of alkali from a dilute distilled water solution is expected to be somewhat slower than that for a solution containing neutral salts. Natural waters found in lakes and streams will contain varying concentrations of neutral salts which should increase the efficiency of alkali removal by this resin. A titration curve for the floating acrylic resin is given in Figure 12.

Samples of floating epoxyamine anion exchange resin were prepared for evaluation in the laboratory. The formula used consisted of a 3:1 ratio of epichlorohydrin to tetraethylene pentamine. Epichlorohydrin was partially reacted with tetraethylene pentamine in an ice bath to form an aqueous syrup containing 49 percent water. This syrup was then allowed to reach room temperature and remain there for 45 minutes or more. A dilute sodium hydroxide solution was added as a catalyst and hollow glass microspheres were mixed into the syrup at a ratio of two cubic centimeters of microspheres to one gram of epichlorohydrin and tetraethylene pentamine. The mixture was then added to rapidly mixed hot mineral oil to complete the polymerization and produce resin beads. The mineral oil contained a small amount (1 percent) of turkey red oil (sulfated castor oil) to aid in reducing the size of the aqueous globules prior to polymerization. Initial batches of resin beads were generally larger in mesh size than desired. Subsequent batches were prepared in smaller mesh sizes by increasing both the mixing speed and the oil to syrup ratio from about 10:1 to about 50:1. The structure of an epoxypolyamine anion exchange resin is shown in Figure 13.

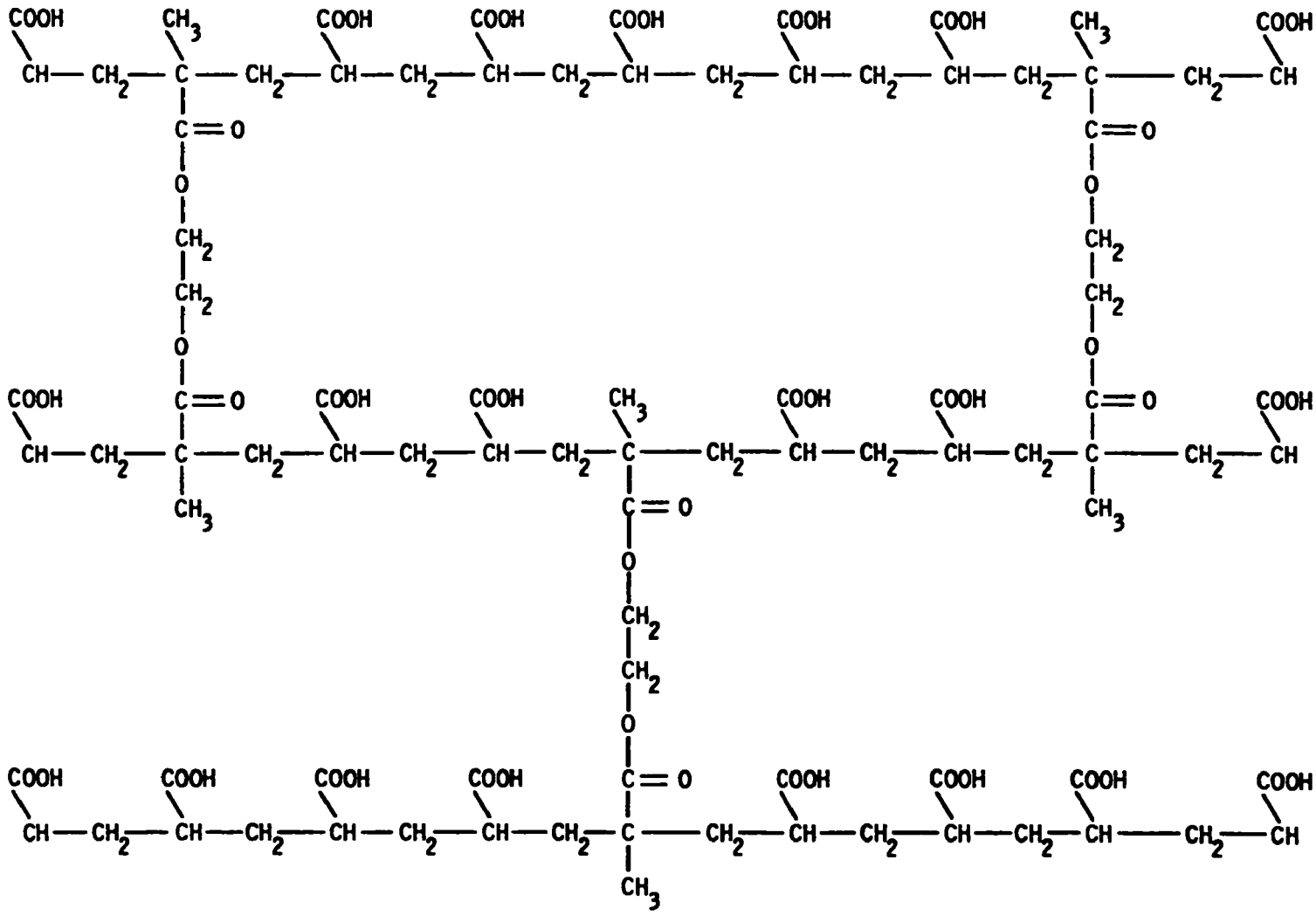


FIGURE 11

POLYMERIZED ACRYLIC ACID CROSSLINKED WITH ETHYLENE GLYCOL DIMETHACRYLATE

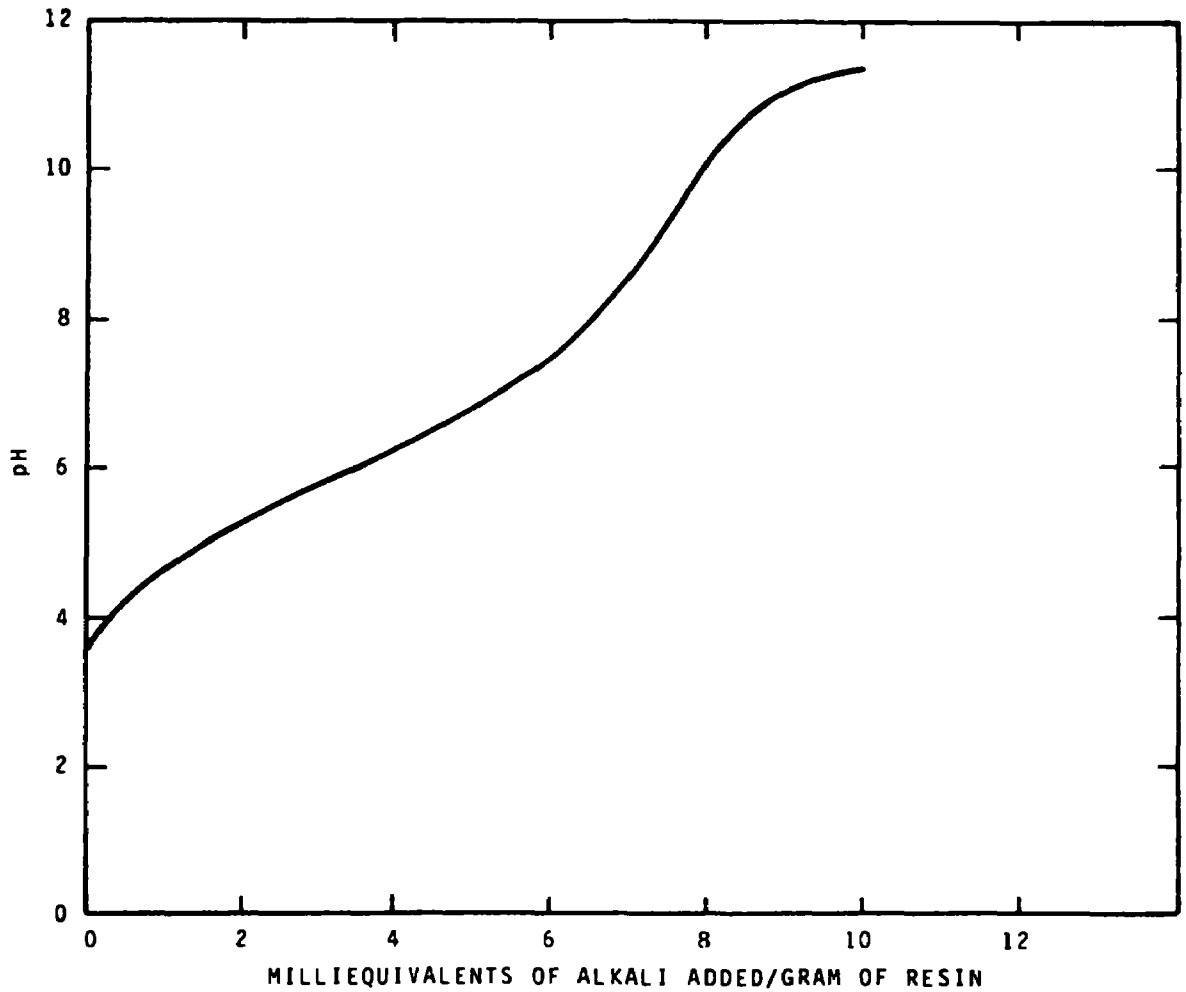


FIGURE 12

TITRATION CURVE FOR FLOATING ACRYLIC ION EXCHANGE RESIN

Titration in 0.2 M NaCl

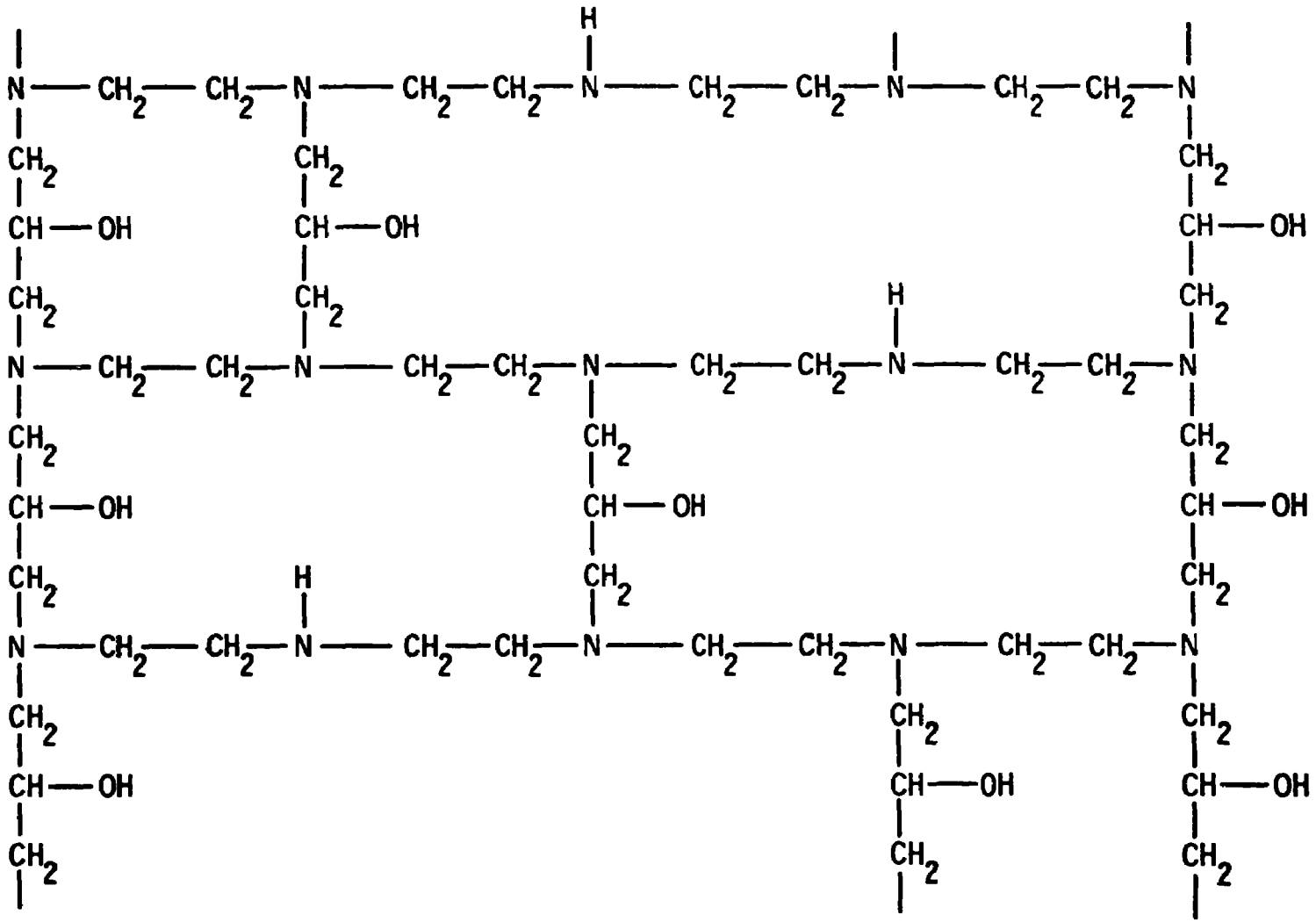


FIGURE 13

EXAMPLE OF STRUCTURE OF AN EPOXYPOLYAMINE ANION EXCHANGE RESIN

The floating anion exchange resin prepared in the manner described above was found to have an ion exchange capacity of four milliequivalents per gram of resin. A titration curve for the resin is given in Figure 14. The resin beads used for evaluation were largely in the 30 to 50 mesh size with 12 percent +30 mesh and 9 percent -50 mesh. When released from an ice cake to float up through a four foot column of water containing 183 mg/l HCl and 200 mg/l NaCl, the resin removed 61 percent of the acid at an application ratio of two grams resin per liter of water. This removal is somewhat less than the removal of NaOH by floating acrylic cation exchange resin under comparable conditions; this is believed due to the smaller ion exchanqe capacity of the epoxyamine resin (4 meq/g vs 8 meq/g). In both cases, however, only a small fraction of the available ion exchange capacity is utilized. A smaller mesh size is considered to be more important in increasing the removal efficiency than adjusting the resin bead density to a level just under that of water. Resin bead density cannot be made too nearly that of water since the density of the bead will increase as it adsorbs ions from the water to replace either H^+ or OH^- ions. Thus, the resin bead rise rate will decrease as the exchange process proceeds. If the resin bead density were initially very close to that of water, the bead might initially rise and then sink as heavier ions are exchanged for H^+ or OH^-.

Following the laboratory development phase, Diamond Shamrock Chemical Company was engaged to investigate the possibility of preparing several hundred pounds of floating epoxyamine resin in their facilities at Redwood City, California. Diamond Shamrock manufactures both a weak base epoxyamine resin (Duolite A30T) and an intermediate base resin (Duolite A30B). These anion exchange resins are reported to have ion exchange capacities of 8-9 meq/gram. It was considered that except for the addition of the hollow glass microspheres, the technique of manufacture of the epoxyamine resin would not be drastically altered from standard production techniques. The major problem lay in the mixing of the microspheres in the syrup just prior to introduction into the oil.

