

H-24-15

Test Results of Surfactant Enhanced Gasoline Recovery In A Large-Scale Model Aquifer

API PUBLICATION 4390
APRIL 1985

American Petroleum Institute
1220 L Street, Northwest
Washington, D.C. 20005



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April 15, 1985

Test Results of Surfactant
Enhanced Gasoline Recovery in
a Large-Scale Model Aquifer

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FORWARD

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TRI gratefully acknowledges the partial support of this work provided by the American Petroleum Institute (API). Technical guidance was furnished by the Groundwater Committee Technical Task Force.

The statements and conclusions contained in this report regarding the effectiveness of surfactant treatment(s) in mobilizing spilled gasoline for soil/groundwater reclamation are those of the authors and may not represent those of API or of the Task Force members.



EXECUTIVE SUMMARY

The objective of this project was to test whether the use of surface active agents (surfactants) would enhance removal or recovery of gasoline from a contaminated aquifer. The effects of surfactants used to mobilize spilled gasoline entrained in the capillary fringe of a modeled aquifer were assessed. The surfactant employed was a 2% solution of Richonate YLA, with 2% Hyonic PE-90 added to enhance flow rate.

A 3m x 3m x 1.2m deep (10ft x 10ft x 4ft) sand-filled concrete tank with a nominal 0.3m (1ft) deep, 3% gradient water table was used as model aquifer. The tank interior was temperature controlled and was instrumented for observation of fluid distribution and measurement of fluid levels and flows. Gasoline was metered into the sand volume just above the capillary fringe of the aquifer. The rate of gasoline removal was monitored by collecting raw gasoline from a simulated producing well and by extraction of dissolved gasoline from samples of the produced effluent. A carbon disulfide (CS₂) extraction technique was employed. Calculation of residual gasoline based on core sampling of the sand volume completed mass accountability.

Three surfactant application techniques were tested: a single application by percolation through the sand volume, a multiple (daily) application by percolation, and a multiple (daily) application by direct injection into the water table. The multiple application techniques proved to be the most effective for removing the spilled contaminants. Based on the amount of gasoline in the tank at the beginning of the surfactant application(s), the percentages of gasoline removed associated with each technique were 6, 76, and 83, respectively.

Ancillary observations performed throughout these tests underscored the uncertainty in predicting fluid distribution and fluid flow in even a simply structured soil (e.g., packed sand).

Recommendations are made for further study of surfactants and surfactant application techniques and of fluid flow behavior in model environments before proceeding to full-scale field tests.

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1.0 INTRODUCTION

Gasoline that escapes from a surface or buried container will permeate the soil downwardly and will diffuse laterally. The extent of lateral diffusion relative to downward travel will be determined principally by the permeability of the soil. In the absence of shelf rock or clay, the limit of downward movement will be the upper surface of the aquifer, which presents a virtually impenetrable barrier to the gasoline. When the gasoline percolates to the aquifer, it then spreads horizontally to form a buoyant layer, or lens, on the water surface. The nature and extent of this lens will be determined by the topography and permeability of the aquifer boundary, by the movement of the ground water, and by complex surface interactions among soil, water, and gasoline.

Gasoline is an obvious contaminant of ground water and its spread may lead to underground seepage into open water containments and potential entry of hazardous fluids and fumes into storm sewers, basements, and underground utilities, often with disastrous results.

Gasoline that permeates the pore structure of the aquifer boundary will be dispersed into droplets whose size (or size range) is determined by the interfacial tension between the gasoline and the ground water and by the capillary dimensions of the pore structure. Capillary forces will act to retain these droplets within the soil pores. Some components of the contaminant will adsorb on surfaces within the aquifer fringe and in the overlying unsaturated soil. The result is a zone of gasoline contamination moving along the surface of the water table at a rate slower than the water movement, plus a relatively small volume of gasoline contaminated soil located beneath the spill site. Water, e.g., rain, that enters the soil over the spill site will percolate through this region to leach gasoline into the water table.