Diamond Shamrock was successful in preparing a floating epoxypolyamine resin both in their laboratory and subsequently with their commercial production equipment. A sample of laboratory prepared epoxypolyamine floating beads was delivered to Battelle for evaluation prior to production of a large batch. Figure 15 shows the titration

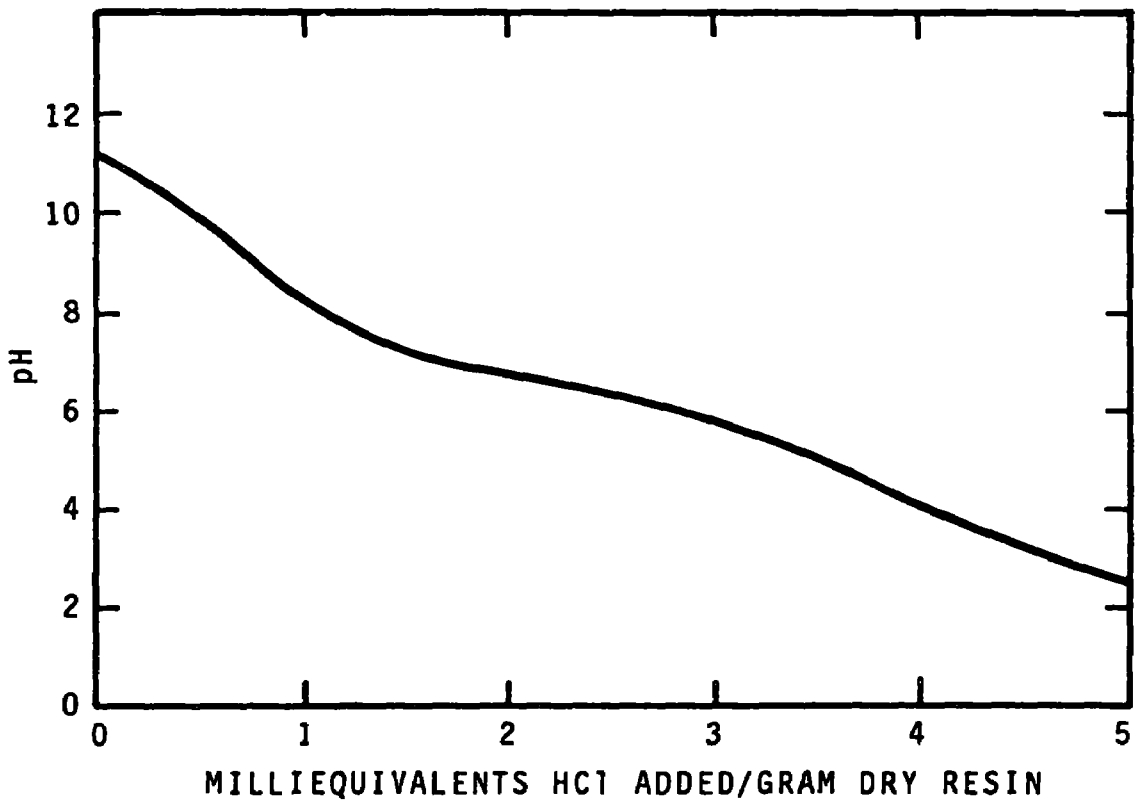


FIGURE 14

TITRATION CURVE FOR FLOATING EPOXY-POLYAMINE ANION EXCHANGE RESIN

Titration in 0.2 M NaCl

curve for this sample. The exchange capacity for this resin was approximately 70 percent greater than that for the resin previously produced. The beads also appeared to have greater structural integrity.

Once the acceptability of the floating resin was substantiated, Battelle contracted with Diamond Shamrock to produce a single lot of 14 cubic feet for use in a field demonstration. The resulting product had the same physical appearance as the earlier sample but showed a greater mesh size dispersion favoring the fraction of larger particle size. The larger mesh size of the resin caused a reduced rate of exchange such that only 37 percent of the acid in a 0.005 N HCl solution was removed at 2000 mg/l resin application. This compares with 53 percent removal under the same conditions with a -30 mesh fraction of resin. It is felt that these size deviations will not be a problem in commercial production once preparation techniques are refined.

Since it is probable that higher concentrations of acid than 0.005 N will be encountered under actual field conditions, an experiment was conducted to measure the uptake of sulfuric acid from a 0.025 N solution with 10 g/l of applied floating epoxypolyamine resin. The removal of acid at this higher level was 94 percent, which is believed to be due to the more rapid diffusion of acid from the solution to the surface of the resin bead since both the acid and the resin were increased by a factor of five. Film diffusion is usually rate limiting for removal of constituents from a dilute solution by ion exchange, whereas particle diffusion becomes rate limiting at the higher concentrations. The higher rate of uptake from concentrated solutions again emphasizes the importance of rapid response to treatment of spills.

While both the bulk polymerized acrylic resin and the suspension polymerized epoxypolyamine resin were successfully produced and demonstrated to be effective for neutralizing contaminated waters when allowed to float up through a water column, suspension polymerization is the preferred production technique.

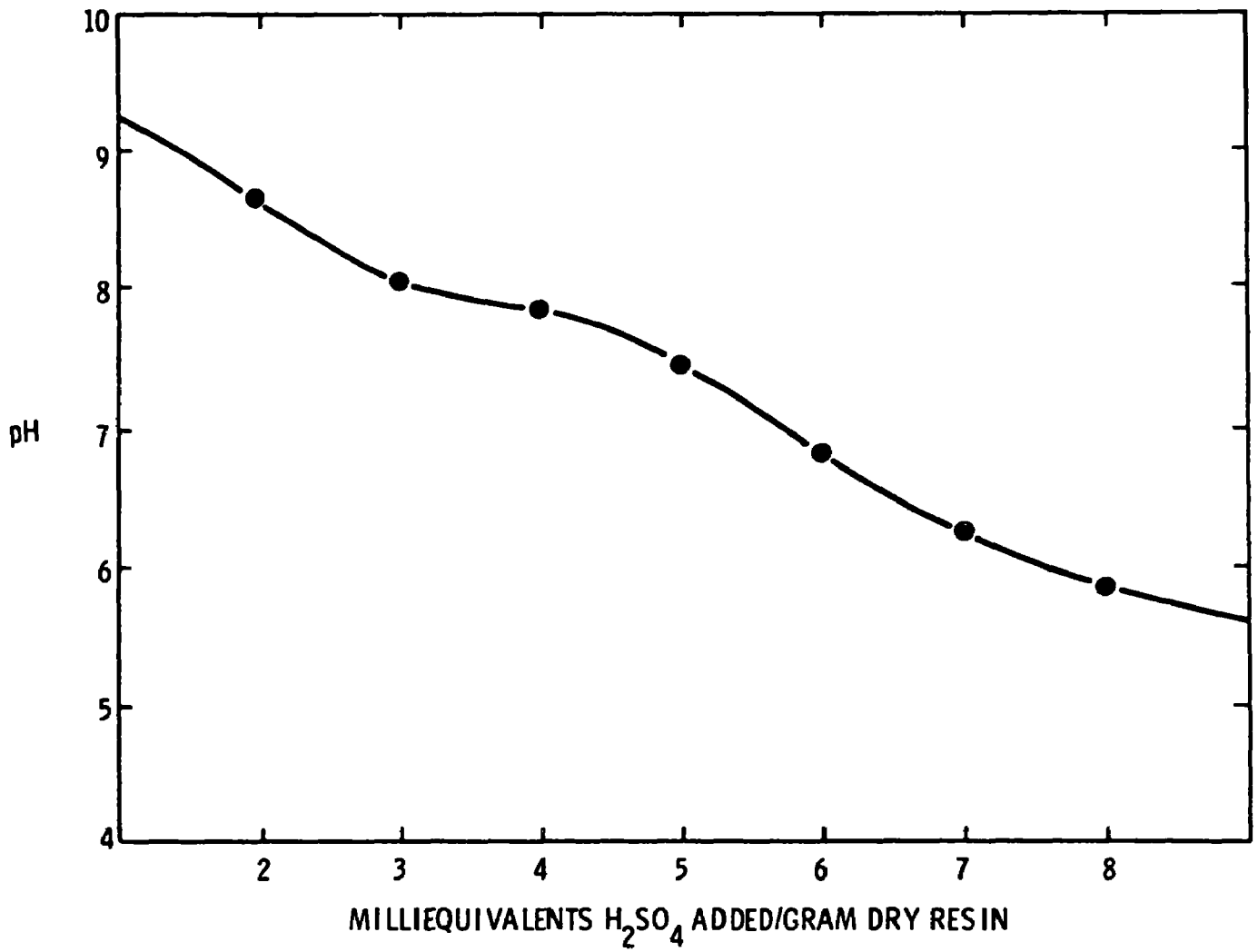


FIGURE 15

TITRATION CURVE FOR DIAMOND SHAMROCK WEAK BASE EPOXYPOLYAMINE RESIN

Bulk techniques prove to be far more expensive because of the associated losses of microspheres. Although no suspension polymerized cationic resins were produced during the program, there is no reason to believe that acrylic resins could not be so produced if acrylic acid-dissolved ethylene glycol dimethacrylate or water soluble sodium acrylate were employed as reagents. Results in the laboratory have demonstrated that the microspheres will remain in the monomer phase, but production techniques were not investigated for the length of time needed to derive a procedure which would produce beads with sufficient strength. The approach still shows great promise.

Regardless of the production technique selected, two considerations remain paramount: 1) small bead sizes are always preferred because of the accelerated exchange kinetics; and 2) resins perform much better in concentrated spills than in dilute ones.

Photomicrographs which show the hollow glass microspheres incorporated in the resin matrices of a floating acrylic resin and a floating epoxypolyamine resin are presented in Figures 16 and 17, respectively.

APPLICATION METHODS

Mechanical subsurface injection by means of slurry pumps installed on ships is probably the most desirable method of delivery in areas such as ports and harbors where equipment of this nature is readily available. However, in remote areas rapid transport of subsurface injection equipment may not be feasible. Therefore, techniques which lend themselves to air transport and injection of the floating sorbents were selected for development in this program.

Air delivery would involve "bombing" the affected area with packages containing the sorption media. In addition to the active media each package unit must contain an appropriate amount of ballast so that it will sink to the bottom of a waterway prior to release of the media. The optimal size of an individual package is dependent upon two separate considerations: 1) achieving uniform distribution of the packages (and thus the media) over a spill area, and 2) overall economics of the concept. While the former consideration tends to favor smaller packages, the latter biases the decision toward larger units.

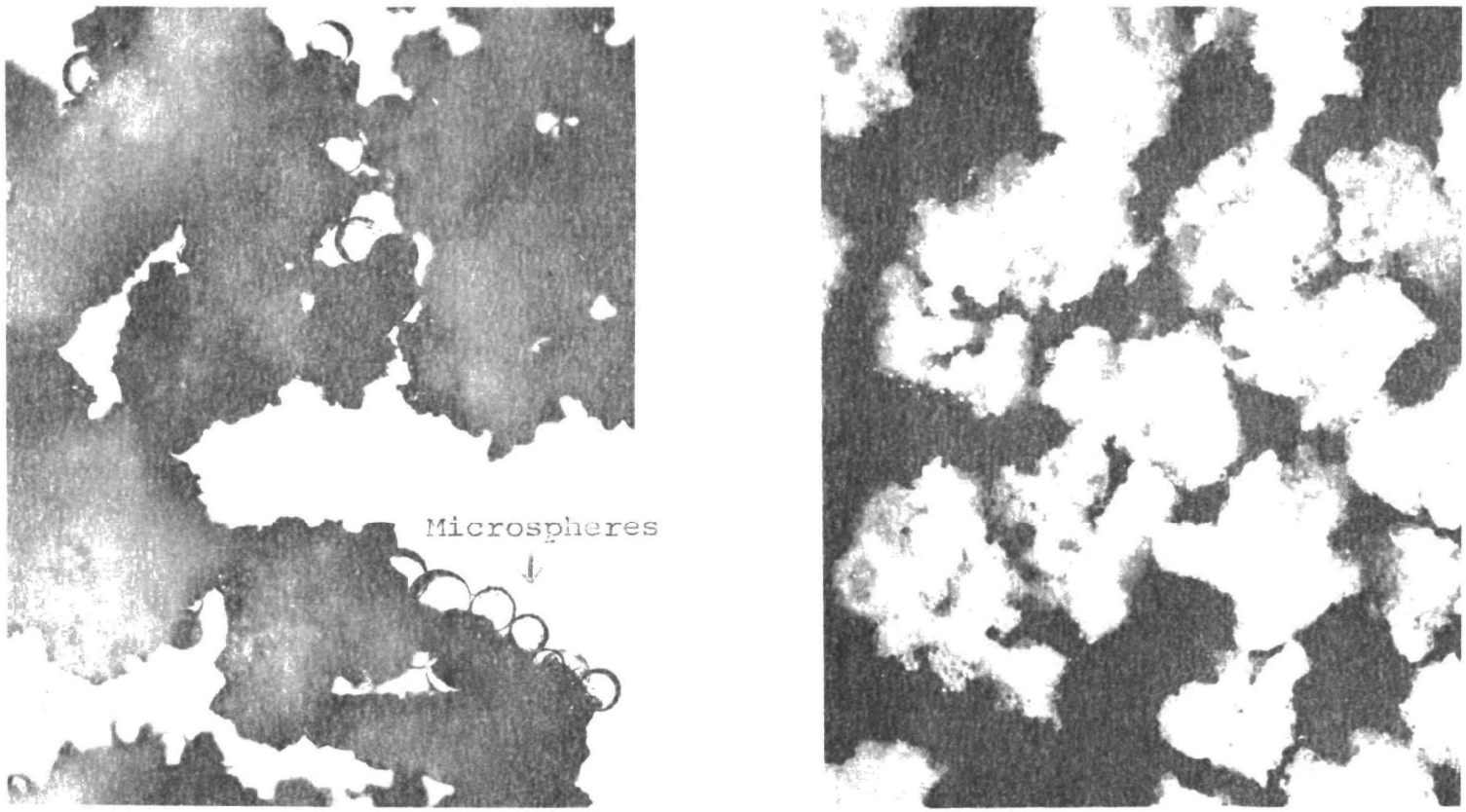
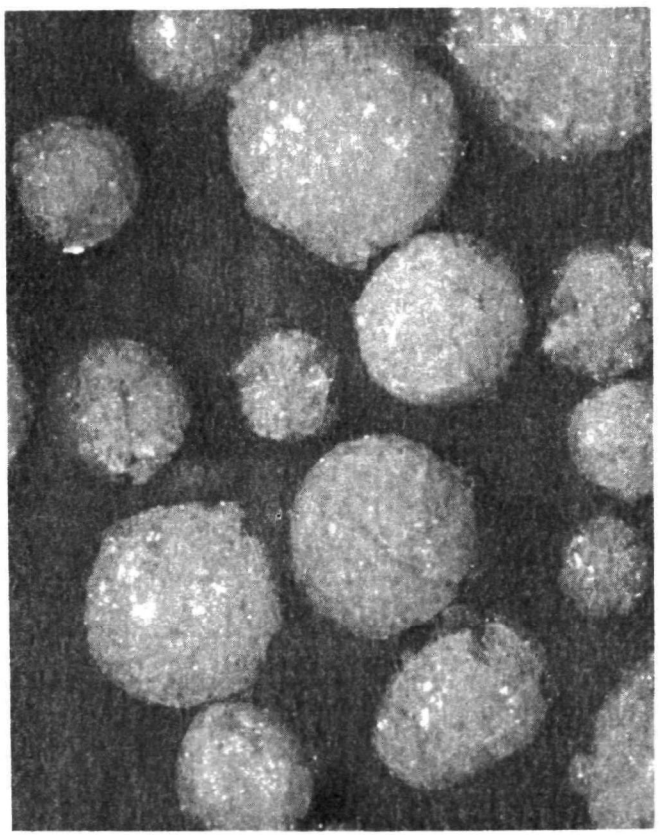