Part of the gasoline spilled to the aquifer can be recovered in raw form at a drawdown well or an intercepting trench. However, a significant portion of the spilled gasoline volume will remain entrapped in the pore structure of the aquifer surface in the form of droplets immobilized by interfacial and capillary forces. Recovery of this entrapped volume of contaminant requires that it be mobilized. This can be accomplished by 1) increasing the driving force, e.g., by flooding with water to increase the hydrostatic head, 2) by forcing air to flow through the soil layer to increase the rate of droplet vaporization while in the pores, or 3) by reducing the surficial forces retaining the droplets, thereby allowing them to flow under the existing driving forces and/or to dissolve. It is the last approach to enhancing contaminant mobility that was addressed in the work reported here.

Texas Research Institute (TRI) identified surface active agents (surfactants) that enhanced the removal of gasoline entrapped in the pore framework of simple soils (packed sands), and that would not themselves permanently contaminate an aquifer, and assessed their utility in recovering the entrapped gasoline in a large-scale physical model experiment. Three surfactant application techniques were evaluated: a single dose that percolated through the spill site to the water table, a multiple (daily) dosage that percolated through the spill site, and multiple (daily) injections directly into the water table below the spill site. In a fourth test, the control, water only was percolated through the spill site. The effectiveness of each technique for recovering the spilled gasoline was evaluated singly and by comparison to the other techniques and to the control.

2.0 EXPERIMENTAL FACILITY

The TRI model aquifer facility is diagrammed in Figs. 1 and 2. It is a steel-reinforced concrete tank measuring 6.1m x 3m x 1.2m deep (20ft x 10ft x 4ft) inside. For the present work the tank was divided by a steel partition to form two 3m x 3m x 1.2m (10ft x 10ft x 10ft) tanks to allow parallel testing of different procedures.

The soil fill of each tank was packed, washed river sand, designated "finish" sand by the aggregate supplier. The four tests--three surfactant application techniques plus water application only--required two fillings of each tank. The characteristics of the sands used in the two fillings differed slightly in grain size distribution and, therefore, porosity and permeability. The sands are characterized below. (See also Appendix C.)

Each tank was equipped and instrumented as follows (see Figs. 1 and 2). A water input pipe for establishing and maintaining the water table was located along the centerline near the steel partition. A 30.5 cm (12 in.) high standpipe/recovery well was located along the centerline adjacent to the opposite (end) wall of the tank. A perforated tube grid for simulating rainfall was positioned just above the top of the sand pack. The sides of the tank and the upper margin of the rainmaker grid were striped with copper tubing for circulating coolant water to maintain tank temperature at nominal 13°C(55°F). Seven observation wells made from 3.2 cm (1.25 in.) i.d. PVC pipe slotted to 61 cm (24 in.) height above the tank floor were positioned as diagrammed in Fig. 1. Four large volume vapor wells made from 10 cm (4 in.) i.d. PVC pipe with 100 mesh screen on bottom were positioned as shown in Fig. 1. Thermocouples were placed at three depths--15 cm (6 in.), 61 cm (24 in.), and in the water table--near the steel divider and the end wall and near the center of the tank to