FIGURE 16

ACRYLIC FLOATING CATIONIC EXCHANGE BEADS



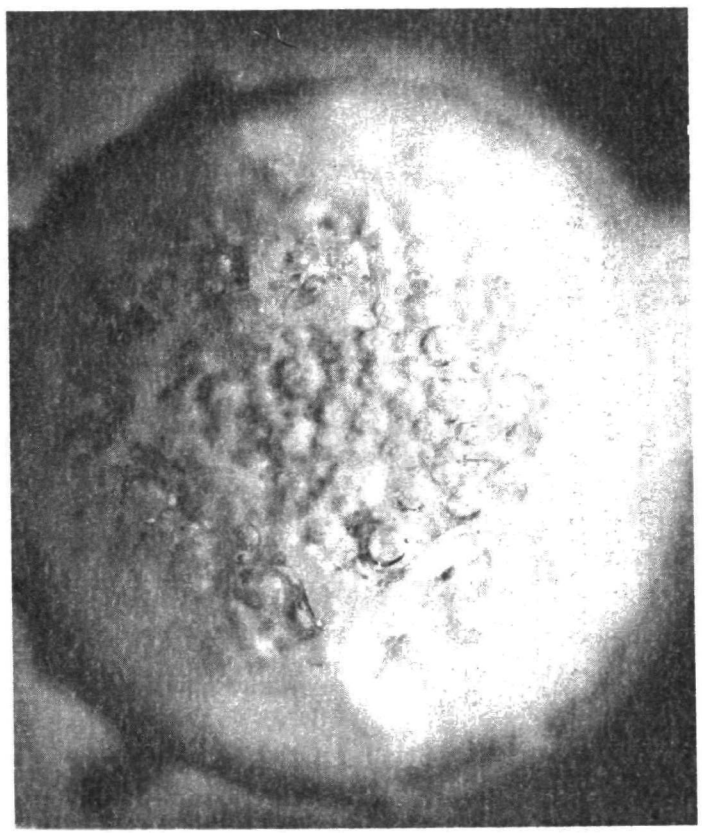


FIGURE 17
EPOXYPOLYAMINE FLOATING ANIONIC EXCHANGE BEADS

Ballast requirements can be determined from the bulk density of the media employed. Media which must be delivered in a dry state will obviously require both larger packages and greater amounts of ballast than media which can be delivered wet. Table 7 contains data on the measured densities of various media and subsequent ballast and package size requirements. Cement ballast with a bulk density of 180 pounds per cubic foot was assumed for the calculation of package size.

TABLE 7

Ballast and Package Size Requirements for Selected Media

Media	Density (lb/ft^3)	Required Ballast (lb/lb Media)	Size of Package Containing One Pound of Media, (ft^3)
Furnace Dried Carbon	8	11.5	0.188
Air Dried Carbon	12	7.9	0.127
Wet Carbon	58.7	0.21	0.018
Dry Epoxy Resin	15.7	5.1	0.092
Wet Epoxy Resin	56.0	0.26	0.019

It is evident that potential packaging techniques for the floating media and ballast for aerial delivery fall into two categories: (1) methods employing retrievable containers, and (2) methods employing non-retrievable containers or containers which will decompose in water over a period of time. Of prime importance in the program has been the identification of a packaging technique which would not result in significant degradation of water quality if the packages were used in spill response activities. Packaging techniques which were considered include plastic containers, soluble synthetic films, unfired clay containers, and ice cakes.

Plastic Bottles

Plastic bottles are an inexpensive, standardized container form potentially useful for packaging floating media.

Plastic containers were employed in column tests to evaluate the effects of various bottle mouth widths on media release rate and release patterns. It was observed that media release from wide mouthed bottles was accompanied by simultaneous release of quantities of large air bubbles. These air bubbles tended to convey clusters of media rapidly to the surface, thus preventing dispersion of the media in the water column. Further tests indicated that this problem could be virtually eliminated by using containers with walls which sloped upward to a mouth of about one inch diameter. Using this type of container, there was a short period of media release followed by a longer period in which small air bubbles escaped but little media was emitted. This venting period preceded a sustained release of clouds of media from the bottle which distributed the media throughout the water column.

Either cement or sand and gravel proved satisfactory as ballast in partially filled plastic bottles. One gallon polyethylene bottles half-filled with cement were found to withstand the impact of a fall from a fifty foot height to a gravel bed. Similarly, these containers withstood drops from a 100 foot height into water.

It was determined that the mouths of the plastic bottles could be sealed with a water soluble material, Quicksol A, to prevent the media from falling from the containers during the air drop. However, in field trials with carbon filled containers, it was observed that no significant quantity of media was spilled during a drop from bottles with open mouths.

Figure 18 is a schematic diagram of a plastic bottle of the type used in the field demonstration containing ballast and floating carbon.

The major drawback associated with plastic containers is the potential aesthetic and/or ecological damage which might result if weighted plastic bottles were allowed to remain permanently in a waterway after treatment of a spill.

Retrieval of plastic containers could be accomplished either manually (e.g., by divers or with grappling hooks) or by use of containers which will surface and float some time after release of the media, thus permitting surface collection. A limited laboratory study showed that cement ballast could be attached to polyethylene bottles with water soluble connections. After several hours' exposure to water these connections dissolved, causing the ballast to separate and allowing the bottles to rise to the surface. However, this or some other technique for producing containers amenable to surface collection would involve significant fabrication costs for the containers. In fact, use of commercially available plastic containers and subsequent manual retrieval from the bottom of a waterway probably would represent a cheaper approach. If plastic containers are to be given further consideration as a potential packaging technique, a thorough economic evaluation will be required in order to determine the most viable alternative from a cost standpoint.

Another approach which was considered but which was not examined in great detail in this program is the use of biodegradable containers. If a container could be identified which would eventually degrade without creating a significant oxygen demand or other pollution problems, it might offer an attractive alternative. Since such materials are still in the experimental development stage, an adequate technical and economic assessment of the feasibility of this approach cannot be made at this time.

Soluble Films

Contacts with several major pharmaceutical firms indicated that both the technology and equipment are presently available for large scale encapsulation of a mixture of ballast and floating media in water soluble capsules.

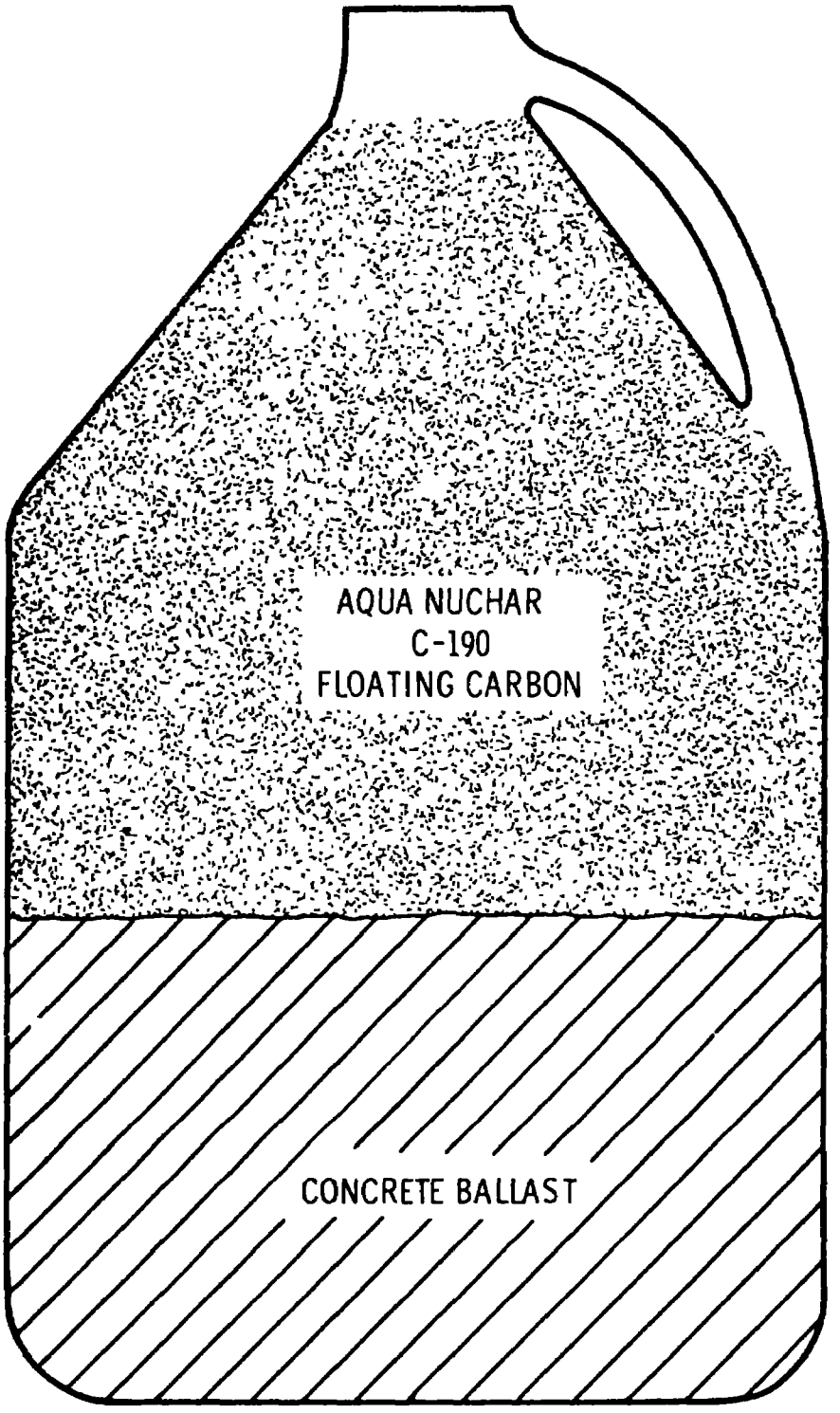


FIGURE 18

SCHEMATIC OF CARBON FILLED PLASTIC BOTTLE

Several samples of water soluble films and bottles were obtained from vendors and subjected to a cursory examination to determine their suitability for containing floating media. Individual packets with volumes of approximately four cubic inches were prepared from each material and loaded with sand ballast and polystyrene chips to simulate media "bombs". Each packet was then immersed in four gallons of tap water (@25°C) to determine the time required for release of the polystyrene chips. Results of this test and pertinent product data are given in Table 8.

Most of the films dissolved uniformly and released the polystyrene chips cleanly with little or no partially dissolved film adhering to them. There was some tendency for the chips to stick to the gelatin capsules and Klucel bottles which dissolved much more slowly. The immersion time required for release could be adjusted by using thicker films or multiple layers of film.

One pound of polymer will yield about 7500 square inches of film with a thickness of three mils. If individual packets with volumes of four cubic inches each were fabricated, a pound of polymer would provide containment for a volume of approximately 1200 cubic inches. The weight of dry carbon thus packaged would be approximately five pounds or a 5:1 ratio of carbon to soluble film. This quantity of soluble film would be equal to or perhaps greater than the spilled organic material being removed from the water.

Experiments were conducted to study the effects resulting from dissolution of one of the films, Quicksol A. It was determined that 160 mg of Quicksol A dissolved in water yielded a total organic carbon concentration of 88 mg/l. Activated carbon at 2000 mg/l removed 47 percent of this TOC. The same dose of activated carbon removed 91 percent of the 171 mg/l phenol solution, but could adsorb only 75 percent of a phenol-Quicksol A mixture. The dissolved film showed a definite tendency to use up available carbon sorption capacity. Biochemical oxygen demand (BOD) tests indicate that a 1000 mg/l solution of Quicksol P has a five day BOD of only 8.2 mg/l. Although the use of these films should not cause excessive oxygen depletion at a spill site, the addition of relatively large quantities of soluble organic matter to the water is a questionable approach. In addition, the tendency of the dissolved films to use up a significant portion of the available sorption capacity of activated carbon is not a desirable characteristic.

TABLE 8

Product Evaluation of Soluble Films

Trade Name	Polymer Type	Thickness (mil)	Release Time (minutes)	Cost ($/lb in 1000 lb lots)
Quicksol A[a]	polyvinyl alcohol	1.25	0.5	1.94
Quicksol P[a]	polyethylene oxide	2.0	0.25	1.94
Quicksol P-U[a]	urethane	2.25	0.75	2.00
Edisol-M[a]	hydroxypropyl cellulose (food grade)	3.0	1.25	2.22
Klucel[b]	hydroxypropyl cellulose (food grade)	10	30-50	1.75[c]
-----	Pharmaceutical gelatin capsule	12	240	-------

(a) Trade Name - Polymer Films, Inc. Woodside, N.Y.- Films
(b) Registered Trademark - Hercules, Inc., Wilmington, Delaware- Molded Bottles
(c) Estimated

Clay Containers

In an attempt to find a packaging agent which could also serve as the ballast material, an effort was initiated to study the feasibility of unfired clay containers. A local pottery shop was engaged to produce various clay container shapes and sizes through a slip molding technique. The resulting products were dried but were not fired so that they displayed an affinity for water which soon caused them to collapse when immersed.

It was found that sand could be added to the clay in varying amounts to increase the speed with which the package lost integrity. Inclusion of approximately 30 percent sand resulted in a decomposition time of 2 to 5 minutes. Pyramidal and cylindrical shapes displayed the cleanest release characteristics, trapping little of the floating media under the collapsed clay.

An impact evaluation was made to determine whether clay containers could withstand the forces encountered when dropped into water. Vessels shaped somewhat like artillery shells (Figure 19) with a one quart capacity (approximately 1 ft. high x 3 in. O.D.) were dropped from a height of 100 feet into the Columbia River. Each clay container was attached to 185 feet of light cord so that it could be retrieved and inspected. Vessels with a wall thickness of 0.25 inch or greater withstood the impact. Those having wall thicknesses of 0.125 inch or less collapsed. Several alignment modifications could potentially increase the effectiveness of the clay cylinders. Walls could be tapered so that heavy sections would absorb the impact while thinner walls at the top would rapidly disintegrate when immersed in water. Alternatively, lids could be loosely molded into place so that soon after coming to rest on the bottom of the water body they would fall off, allowing the media to escape. It might also be desirable to add fins to the design since the models tested continued to tumble when initially given angular momentum.

Clay containers would require use of dry media and would thus have a low payload to ballast ratio. A further disadvantage of unfired clay is the turbidity caused by suspension of the fine clay particles in water. The mixing

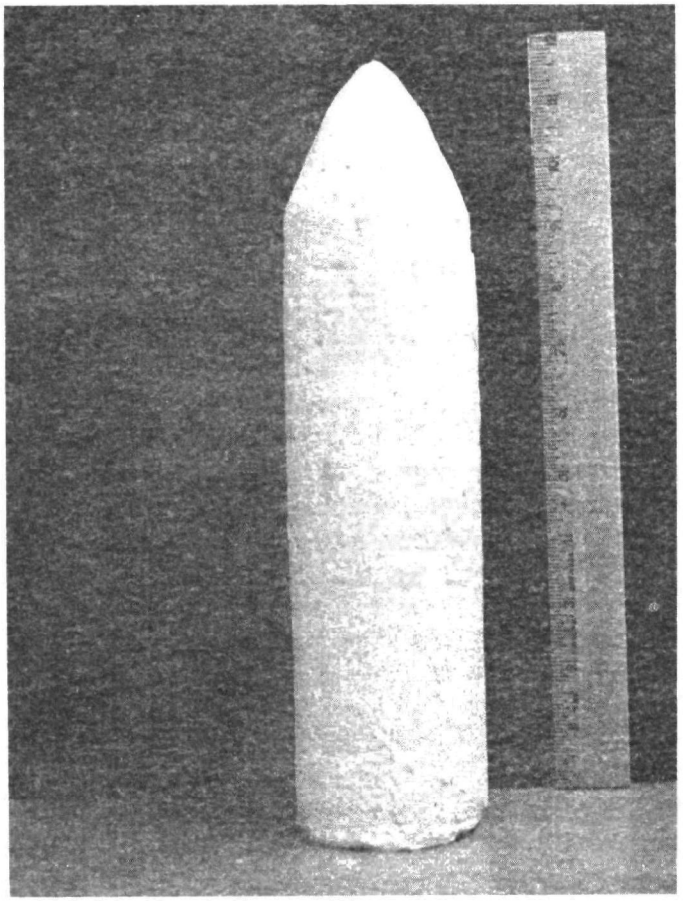


FIGURE 19

PHOTOGRAPH OF CLAY CONTAINER

action caused by the release of air and media suspends a significant amount of clay in the water. Use of a fired clay container with an unfired clay seal is a possible alternative to minimize the amount of suspended clay formed.

Ice Cakes

The search for a completely innocuous encapsulation agent led to an attractive possibility--the use of ice as a binding agent. Ballast and media could either be layered and frozen into discrete packages for aerial distribution or intimately mixed and frozen into blocks which could be shattered into any size desired at the time of release.

Advance production and stockpiling of media ice cakes would have associated high storage costs since refrigerated storage would be required. In addition, sublimation might be a problem associated with long term storage of ice cakes. One possible solution to these drawbacks would be dry storage of components (media and ballast) and subsequent quick freezing when use of the media is required. Transport of the ice cakes might not involve too many difficulties since low temperatures prevail in the higher altitude flying lanes.

Column evaluations showed media release from ice packages to have several excellent characteristics. Media release begins almost immediately after the ice cake reaches the bottom of the water column and the media soon distributes itself evenly throughout the water column. Release of the media is spread out over the period of time required for the ice to melt and thus the release is smooth. Problems with air bubbles are avoided and ballast requirements are much less than when dry media is utilized.

Freezing the media in an ice matrix was found to have no debilitating effects on the performance of floating ion exchange resins. Packaging in ice did, however, appear to result in some loss of capacity in the case of the floating carbon. Parallel column removal tests run with a standard phenol solution showed that unfrozen carbon removed 65 percent of the phenol while an equal quantity of carbon frozen in an ice cake achieved only 51 percent phenol removal. Removal differences fluctuated in subsequent tests, but the carbon ice cakes were always found to be somewhat less effective than unfrozen carbon.

Parallel column runs with unfrozen carbon at solution temperatures of 0°C and 17°C showed little difference in phenol removal efficiencies (75 percent at the lower temperature and 77 percent at the higher). This observation led to the conclusion that the reduced efficiency of the carbon frozen in ice cakes was not a function of temperature so much as the result of interactions between the ice and the carbon. It was noted that finer carbon particles appeared to floc when released from the ice cake. Flocculation of carbon particles was not observed in release from plastic bottles. This flocculation effect could reduce the actual coverage of the media and hence reduce removal efficiency. In addition, it is possible that residual ice crystals on the carbon may interfere with surface forces and hence reduce sorption.

In deference to the major objectives of the program, these apparent interactions were not fully explored. Because of the lower ballast requirements and superior dispersion of the carbon near the bottom of the stream or lake, the carbon ice cake approach appears preferable in spite of the somewhat lower sorption capacity or rate. However, further work is needed to establish the feasibility of the carbon ice cake packaging concept. Clearly, there is great promise in the use of ice with floating ion exchange resins.

SECTION VI

FIELD DEMONSTRATIONS

In order to test the effectiveness of the floating media concept on the scale and under the conditions of actual hazardous materials spills, field demonstrations were conducted using both the floating epoxypolyamine anion exchange resin and the floating Nuchar C-190 carbon. These demonstrations concerned application of the floating media concept to static or impounded water only. Treatment of flowing streams may involve different techniques because of the turbulence of the water.

DIAZINON SPILL

A 10 million gallon water storage basin was selected for the spill treatment demonstration. The basin was filled with Columbia River water to a depth of 12 feet and calibrated ropes were placed across the western end of the 200 x 400 foot structure as illustrated in Figure 20.

A commercial grade of the organophosphorus pesticide, Diazinon, was selected for the spill. Diazinon is highly toxic to aquatic life forms and hence causes major concern when spilled. It is not persistent beyond several weeks, however, so immediate complete cleanup by the floating carbon was not required in the event discharge of the basin water was required at some future date. The composition of the 48 percent Diazinon in an emulsifiable solution is given in Table 9. Seventy-eight pounds of the organic solution emulsified in 160 pounds of water was employed for the spill.

TABLE 9

Composition of Emulsifiable Diazinon Solution

Ingredient	Percent
0,0-diethyl 0-(2-isopropyl-4-methyl-6-pyrimidinyl) phosphorothioate	48
Xylene	36
Inert Ingredients	16

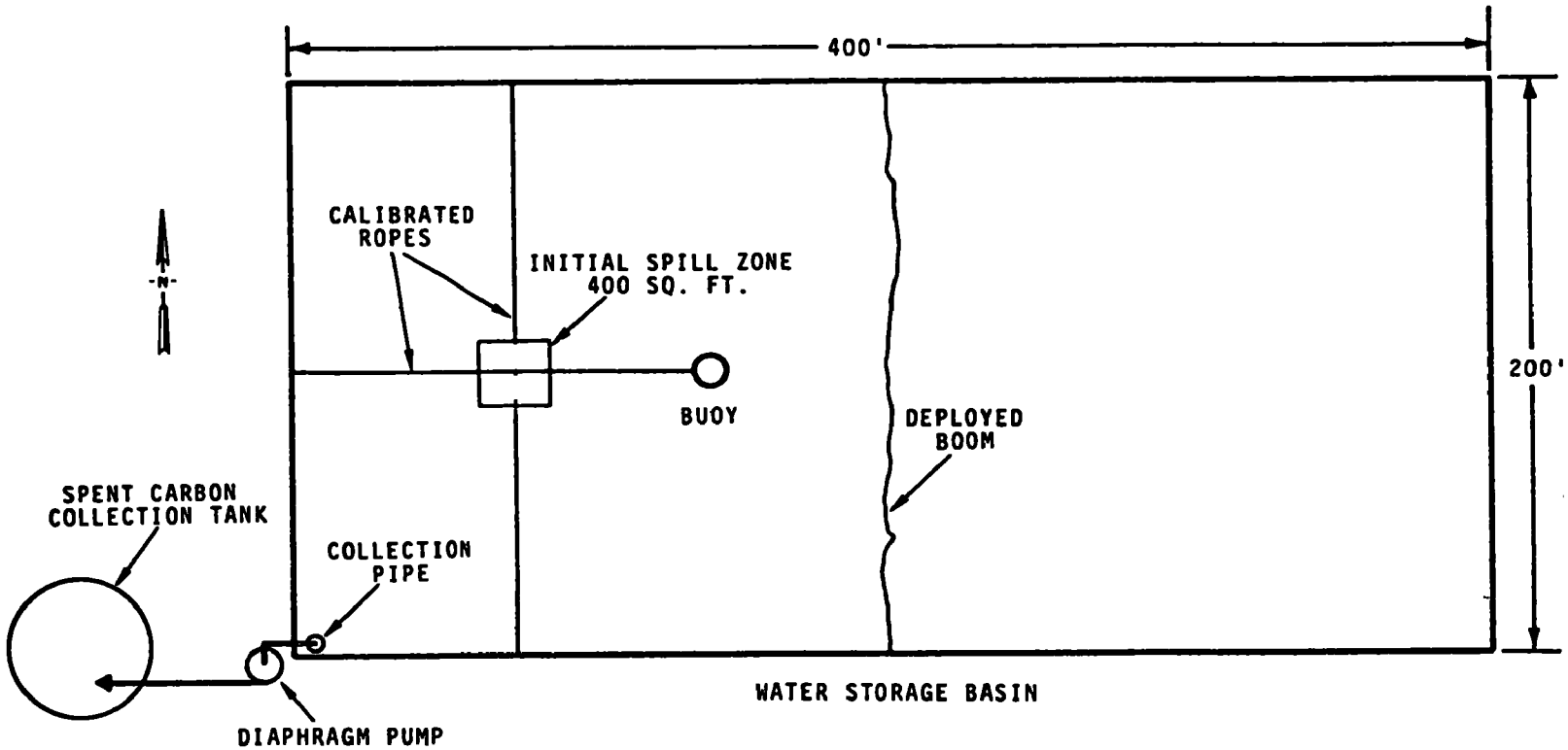


FIGURE 20

LOCATION OF FACILITIES FOR DIAZINON SPILL

The Diazinon was spilled at 0700 by spreading the 25 gallons of emulsion from a rowboat in a 20 foot by 20 foot square as illustrated in Figure 20. Aerial photographs of the spill taken at 0715 are given in Figures 21-22. Sampling of the spill area began at 0730. Samples were taken with ten foot aluminum tubes connected by flexible tubing to peristaltic pumps. One liter glass bottles were filled with water withdrawn from 1, 5, and 10 foot depths. Sample lines were thoroughly flushed between sampling points.

A total of 845 pounds of Nuchar C-190 activated carbon was employed in treating the spill which is about a 10:1 ratio of carbon to Diazinon. The carbon included 675 pounds of 40 x 325 mesh carbon and 170 pounds of 12 x 325 mesh carbon packaged in 1,128 one gallon polyethylene bottles each of which contained 1/2 gallon of carbon (3/4 pound) and 1/2 gallon of concrete (8 pounds).

Bottles of carbon and ballast were dropped into the spill area from a helicopter equipped with a platform suspended beneath the helicopter with a sling. Servo-motors mounted on a drop gate of the platform were wired for control from within the helicopter. The slings were fixed with an offset harness so that under normal flight conditions they would hang at an oblique angle with 60 carbon-filled bottles (540 pounds) resting against the drop gate. Over the drop site the gate was opened and the bottles were allowed to slide down into the water. Figure 23 shows the platform in place beneath the helicopter. Two platforms were employed so that one could be loaded while the other was in use.

The actual treatment phase of the demonstration was begun at 0810 when the first of 17 loads of carbon were dropped into the spill area as shown in Figure 24. Flags were used to mark the drop lane and a flagman was employed to signal the helicopter pilot to release the gate. In this manner drops were distributed evenly across the contaminant plume. Due to a failure in the gate control of both platforms, the 18th and final load could not be dropped from the helicopter. These bottles were subsequently distributed by hand from the side of the basin and from a rowboat. The application work was completed by 1100; however more than half the carbon was dropped by 0915. Intermittent failure of the tailgate release on the platforms increased the time between subsequent drops after 0915. Three of the 1128 bottles contained insufficient ballast and consequently floated to the surface without releasing their carbon.