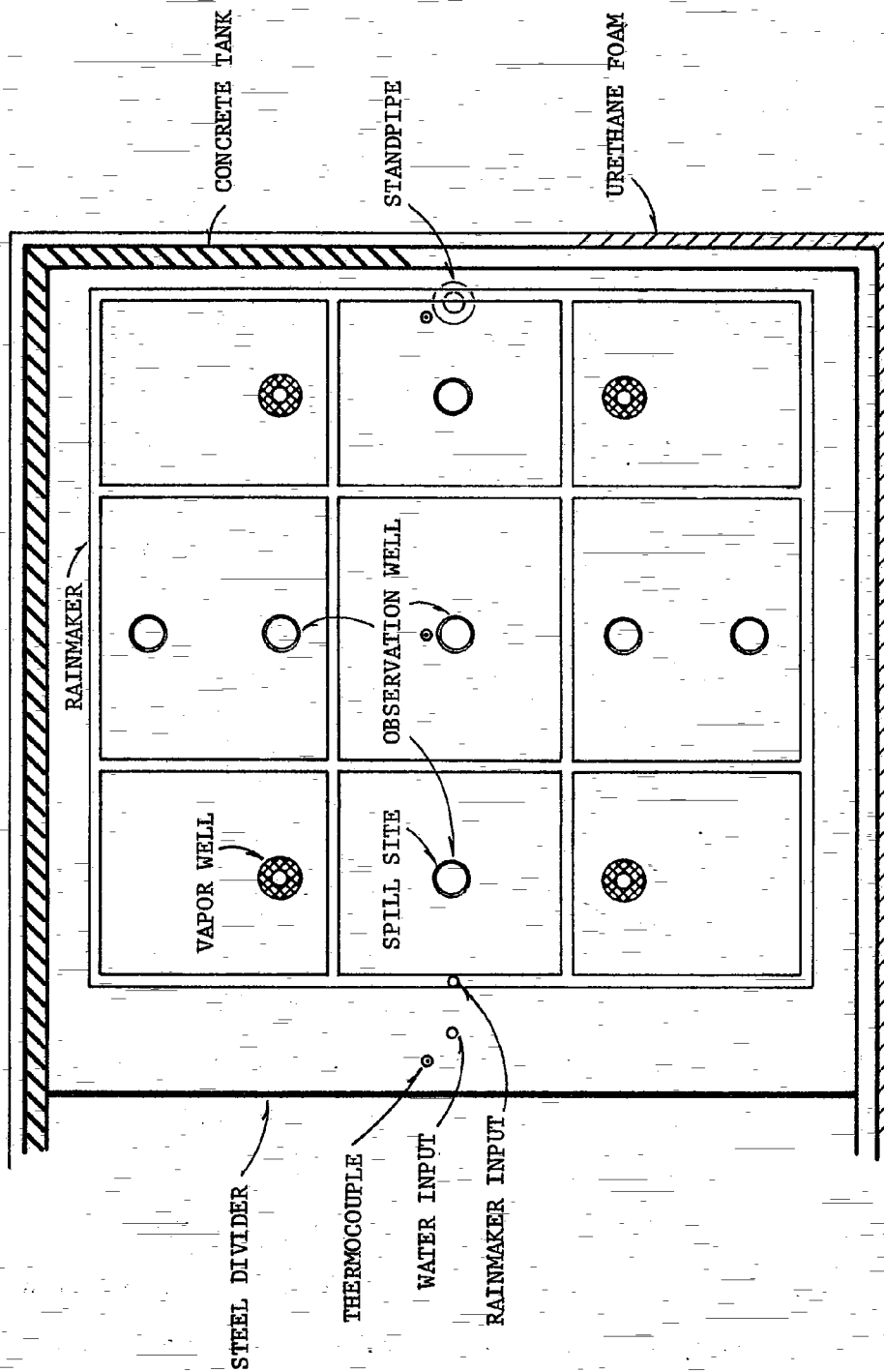


Figure 1
TRI Soil/Aquifer Model Facility
Plan View

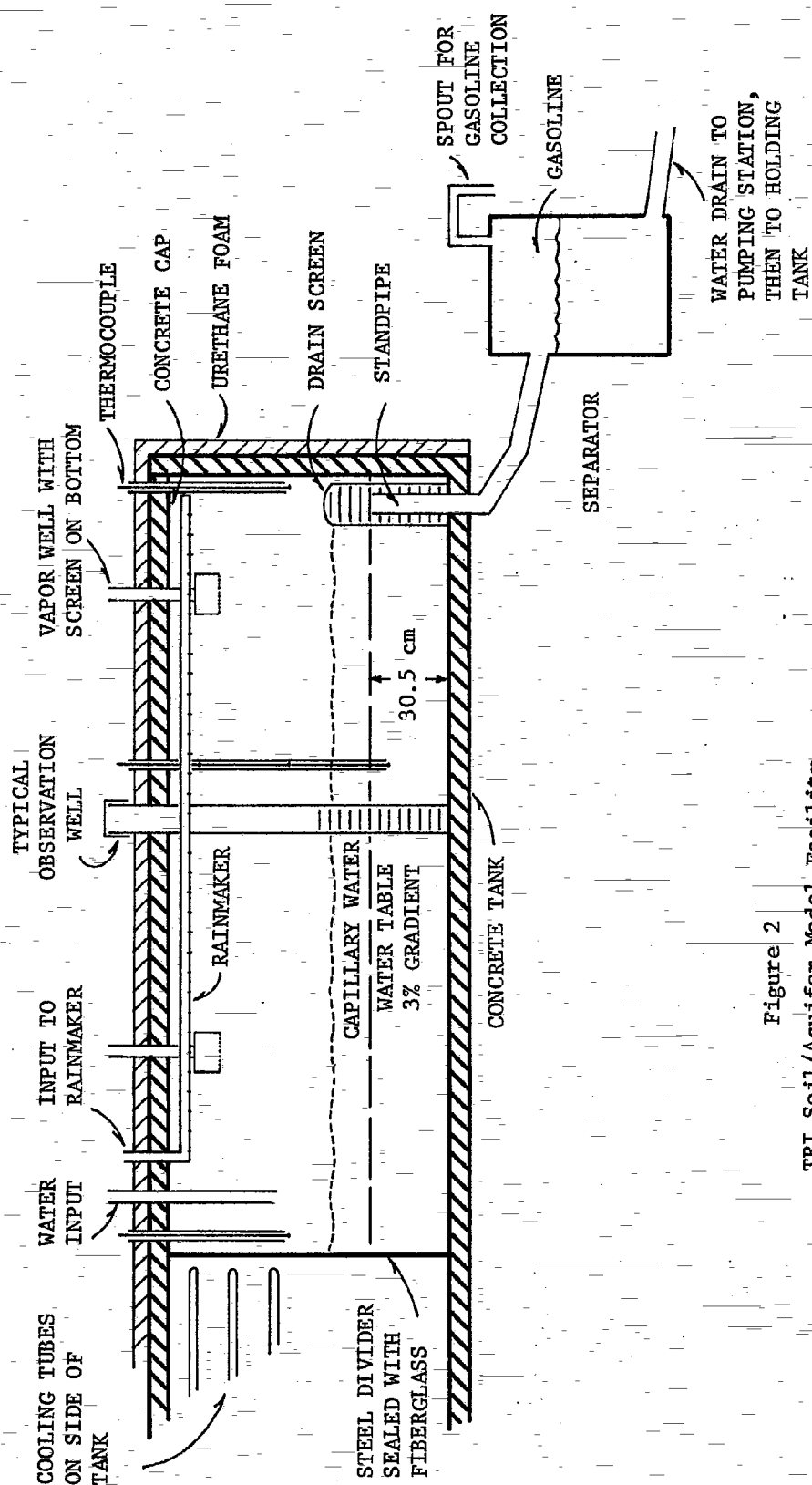


Figure 2
TRI Soil/Aquifer Model Facility
Side View

monitor the temperature profile of the model aquifer; an additional thermocouple was located externally to monitor ambient temperature.

A plywood barrier was laid over the cooling coils above the sand pack and a nominal 5 cm (2 in.) thick concrete cap was poured in place to reduce evaporative losses from the tank and, by acting as an oxygen barrier, to reduce bacterial activity in the model aquifer. The entire structure was then spray coated with polyurethane foam to a thickness of 5 cm (2 in.) for insulation and further sealing. Photographs of the surface of a filled tank before the concrete cap was poured and after it was spray coated with foam are included as Appendix A.

The water table was set at 30.5 cm (12 in.) above the tank floor. Untreated City of Austin tap water--pH 9.7 to 10.0--was used. The input flow was adjusted to establish and maintain a nominal 3% water table gradient.

Effluent was passed through a separator for removal of raw gasoline. The effluent water was sampled for analysis and the remainder was pumped to a holding tank for subsequent disposal (transport to a sewage treatment facility).

The grain sizes of the sand used in the first pack are represented by the following sieve analysis results.

Mesh Size	Wt % Passing
5	99.9
10	96.8
20	81.0
35	51.1
50	22.5
100	4.8

The porosity of this sand was 33%. Its permeability was 19 darcies.