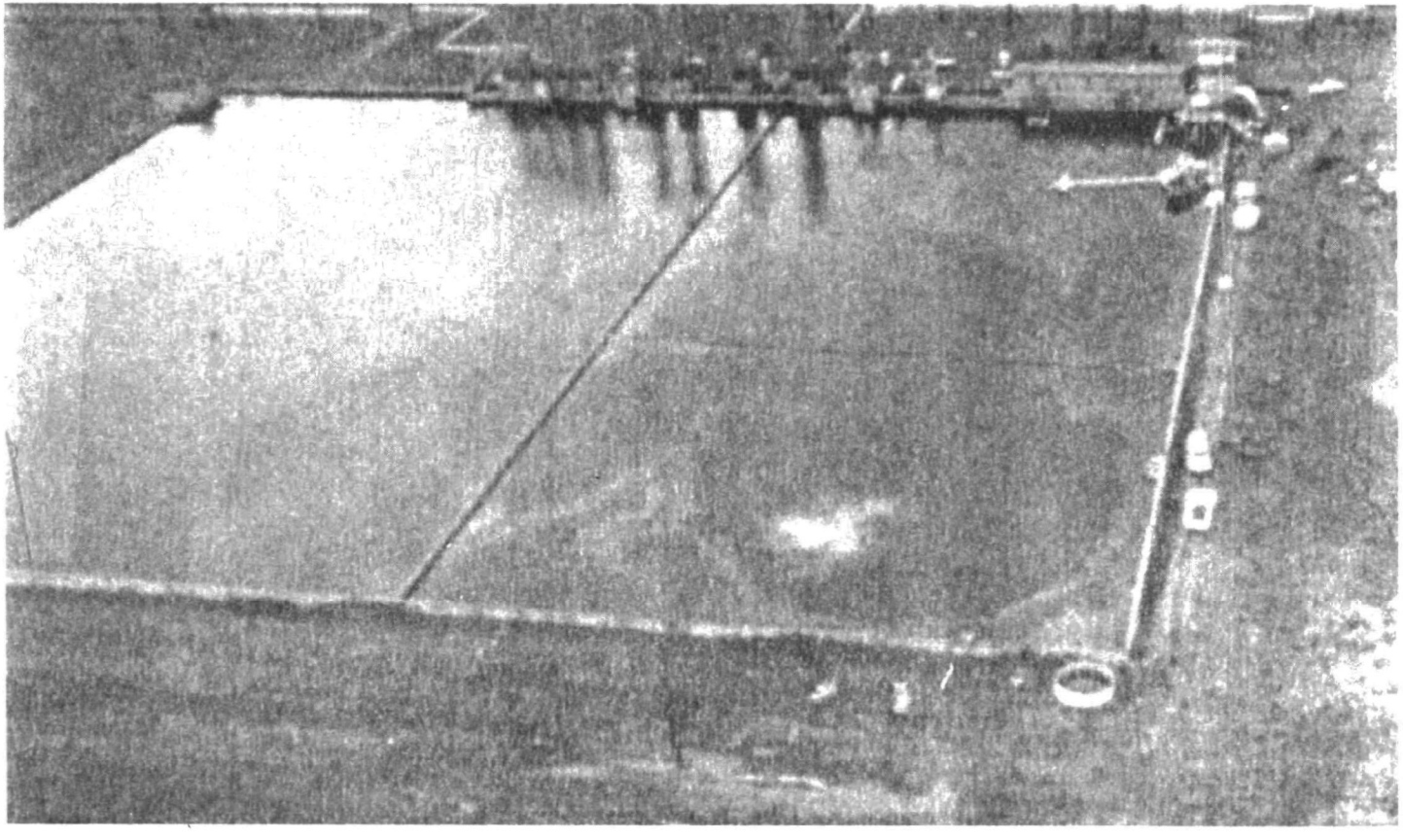


FIGURE 21

AERIAL PHOTOGRAPH OF DIAZINON SPILL

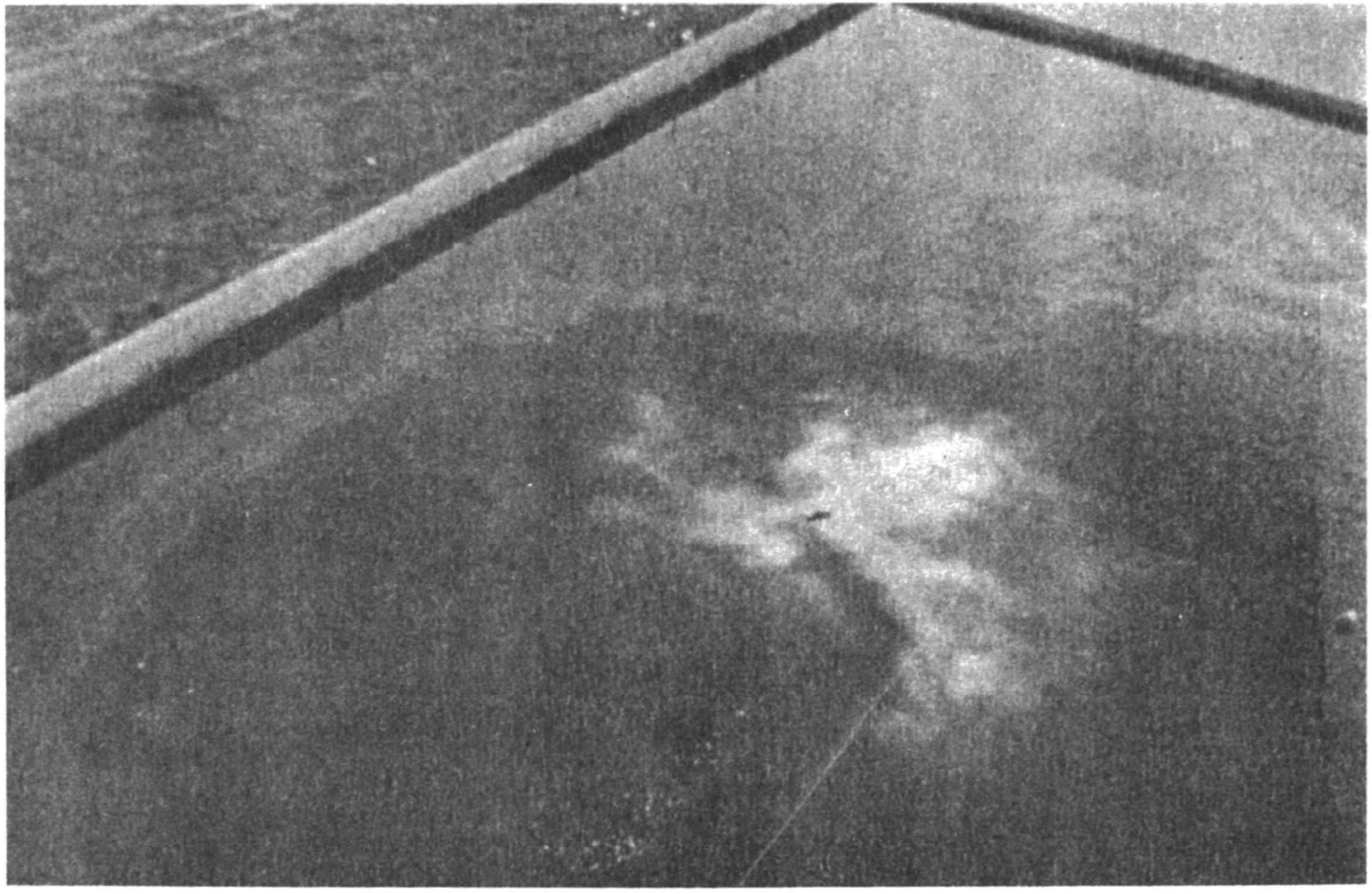


FIGURE 22

CLOSEUP OF DIAZINON SPILL IN SAMPLING GRID

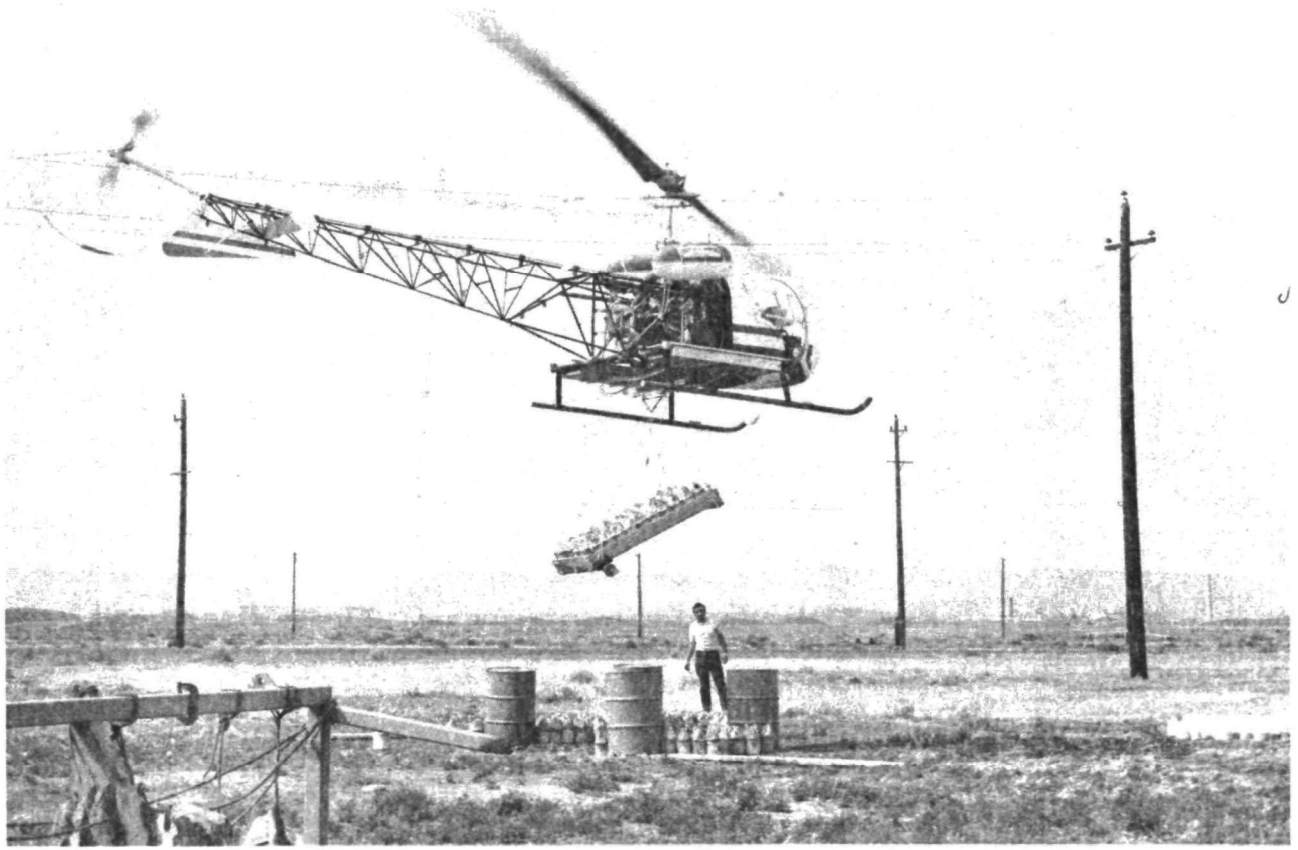


FIGURE 23

PHOTOGRAPH OF HELICOPTER WITH SLING

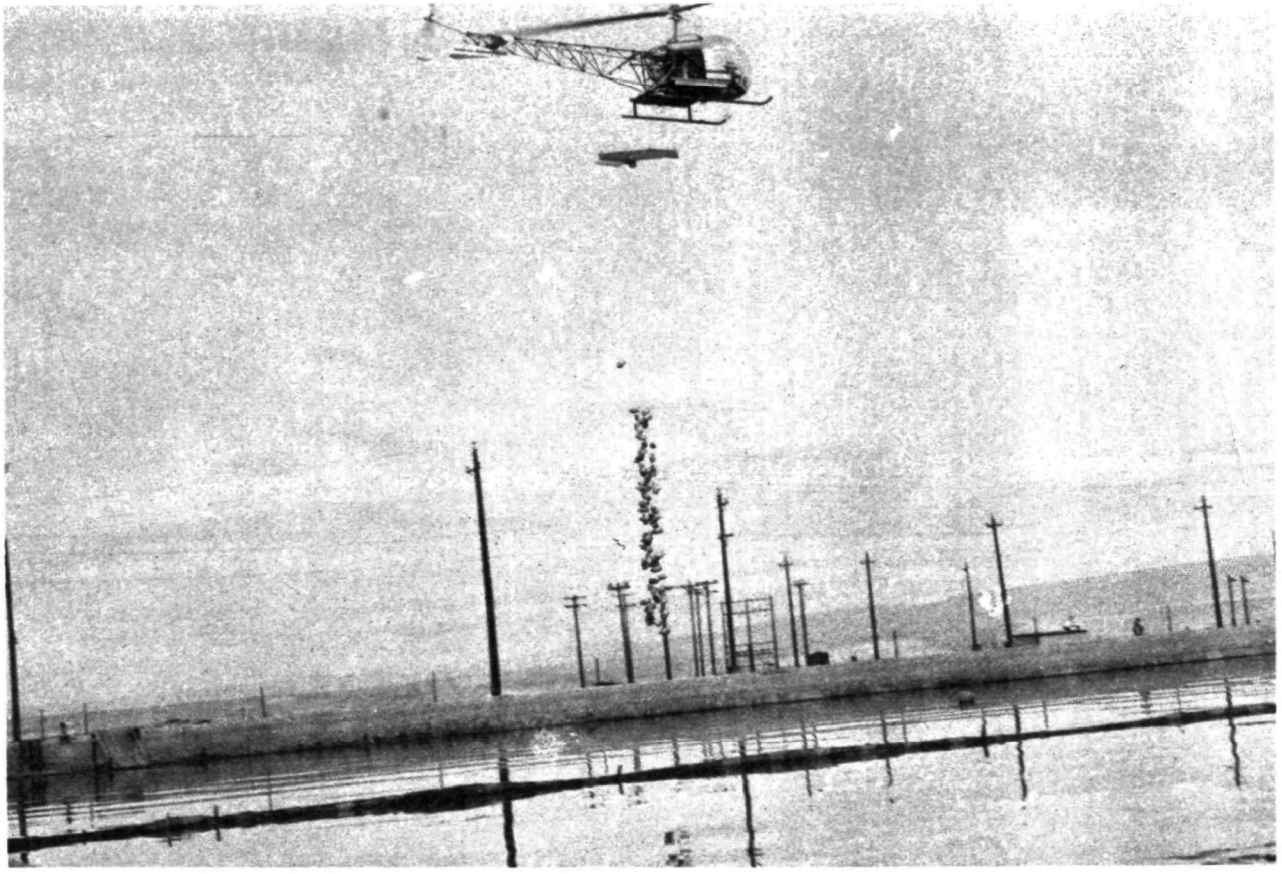


FIGURE 24

PHOTOGRAPH OF AIR DROP INTO SPILL AREA

By 1000 carbon was very evident in the surface waters around the spill. Many portions of the contained area were too dark to allow observance of objects more than six inches beneath the surface. A thin oil slick was also visible on the water since, as previously mentioned, prior to this field demonstration the basin was used for numerous oil spill contaminant demonstrations and residue oils remained behind after this work. As the bottles disturbed the water and moved down through the weeds on the bottom of the pond, globules of this residual oil were freed to rise and form a slick. The carbon appeared fairly effective in removing this oil as well as the Diazinon.

At 1400 two sampling boats set out to scoop random carbon samples from the surface of the spill area. These were composited for evaluation at a later time. Post spill water sampling was then initiated using the same procedure as before but this time with a greater number of sampling points.

The samples were analyzed for both phosphate and total organic carbon (TOC). The latter determination may be subject to some error due to the presence of oil slicks from previous spill studies in the basin water. Phosphate was determined by digesting an aliquot of the sample with a sulfuric acid-nitric acid mixture prior to colorimetric measurement of the phosphate concentration by the ascorbic acid-phosphomolybdate method[7]. Analysis of basin water with known concentrations of Diazinon gave 98 percent recovery of the phosphate by this procedure. The TOC analyses were performed with a Beckman Model 915 carbon analyzer.

Results of the phosphate analyses of the pretreatment and posttreatment samples are given in Figure 25, with the locations on the sample grid. Several increases in phosphate concentrations are noted between pretreatment and posttreatment samples which are believed to be largely caused by analytical variations. Additional posttreatment phosphate analyses are given in Figure 26. The data illustrate that the emulsion was relatively dense and the bulk of the spilled Diazinon formed a layer near the bottom of the basin. Laboratory studies conducted with the six inch diameter column did not indicate bulk movement of a fine emulsion to the bottom of the column. The density of the Diazinon is greater than water while the density of the xylene in the emulsifiable solution is less than water. Large droplets of the emulsifiable solution will float when initially dropped in water but will slowly sink after a few minutes. It is believed that the lighter xylene is either evaporated or extracted into the water causing the density of the droplet to increase.