Capillary height was approximately 15 cm (6 in.). Surfactant adsorption studies indicated that 20-30% of the surfactant in one pore volume of solution was retained by the sand.

The grain sizes of the sand used in the second pack are represented by the following sieve-analysis results.

Mesh Size	Wt % Passing
5	100
10	98.4
20	81.5
35	44.2
50	14.9
100	2.8

That is, the median grain size of this sand was slightly larger than that of the earlier sand. Its porosity was 34%, an insignificant difference from the earlier sand, but its permeability was 37 darcies, a two-fold increase. Capillary height was approximately 13 cm (5 in.). Surfactant adsorption studies on this sand indicated that about 20% of the surfactant was removed from solution by the sand.

3.0 EXPERIMENTAL PROCEDURE

Four experiments were conducted using the model aquifer facility described above. Three of these were to assess the effectiveness of different surfactant application techniques in mobilizing soil and gasoline trapped in ground water for removal and/or recovery. The fourth was a comparison or control test to assess recovery in the absence of mobilizing agents.

The surfactant employed was a 2% solution of Richonate YLA (Richardson), with 2% Hynic PE-90 (Diamond Shamrock) added to enhance flow rate. Earlier work at TRI* has shown that the anionic Richonate YLA was effective in displacing gasoline from a sand pore framework by reducing the gasoline-water interfacial tension. However, used alone it formed a viscous emulsion with an intolerably low flow rate. The addition of the nonionic Hynic PE-90 increased the flow rate without decreasing the effectiveness of the YLA.

The original test plan specified that during the first phase of the experimental program, one of the surfactant application techniques would be compared to the control. Then, in the following phase, this application technique would be repeated for comparison with a second application technique. However, the results from the Phase I assessment revealed a need to modify the testing program. Therefore, during Phase II, two additional surfactant application techniques were assessed. (See below.)

The Phase I tests consisted of the control--no surfactant applied--and a single application of surfactant by percolation through the sand. The experimental procedure for these tests was as follows.

*Texas Research Institute, Inc., "Underground Movement of Gasoline on Groundwater and Enhanced Recovery by Surfactants," Final Report (September 14, 1979) submitted to the American Petroleum Institute.

1. On Day 1 a nominal 3% gradient of the water table was established, and
2. 75.7 liters (20 gal) of gasoline (unleaded, 87 octane) were "spilled" into each tank at the high end of the water table through the observation well identified in Fig. 1. The gasoline was siphoned from 19 liter (5 gal) cans through a small tube over a 4 hour period.
3. On Day 18, 94.6 liters (25 gal) of surfactant solution (water in the control) were trickled onto the soil surface via the rainmaker grid.
4. On the following two days, Days 19 and 20, 208 liters (55 gal) of water per day were added through the rainmaker to wash any pore-space-entrapped surfactant down to the gasoline contaminated soil above the water table. Equal volumes of water were similarly applied in the control test.
5. On Day 26 a third washdown, not originally scheduled, with 208 liters of water was applied to determine whether any additional surfactant could be removed from the soil. Again, a similar volume of water was percolated through the control soil.
6. All measurements were terminated on Day 30.
7. Core samples of the sand pack in each tank were taken on Day 32 for use in determining residual gasoline contents.

The Phase II tests consisted of multiple (daily) applications of surfactant, without washdown, in one case via the rainmaker to percolate through the contaminated soil, in the other case by direct injection into the water table via an observation well. The experimental procedure for these tests was as follows.

1. The water table gradient, nominal 3%, was established on Day 1, and,
2. 75.7 liters of gasoline were spilled into each tank via the observation well identified in Fig. 1. Again, the gasoline was siphoned from 19 liter (5 gal) cans through a small tube but this time over a 6 hour period.
3. Beginning on Day 17 and continuing through Day 29, 94.6 liters of surfactant solution per day were, in one tank, trickled onto the soil surface via the rainmaker to percolate through the gasoline contaminated soil to the water table, and in the other tank were injected directly into the water table via an observation well.
4. Measurements of gasoline recovery and/or removal were terminated on Day 30.
5. Core samples of the sand pack in each tank were taken on Day 31 for use in determining the residual gasoline contents.

The measurements and analyses described below were performed during each Phase of the experimental program.

1. The volume of raw (liquid) gasoline in the separator (see Fig. 2) was measured twice daily. Samples of the effluent water were collected at the same time for later analysis for dissolved hydrocarbon content. The raw gasoline was analyzed by gas chromatography (GC) to evaluate the percentages of heavy and light fractions. Immediately upon collection of effluent a 20 ml sample was extracted with 2 ml of CS₂ in a separatory funnel; extracts were stored at -10°C and analyzed weekly for dissolved hydrocarbon content.

Analysis was by GC using a 6m FFAP column and a flame ionization detector (2 1 injections; temperature program from 75°C to 200°C at 49°C/min after 2 min initial hold). The CS₂ peak was arbitrarily chosen as the demarcation between light and heavy fractions. The selection of the CS₂ extraction technique vis-a-vis other techniques was predicated on development work at TRI that demonstrated its effectiveness in these applications.

2. Samples of the effluent were collected daily but were frozen for weekly analysis of surfactant content. Analysis involved complexing the anionic Richonate YLA with methylene blue, followed by colorimetric determination (see Appendix C).
3. Gasoline and water levels in the observation wells were determined twice daily using a dipstick. Water level was measured by detecting electrical conductivity; gasoline depth was measured using a wettable surface.
4. CO₂ in the sand pore spaces was monitored on a daily schedule. Samples were drawn from one of the four vapor wells on a rotating basis and passed through a dry ice/ethanol cold trap and a charcoal tube to remove hydrocarbon vapors. Evaluation was by GC using a 2m Porapak Q Column with a reducing catalyst (conversion of CO₂ to CH₄) and a flame ionization detector.
5. CO₂ and O₂ contents in the input water and effluent were determined twice daily. CO₂ was evaluated by ion selective electrode (Orion Model 95-02). O₂ was measured by use of a membrane electrode (Yellow Springs Instruments Model 5331).
6. The pHs of the input and effluent waters were measured daily using a research grade combination pH-electrode.

7. Model aquifer and ambient temperatures were recorded continuously on a 24 channel strip chart recorder.
8. At the end of each phase, a number of core samples from each tank were removed and the residual gasoline was extracted with 1.5 liters of CS_2 . A 5.7 cm (2.25 in.) diam core from the sand surface to the piezometric level was removed. Extraction took place in one gallon glass vessels with intermittent agitation. Quantification of gasoline content was by GC.
9. The porosity, permeability, capillary height, particle size distribution, and surfactant adsorption of the sand used in each phase were determined using the techniques described in Appendix C.