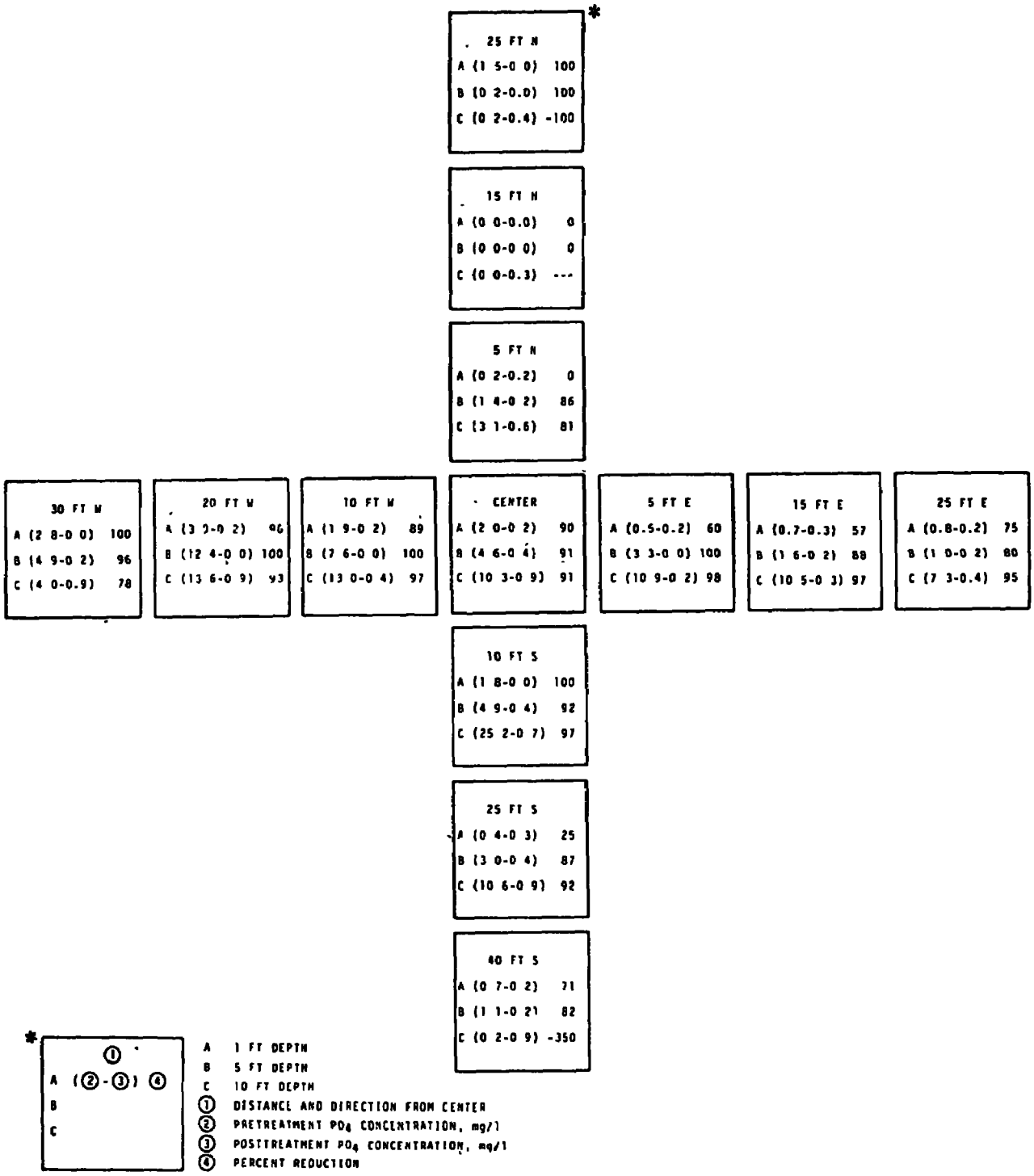


FIGURE 25.

RESULTS OF PHOSPHATE ANALYSIS ON PRETREATMENT AND POSTTREATMENT SAMPLES

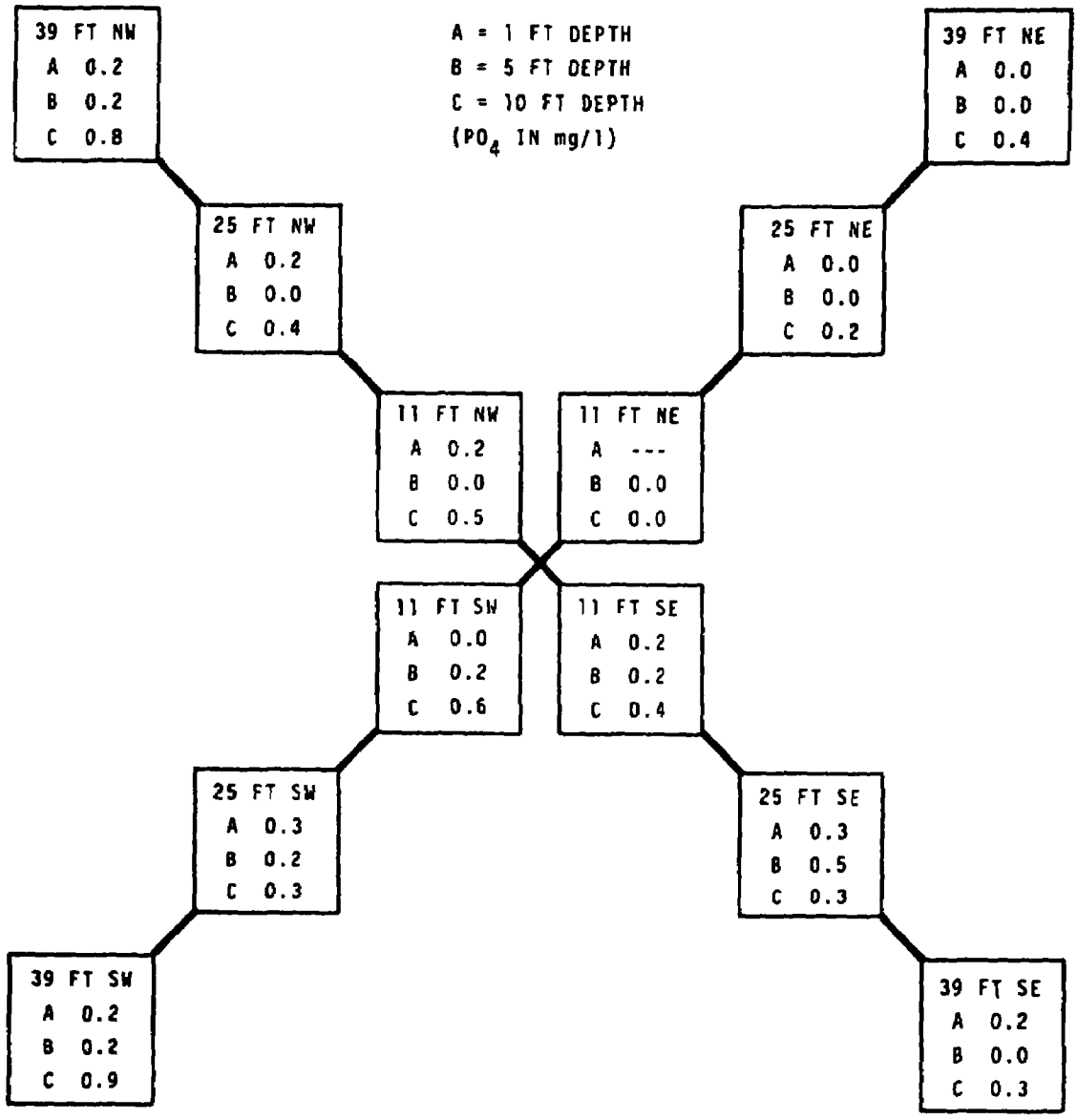


FIGURE 26

ADDITIONAL RESULTS OF PHOSPHATE ANALYSIS
ON POSTTREATMENT SAMPLES

Observations indicated that the wind drifted the emulsion briefly to the south and east while the emulsion was near the surface, but once the emulsion settled several inches into the water it appeared to remain stationary. The bulk movement to the west as indicated in the data of Figure 25 and in the aerial photograph, Figure 21, was not observed visually at ground level following the spill.

Results of the TOC analyses presented in Figures 27 and 28 correlate reasonably well with the phosphate analyses. As in the case of the phosphate results, several increases occurred between pretreatment TOC concentrations and post-treatment TOC concentrations. Analytical variations and oil contamination of the samples are believed to have caused these increases. Interpolation of the TOC data over the affected water column accounts for 66 pounds of the Diazinon solution or 85 percent of the 78 pounds originally spilled. Similarly, the phosphate data accounts for 68 pounds or 87 percent of the original solution spilled.

Based upon the water sampling data, the total quantity of Diazinon remaining in the water column after treatment was calculated in the same manner as had been the spill accountability numbers from the pretreatment data.

Phosphate analyses indicated a total of 4.2 pounds of Diazinon solution left in the water, or five percent of the original 78 pounds. Total organic carbon analyses indicated a residual of five pounds or six percent of the original spill. This suggests an average of 94.5 percent removal from combined dilution and treatment effects. However, examination of the post treatment data revealed that low concentrations of Diazinon might occur for some distance outside the sampling grid. Since most of the carbon was applied rapidly to the major dispersion of the spill in the southwesterly direction it is believed that good contact was made between the carbon and the bulk of the spill. Eddy currents set up by bottles descending to the bottom of the basin may have persisted for some time after the treatment and may have caused dispersion of the treated water containing low concentrations of the Diazinon. As a worst case estimate, a volume six times that of the sample grid could be assumed to have the same average posttreatment Diazinon concentration as that found within the sample grid. In such a case the removal would be 67 percent. The volume of water would then include both that in the sample grid and all of the water contained outside the grid in the basin west of the eastern edge of the sample grid. Thus, the actual removal of Diazinon should be between 67 and 94 percent.

Composite samples of carbon collected after treatment of the Diazinon spill were analyzed in an effort to determine the amount of Diazinon recovered by the carbon. The results of

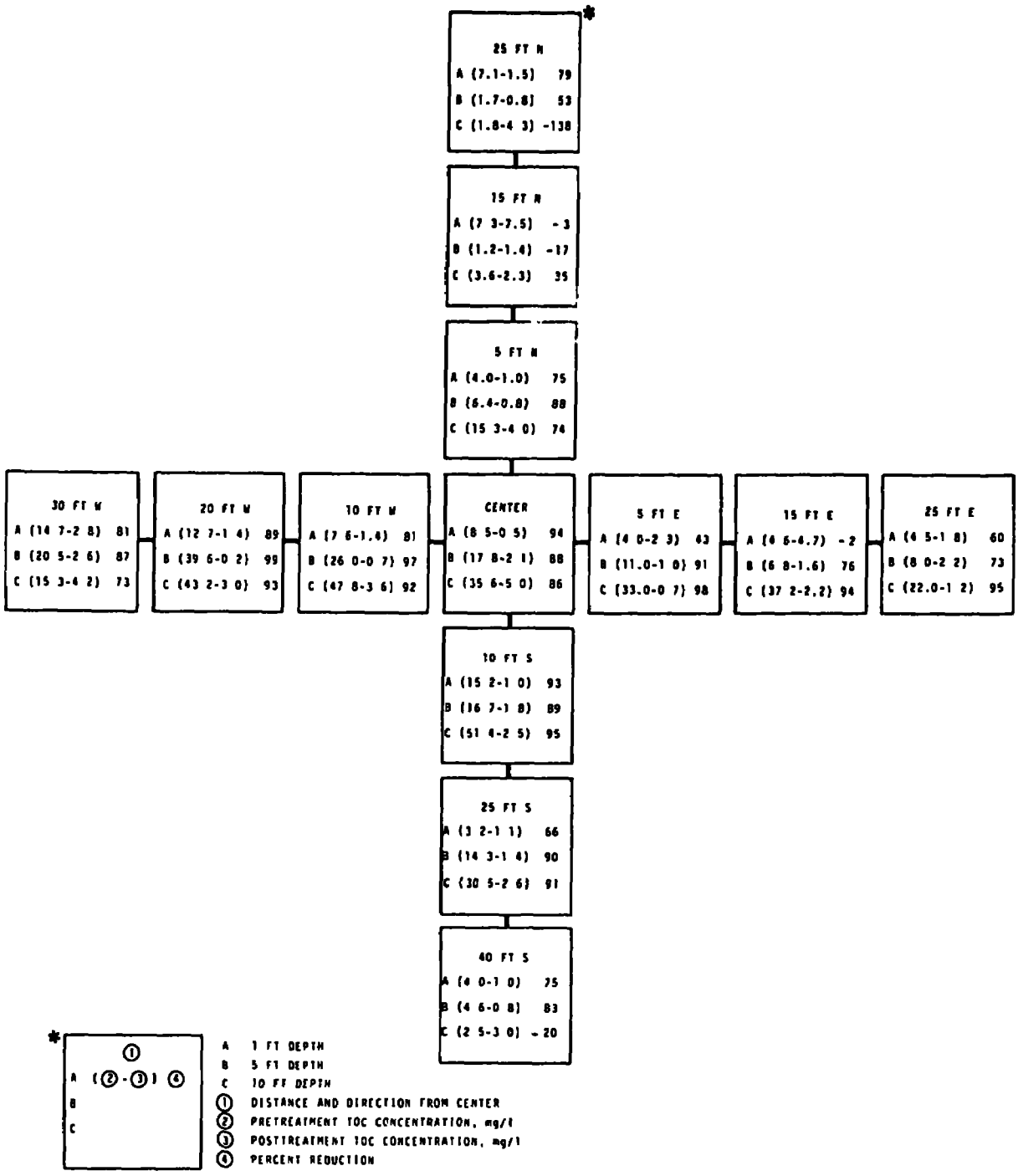


FIGURE 27

RESULTS OF TOC ANALYSIS ON PRETREATMENT AND POSTTREATMENT SAMPLES

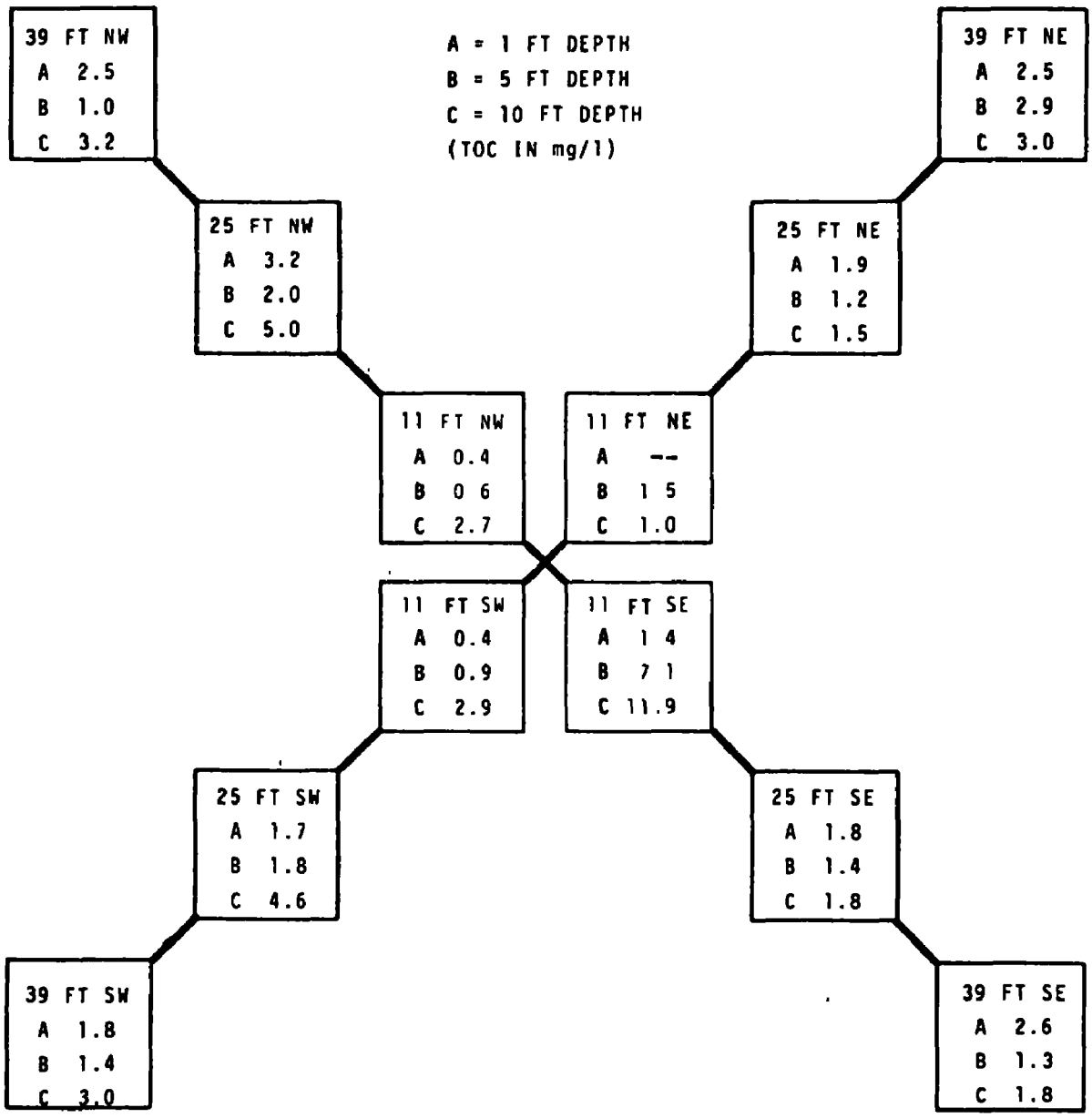


FIGURE 28

ADDITIONAL RESULTS OF TOC ANALYSIS
ON POSTTREATMENT SAMPLES

these analyses were inconclusive, however, due to considerable variation between analytical results. Insufficient information was found in the literature concerning the extraction of Diazinon from carbon for subsequent analyses. The development of adequate analytical procedures for analyzing the carbon for Diazinon content would require a level of effort for which time and funding were not available.