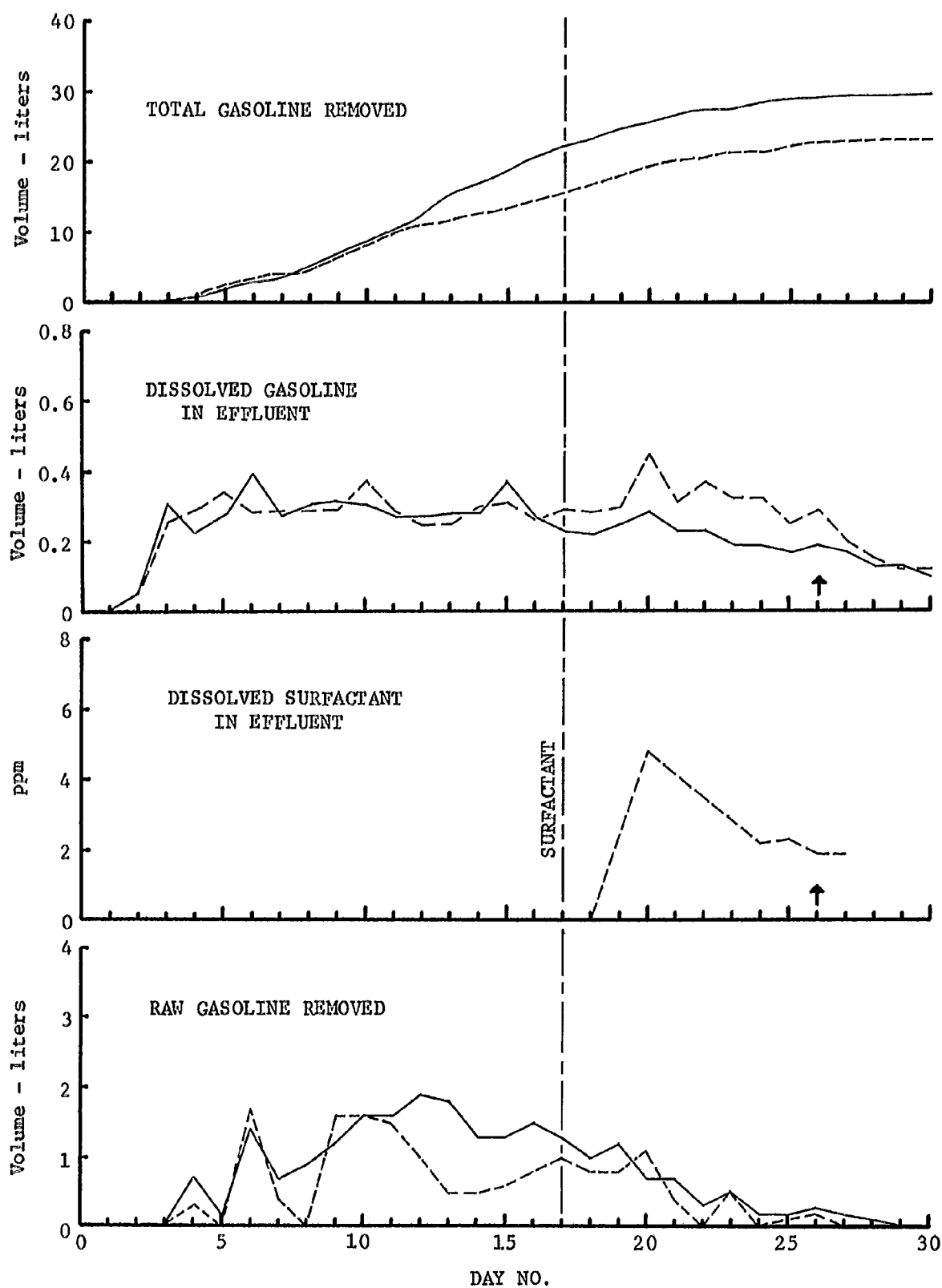
4.0 RESULTS AND DISCUSSION

4.1 Phase 1

Figure 3 displays gasoline recovery and removal during the two tests constituting Phase I of the experimental program: the no-surfactant control and a single application of surfactant followed by sequential washdowns (see Sec. 3.0). Each plot is identified in the figure; the control test data in each plot are shown by the solid curve. The vertical line labelled "surfactant" (Day 18) identifies the day on which surfactant was applied in the surfactant application test and on which water was first applied in the control test.

Daily totals of raw gasoline collected from the separators are displayed in the lower plot; the ordinate is in liters. The total volume of raw gasoline recovered in the control test was 23.4 liters, or 30.9% of the spilled volume. The total volume of raw gasoline recovered in the surfactant application test was 15.3 liters, or 20.2% of that spilled. The difference is presumed to be due to differences in the flow characteristics of the sand packs in the two test tanks.

The application and subsequent percolation of surfactant through the soil/aquifer is represented by the plot second from the bottom in Fig. 3, labeled "Dissolved Surfactant in Effluent;" the ordinate is in ppm (see Appendix C for details of the analysis). The volumes of dissolved gasoline in the daily samples of the effluents are shown in the third plot up, labeled "Dissolved Gasoline in Effluent." Following the application of surfactant and subsequent washdowns, there is a noticeable peak in the data (curve) for this test; also, the amounts of dissolved gasoline are henceforth greater than in the control. The total volumes of dissolved gasoline in the control and in the surfactant tests, respectively, were



DAY NO.

Figure 3

Time Course of Gasoline Removal during Phase I Tests

— Control test (no surfactant)
 --- Surfactant test