Sediment samples were analyzed to verify that the pesticide had not settled and associated itself with the bottom sediments. No change in sediment phosphate levels was detected. Sediment supernatant samples showed a slight increase in phosphate level. This increase, however, when extrapolated to the total spill area could account for less than 50 grams of Diazinon. It is clear that the floating carbon proved highly effective in removing the spilled Diazinon emulsion. Even greater efficiencies could be expected for light organics which would remain near the surface. In such cases, the rising carbon would simulate a countercurrent contacting process. Carbon resting on the surface or gently circulating nearby with wave action would remain in contact for greater periods of time and thus remove larger amounts of the organic contaminant.

Booming operations were begun at 1415. A 200 foot spliced section of a plastic Rodeorm Oil Containment boom manufactured by Trelledorg, Inc. was used to herd the carbon into the southeast corner of the basin.

The boom was pulled through the water manually with the aid of rope attached to the end of the boom. The northern end was first brought into the western wall, and then the triangle thus formed was diminished by moving both ends of the boom towards the apex. It was found that the carbon herded easily with no underwash evidenced.

At the beginning of the booming operation the wind had driven most of the carbon to the collection corner. During the operation the wind shifted causing the carbon to drift out against the boom. Some carbon escaped by moving out through the gap left between the end of the boom and the basin wall. Most of the carbon, however, appeared to pile up against the boom.

When the boom was well into the corner, carbon appeared to form a blanket up to two inches deep in places. A "J" shaped pipe was lowered into the corner of the basin and connected to a gasoline powered diaphragm pump. Figure 29 illustrates the placement of the pipe. The suction from the pump drew down a vortex from the surface of the basin and thus removed the carbon, which was then pumped to a 15 foot diameter portable swimming pool. The booming operation was completed by 1645. Water in the pond appeared to have returned to its original clarity with no noticeable carbon residues.

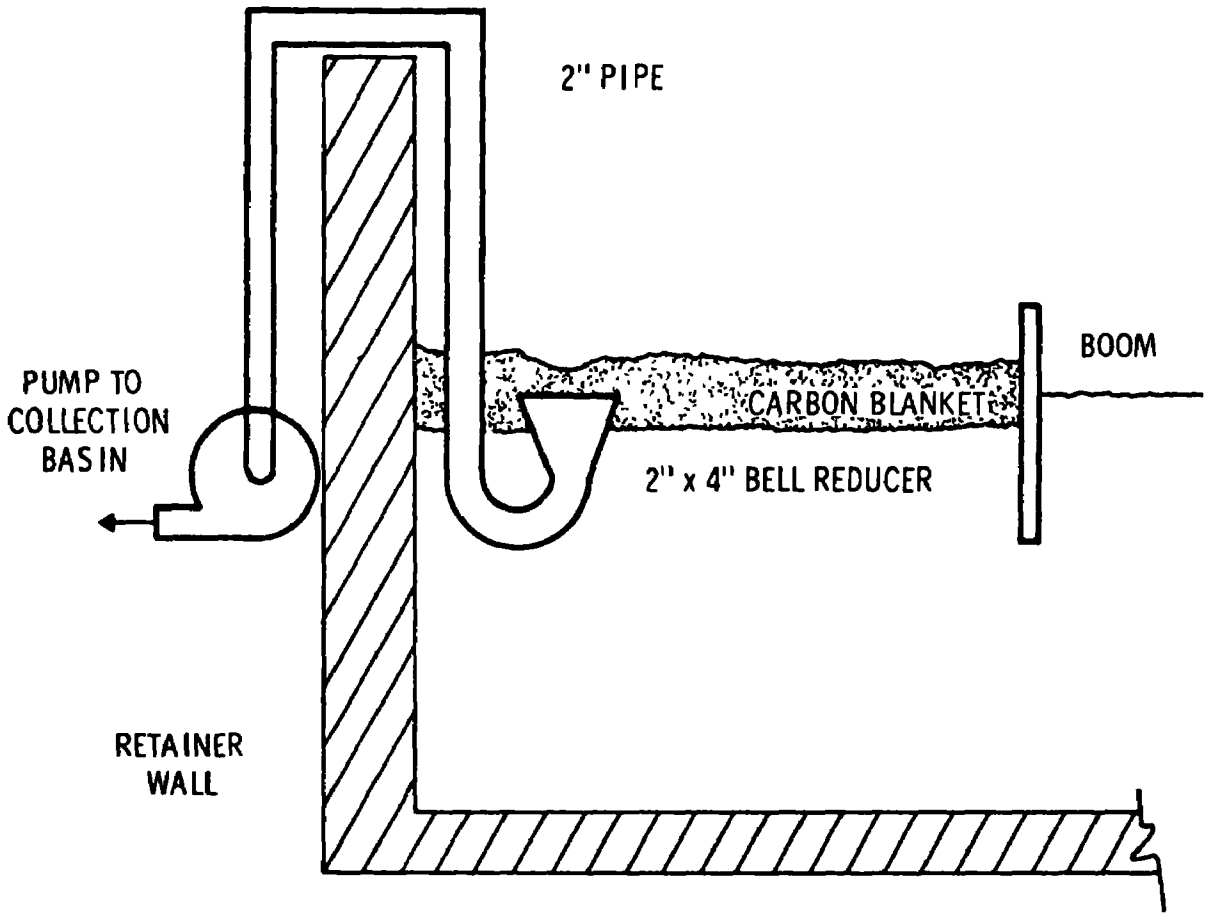


FIGURE 29

PLACEMENT OF THE COLLECTION PIPE AND BOOM

Water was subsequently drained from the carbon storage tank and the remaining carbon was allowed to dry. Measurements of the total volume and bulk density of the recovered carbon indicated that 90 percent of the original volume of carbon was recovered. Laboratory tests show that two percent of the carbon employed in the demonstration does not float and an additional one percent remains in the plastic container. A substantial portion of the remaining seven percent lost in the demonstration may have been trapped on weeds in the bottom of the basin and may not have floated to the surface. The 90 percent recovery was considered to be good.

No alternative skimming or booming devices were tested for comparison of effectiveness.

SULFURIC ACID SPILL

An abandoned sedimentation basin on the Hanford Reservation was selected for evaluation of the floating epoxypolyamine anion exchange resin. The 30 x 50 foot concrete lined basin was filled to a depth of six feet with water from a nearby fire hydrant.

Sulfuric acid was selected for the field demonstration since it is the chemical produced in the greatest quantity in the United States and it represents one of the major hazardous spill threats. During predemonstration tests it was found that concentrated solutions of sulfuric acid would rapidly sink and spread out over the bottom of the test basin when introduced at the surface of the water.

It was also observed that lateral movement of a dilute acid spill was too rapid in the basin to allow effective spill treatment with the quantity (13.7 cu. ft.) of floating ion exchange resin available for the demonstration. Water currents in the basin appeared to be largely responsible for the movement rather than dispersion of the acid in the water. It was therefore decided to conduct the demonstration spill of sulfuric acid in a small submerged open tank (five feet in diameter by two feet high) placed in the basin. The tank served to simulate the kind of natural depression found in most river beds or lake bottoms. Further predemonstration testing with a submerged tank showed some loss of sulfuric acid when the spill occurred at the surface of the water directly over the center of the submerged tank. The concentrated acid descended rapidly, thereby gaining sufficient momentum to travel across the bottom of the tank and up the wall to spill a portion of the acid over the wall of the tank. In order to avoid any loss of acid from the simulated depression, a subsurface spill of concentrated sulfuric acid was planned for the spill treatment demonstration.

The acid spill treatment demonstration was conducted with 45 pounds of concentrated sulfuric acid containing one ounce of m-cresol purple indicator which imparted a red color to the acid, thus allowing visual observation of the acid beneath the water surface. Sulfuric acid was transferred to the submerged tank in the basin via a one inch diameter PVC pipe. At the completion of the transfer, the acid blanketed the floor of the tank in a thin layer less than two inches deep.

Pretreatment sampling was performed using a six foot length of 1/4 inch diameter stainless steel tubing connected to flexible tubing and a peristaltic pump. Analysis of the pretreatment samples showed acid to be virtually completely contained in the thin layer on the bottom of the tank. A pH reading of 3.8 was recorded at the top wall (two feet above the bottom) of the tank. Directly above the tank and one foot below the water surface the pH was determined to be 6.9 as opposed to a prespill pH of 7.2.

Fifty media ice blocks containing epoxypolyamine anion resin and gravel ballast were used in the spill treatment operations. The media ice blocks were prepared by covering a layer of gravel in a mold with a layer of 30 percent resin slurried in water and freezing in a home freezer unit. Each media ice block was packaged in a plastic bag and stored in a freezer until use. A schematic diagram and a photograph of the media ice blocks used in the demonstration are given in Figures 30 and 31, respectively.

During the spill treatment operation, the media ice blocks were removed from the plastic bags and were dropped into the spill area approximately 30 minutes after the sulfuric acid was spilled. Nearly half of the media was dropped around the periphery of the submerged tank and the remainder was fairly evenly distributed on the bottom of the tank. It was planned that a substantial portion of the resin ice cakes should fall outside of the tank to provide resin for acid sorption above the periphery of the submerged tank. Laboratory studies had suggested that resin rising from the tank would cause vertical mixing and dispersion of the acid above the tank. However, little of the anticipated mixing actually occurred, because transferring the acid directly to the bottom of the tank caused formation of a thin, dense acid layer. It is believed that the layer of gravel ballast on the bottom of the resin ice cakes held the resin above the acid layer thus virtually eliminating contact between the resin and the acid.

Analysis of samples taken after the spill confirmed that only a small portion of the acid was removed from the water by the resin. Post spill sampling was carried out in the same manner as the pretreatment sampling. The only real change in acidity appears to have occurred in the center of the tank near the top, where the pH rose from 3.8 to 6.6. Apparently a small amount of vertical mixing occurred at this point.

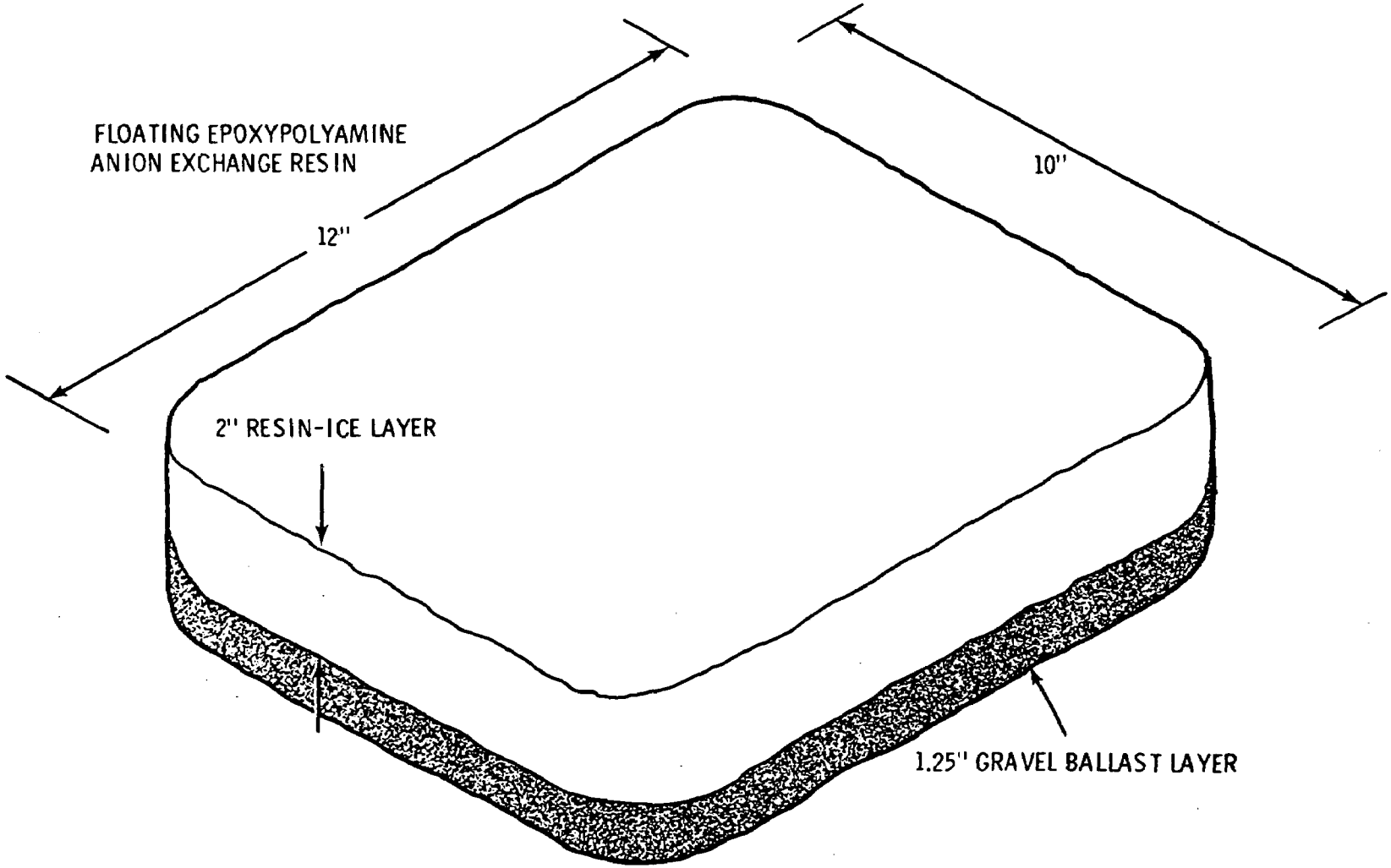


FIGURE 30

TYPICAL "MEDIA CAKE" EMPLOYED IN BASIN DEMONSTRATION

FIGURE 31

PHOTOGRAPH OF RESIN ICE CAKE

Within two hours, all of the resin had reached the surface (Figure 32). Samples of the floating resin were continuously taken and composited as the media surfaced. The resin samples were thoroughly mixed and a composite sample was then analyzed to determine the capacity utilization and sulfate sorption. The unused ion exchange capacity of the spent resin was determined by titrating samples of the resin with standard acid. The results showed a difference of 0.405 milliequivalents per gram when compared to the capacity of virgin floating resin. This represents 4.43 pounds of sulfuric acid when extrapolated to the total of 13.7 cubic feet of resin dropped, or ten percent of the original 45 pounds of concentrated acid spilled.

Similarly, analysis of the spent resin for sorbed sulfate ion revealed 22.1 mg more sulfate per gram of resin than in the virgin floating resin. This accounts for 5.3 pounds of sulfuric acid or 12 percent removal. The sorbed sulfate on the spent resin was determined by eluting samples of the resin with 1 N NaOH and measuring the eluted sulfate by a turbidimetric $BaSO_4$ procedure.

This low level of removal is not considered representative of the potential of the floating ion exchange resins for treating spills of electrolytes. There is no reason to believe that the resin would not be effective for a diffuse or diluted spill. A demonstration of this type to treat an unconfined spill would require considerably more resin than could be feasibly produced in this program.

The acid spill demonstration does, however, point out the need for sufficient contact of the sorbent with the material to be removed since densely layered spills are certainly within the realm of possibility. The sorbent-ice cake represents the most logical approach to attaining good bottom contact. Neither bottles nor clay containers would approach the same degree of bottom contact. Placement of the ballast in the center of the resin-ice cake rather than on the bottom would be expected to improve bottom contact. To be fully effective, however, the material to be removed must be dispersed above the resin-ice cake for good contact with the main plume of resin rising above the cake.

Two days after the acid spill, operations to recover the ion exchange resin were initiated. The resin was easily boomed and herded to a corner of the water basin where it was skimmed from the surface and dewatered by screening through a 100 mesh screen. Virtually complete recovery of the total quantity of floating resin used in the spill treatment demonstration was achieved in this manner.

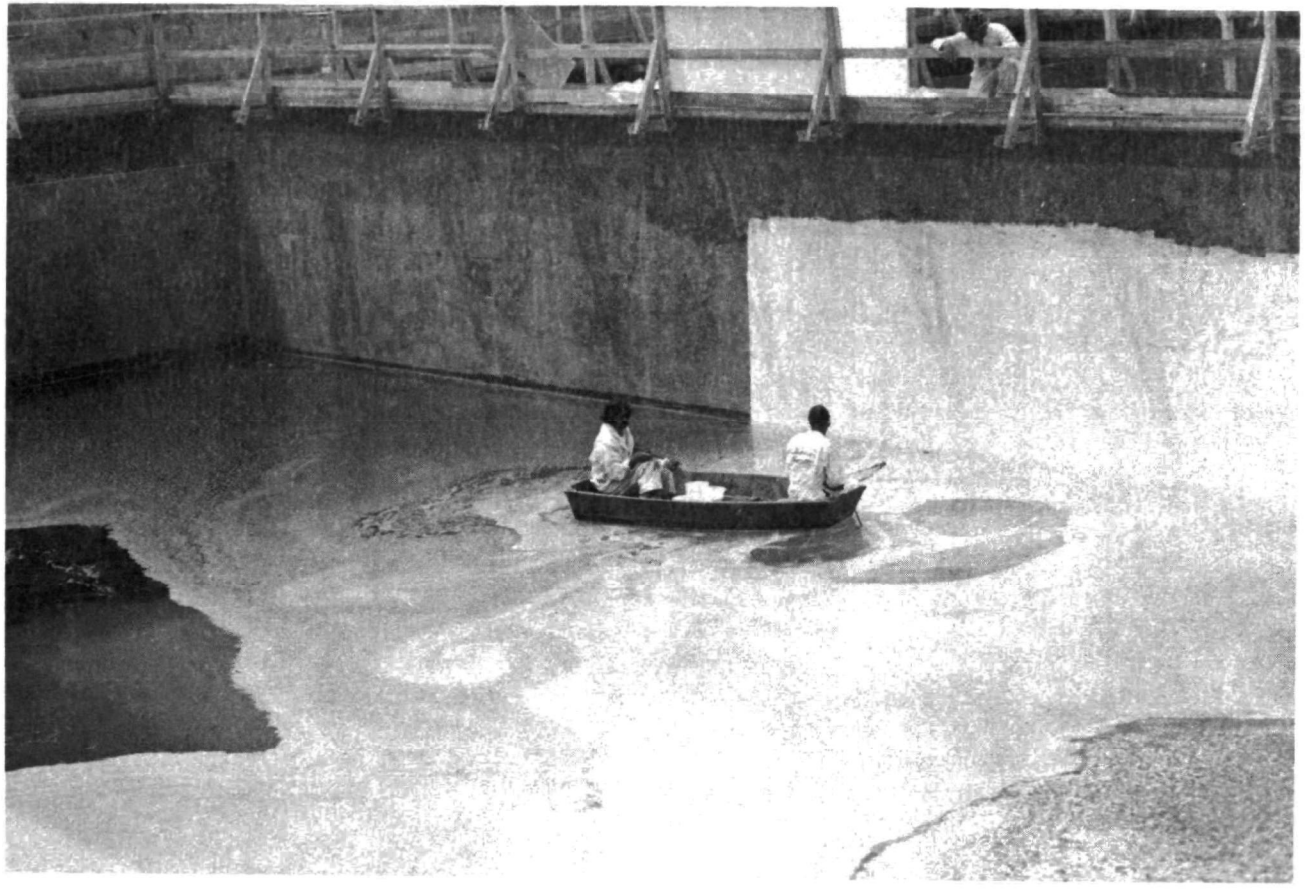


FIGURE 32

SAMPLING FLOATING RESIN AFTER TREATMENT

SECTION VII

APPLICATION

Although the basic concept of utilizing floating media for spill treatment has been successfully demonstrated, it is emphasized that neither media production methods nor application techniques have been fully optimized. The following discussion will summarize the status of the technology developed for treating hazardous material spills with floating mass transfer media, however, and provide some understanding of its use.

Floating activated carbon represents the most versatile media evaluated in this work because of its ability to remove a broad range of hazardous materials, principally organics, from water. Although only a few hazardous materials (phenol, benzene, toluene, styrene, Diazinon, Malathion, and acrylonitrile) were investigated in this study, activated carbon could be effectively used for adsorbing many other organic substances which have limited solubility in water and/or consist of long-chained molecular structures. Included in this category are a wide variety of hydrocarbons; organic halogen compounds (e.g., pesticides); long-chained monofunctional alcohols, aldehydes, ketones, and fatty acids; low solubility esters; and many others. Examples of common organic compounds which are not readily adsorbed from aqueous solutions are methanol, ethanol, urea, sugars, and ethylene glycol.

Effective treatment of hazardous organic material spills with floating activated carbon will depend on the following factors.

1. The material must be readily adsorbed by the carbon from aqueous solutions.

2. The carbon grain size should be small, preferably in the 50 x 325 mesh size range, with a significant fraction passing a 100 mesh sieve.

3. The carbon must be pretreated by soaking in water and drying at a low temperature (100°C or less) to assure proper wetting and dispersion when released from packages beneath the spill zone.

4. The spill zone must be accurately defined and the carbon applied accordingly. On-the-spot judgments may necessitate application of a larger amount of carbon where higher concentrations of spilled material are believed to exist. A 10:1 ratio of carbon to spilled material is recommended for application.

5. Response to the spill must be rapid since dispersion of the spilled material over a wide area will decrease the effectiveness of the carbon and may prevent accurate location of the material.

6. The floating carbon containing the sorbed hazardous material must be collected and removed to prevent desorption of the material into uncontaminated water (desorption will be slow unless wave action or other surface turbulence disperses the carbon in the water).

Release of the floating carbon from weighted plastic bottles in a hazardous material spill zone has been demonstrated, but only in static or impounded waters. Application to flowing streams may require a different technique. Other methods of application such as subsurface injection by infusion pumps and release from ice cakes or unfired clay containers appear practical but have not been demonstrated on a large scale.

The use of a floating epoxypolyamine ion exchange resin for removing hazardous substances has also proved successful. The resin was prepared by incorporating buoyant hollow glass microspheres in the resin matrix. As is the case with activated carbon, a small resin particle size is required to maximize the effectiveness of this medium. The floating epoxypolyamine ion exchange resin obtained for the field demonstration had a particle size range of 16 x 100 mesh with the bulk of the resin particles in the 16 x 40 mesh range. A particle size passing a 50 mesh screen would be more desirable; however, production methods must be refined to accomplish this.

The floating epoxypolyamine resin evaluated during this program was found to be quite effective in removing acid from water. The field demonstration pointed out, however, that spills of high density acids may be difficult to treat because the acid forms a dense layer at the bottom

which cannot be readily contacted by the resin. The ice cake method of applying the resin represents the most favorable packaging concept investigated for use in treating hazardous materials concentrated near the bottom of a body of water. Although the floating epoxypolyamine resin has been evaluated for use in treating only acids in this study it is anticipated that the resin will be useful for removing toxic anions (e.g., cyanide) also.

The effective use of the floating ion exchange resin in treating spills will be governed by the same conditions as those for carbon listed above with the exception of pretreatment (item 3). The ion exchange resin is maintained in a moist condition and should not be allowed to dry out.

The feasibility of commercial production of floating activated carbon and floating epoxypolyamine resin has been demonstrated. Although production methods have not been optimized, sizable quantities of these materials can be obtained for further studies or for application in the field. The sources of these materials and costs are given in the Appendix.

SECTION VIII

ACKNOWLEDGMENTS

The assistance and advice provided by Mr. Ira Wilder, EPA Project Officer, are gratefully acknowledged. The authors also wish to express their appreciation to Westvaco for samples of activated carbon provided for experimental studies; to Dr. Irving M. Abrams, of the Diamond Shamrock Chemical Company, who provided information and suggestions concerning the preparation of ion exchange resins; and to Battelle-Northwest personnel, Mr. James Coates, Mr. Marvin Mason, Mr. Richard Parkhurst, Mr. Greg Swank, Mr. Robert Upchurch, Mr. Gary Schiefelbein, and Mr. Terry Brix, who assisted in the carrying out of the experimental work.

SECTION IX

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SECTION X

APPENDIX

SOURCES, PREPARATION, AND COSTS OF FLOATING MASS TRANSFER MEDIA

ACTIVATED CARBON

The floating activated carbon used in the field demonstration was prepared from Nuchar C-190, +30 mesh carbon manufactured by Westvaco of Covington, Virginia. Four thousand pounds of this carbon were purchased at a cost of $1,693 delivered to Majac, Inc., of Pittsburgh, Pennsylvania. The carbon was pulverized and air classified to remove the fines (-325 mesh) by Majac at a cost of $1,200. The carbon was then shipped to Battelle-Northwest for the remaining processing steps which consisted of dry sieving to separate the 40 x 325 mesh fraction and washing and drying to condition the carbon to wet and disperse properly when applied for spill treatment.

The production rate of the continuous sieving apparatus used to separate the desired mesh fraction was limited to about four pounds of 40 x 325 mesh carbon per hour. Washing was accomplished by mixing the carbon with water in a 50 gallon tank to thoroughly wet the carbon particles. The carbon was then allowed to rise to the surface, removed from the tank by skimming, and placed in canvas bags for draining.

Drying was accomplished in about one week at ambient air temperatures by spreading the damp carbon to a depth of 1-2 inches on diamond mesh sisal paper in well ventilated rooms. The average temperature and relative humidity during the drying period were 70°F and 48 percent, respectively.

Seventy-one percent or 1700 pounds of the carbon received from Majac was processed through the sieving apparatus. The final yield of treated 40 x 325 mesh carbon was 675 pounds which cost $1539 to process through the sieving, washing, and drying steps. The total cost of the 675 pounds of 40 x 325 mesh carbon was $3,593, which includes the $1,539 above and 71 percent of the purchase and pulverizing/air classifying costs.

Since the completion of this work Westvaco has discontinued sales of the +30 mesh and unground grades of Nuchar C-190 and will soon discontinue sales of the same grades of Nuchar WA. Westvaco will continue to market a fine mesh size of Nuchar C-190 (Nuchar C-190 N) with about one-third of the carbon in the 100 x 325 mesh range. This material costs approximately 17 cents per pound (excluding delivery costs) in quantities of 30,000 pounds or more, which is about half the cost of the +30 mesh grades formerly marketed. The Nuchar C-190 N carbon has not been evaluated as a floating mass transfer media; however, there is no reason to expect that it would not function as well as the other grades tested. In addition to the lower purchase price, the Nuchar C-190 N could be processed to give the desired mesh size at a lower cost since no pulverization would be required.

Westvaco also markets another grade of powdered carbon, Nuchar C-115 N, which has about one-third of the carbon in the 100 x 325 mesh range. A cursory examination indicates a high percentage of floating particles in the desired mesh size range.

EPOXYPOLYAMINE RESIN

The floating epoxypolyamine ion exchange resin was obtained by special order from the Diamond Shamrock Chemical Company, Nopco Chemical Division, Duolite Ion Exchange Resins, Redwood City, California. Five hundred pounds (14 cu. ft.) of this resin were purchased for $4,000.

The floating anion exchange resin prepared in the Diamond Shamrock Chemical Company's development laboratories was characterized as follows:

Reference number	1,219, 67
Free base form	100 percent floaters
Chloride form	100 percent floaters
Sulfate form	95 percent floaters
Total acid absorption capacity (dry weight basis)	7.2 mg/gm
Moisture retention capacity	59 percent
Granule strength	Fairly hard
Particle size	30 to 70 mesh

The 500 pounds of resin produced in plant facilities had essentially the same characteristics except that the particles were largely in the 16 to 100 mesh size range.

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16 Abstract An approach for the in situ treatment of spills of soluble hazardous polluting substances was developed and demonstrated on a field scale for a static body of water. Laboratory scale experimentation showed that floating sorbents and ion exchange resins could be highly effective removal agents when applied as small particles beneath the surface of contaminated waters.

A lightweight commercial activated carbon was found to be particularly effective for removing organic substances such as phenol, aromatic hydrocarbons, and organophosphorus insecticides from water.

Floating ion exchange resins were also prepared for use on spills of acid, alkalis, and toxic salts. Hollow glass microspheres are incorporated in the resin granules for buoyancy.

Field demonstrations were conducted using carbon contained in weighted plastic gallon bottles. The carbon proved highly effective in removing an organophosphorus pesticide spilled in a large basin, and was easily collected through use of an oil containment boom. Ice encapsulated floating anion exchange resin beads were similarly employed to neutralize a spill of sulfuric acid.

17a Descriptors

*Activated Carbon, *Ion Exchange, *Resins, *Water Pollution Treatment, Water Pollution Control

17b Identifiers

*Spills, *Hazardous Materials, *Hazardous Chemicals, *Mass Transfer Media

17c COWRR Field & Group 05G

18. Availability

19. Security Class. (Report)

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