

Laboratory and Pilot Field-Scale Testing of Surfactants for Environmental Restoration of Chlorinated Solvent DNAPLs

Author:

Richard E. Jackson
John C. Fountain

Contractor:

INTERA, Inc.
6850 Austin Center Boulevard, Suite 300
Austin, Texas 78753

Contract Number:

DE-AC21-92MC29111

Conference Title:

Opportunity '95 - Environmental Technology Through
Small Business

Conference Location:

Morgantown, West Virginia

Conference Dates:

November 16 - 17, 1994

Conference Sponsor:

U.S. Department of Energy - Morgantown Energy Technology Center

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, 175 Oak Ridge Turnpike, Oak Ridge, TN 37831; prices available at (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

**Laboratory and Pilot Field-Scale Testing of
Surfactants for Environmental Restoration
of Chlorinated Solvent DNAPLs**

CONTRACT INFORMATION

| | |
|----------------------------|---|
| Contract Number | DE-AC21-92MC29111 (In Situ Decontamination of Aquifers for Surfactant Solubilization of DNAPLs) |
| Contractor | INTERA Inc. 6850 Austin Center Boulevard Suite 300 Austin, Texas 78753 |
| Contractor Project Manager | John F. Pickens |
| Principal Investigators | Richard E. Jackson John C. Fountain (SUNY-Buffalo) |
| METC Project Manager | T. Robert McLendon (from 6/94) J.L. Harness (from 9/92 to 6/94) |
| Period of Performance | 9/30/92 - 12/31/94 |
| Schedule and Milestones | |

FY94 Program Schedule

| | O | N | D | J | F | M | A | M | J | J | A | S |
|-------------------------|---|---|---|---|---|---|---|---|---|---|---|---|
| Task 1: NEPA | | | | | | | | | | | | |
| Task 2: Lab Experiments | | | | | | | | | | | | |
| Task 3: Field Testing | | | | | | | | | | | | |
| Task 4: Topical Report | | | | | | | | | | | | |

OBJECTIVES

This project is composed of two phases and has the objective of demonstrating surfactant-enhanced aquifer remediation (SEAR) as a practical remediation technology at DOE sites with ground water contaminated by dense, non-aqueous phase liquids (DNAPLs), in particular, chlorinated solvents. The first phase of this project, *Laboratory and Pilot Field Scale Testing*, which is the subject of the work so far, involves (1) laboratory experiments to examine the solubilization of multiple component DNAPLs, e.g., solvents such as perchloroethylene (PCE) and trichloroethylene (TCE), by dilute surfactant solutions, and (2) a field test to demonstrate SEAR technology on a small scale and in an existing well.

The specific objectives of this first phase were:

1. to identify surfactants or blends of surfactants in the laboratory that will efficiently extract PCE and TCE from a sand aquifer by micellar solubilization;
2. to test the efficacy of the surfactant or surfactant blend(s) to solubilize the DNAPLs, PCE, and TCE *in situ* by injection and then withdrawal of a surfactant solution through an existing well within the sand aquifer at a Government-owned contaminated site.

These specific objectives became tasks in the Phase 1 project as follows:

Task 1.1: Information required for the National Environmental Policy Act (NEPA);

Task 1.2: Laboratory experiments to identify and characterize surfactants and their solubilization activity;

Task 1.3: Single-well, injection-withdrawal test for DNAPL solubilization;

Task 1.4: Phase 1 topical report.

The project is the responsibility of INTERA Inc. of Austin, Texas, which has subcontracted the laboratory screening of surfactants to the State University of New York at Buffalo, where Dr. John Fountain has been conducting research into SEAR since the late 1980s. The original contract signed by METC provided for additional laboratory testing of the preferred surfactants by Sandia National Laboratories. However, DOE Albuquerque did not allow Sandia to be subcontracted by INTERA to undertake such work.

BACKGROUND INFORMATION

Dense, non-aqueous phase liquids or DNAPLs, in particular chlorinated solvents such as TCE, pose an as-yet unresolved ground-water contamination problem at DOE facilities and hazardous waste sites across the nation. Figure 1 shows the migration of DNAPL in a sand and gravel aquifer system and the development of a DNAPL zone, comprising several vertical fingers and horizontal pools. Also shown are two dissolved-phase plumes, one partially due to vapor migration to the water table, the other due solely to DNAPL dissolution beneath the water table. The mobility of DNAPLs in the subsurface, their low aqueous solubility, and the heterogeneity of typical aquifer systems combine to create conditions that inhibit rapid

in situ remediation by traditional pump-and-treat methods. Thus, tens to hundreds of liters of DNAPL may require tens to hundreds of years to be dissolved by ground-water extraction (Johnson and Pankow, 1992).

Such long remediation times mean that short-term remediation target dates will not be met. The hazardous waste clean-up program presently being undertaken by the U.S. Department of Energy is committed to the decontamination of the Weapons Complex facilities in 30 years (i.e., by the year 2019). As Mackay and Cherry (1989) have noted about DNAPLs in general, ". . . very little success has been achieved in even locating the subsurface sources, let alone removing them." Thus, it is essential that methods be developed to permit the rapid location, characterization and remediation of such DNAPL sources if DOE's deadline is to be met.

A particularly attractive approach to the remediation of DNAPL sites involves the use of surfactants to enhance the dissolution of DNAPLs by a process known as solubilization. Surfactant-enhanced aquifer remediation (SEAR) is the name given to this process of *in situ* DNAPL remediation employing micellar surfactant solutions (Jackson, 1993).

The mechanism of solubilization displayed by nonionic and anionic surfactants arises from the formation of micelles by the surfactant in aqueous solutions (Rosen, 1989). Surfactants, or surface-active solutes, have polar and nonpolar groups that exhibit hydrophilic and hydrophobic properties, respectively. At certain characteristic concentrations, surfactants exhibit marked changes in several physical and chemical properties, e.g., electrical conductivity, interfacial tension, and detergency. The concentration of the

surfactant at which these phenomena occur is known as the critical micelle concentration, or CMC. At this concentration, the polar and nonpolar groups become oriented such that they form colloidal clusters of molecules in solution. The clusters are characterized by the interfacing of the hydrophilic groups with the water molecules on the outside of the cluster, while the hydrophobic groups are arranged pointing toward the interior of the cluster.

At the CMC, aqueous solutions of surfactants show a greatly enhanced ability to dissolve compounds that are otherwise sparingly soluble in aqueous solution. The hydrophobic interior of the micelles creates a non-polar environment in the center of the cell which is capable of accommodating non-polar molecules, effectively bringing the contaminants into solution. This process of solubilization has been defined by Rosen (1989) as "the spontaneous dissolving of a substance (solid, liquid, or gas) by reversible interaction with the micelles of a surfactant in activity of the solubilized material." Figure 2 shows a schematic interpretation of solubilization and Figure 3 presents a schematic of a SEAR operation for DNAPL remediation.

It is well known in the petroleum industry that extremely high effective aqueous solubilities for organic compounds can be obtained by lowering the interfacial tensions of oil/surfactant mixtures to values less than 0.1 dynes/cm (Lake, 1989). By this method, it is possible to mobilize and displace petroleum hydrocarbons as an "oil bank." Such mobilization of DNAPLs could, under certain conditions, result in their vertical displacement through permeable windows in sedimentary aquitards and through fractures in rock resulting in deeper contamination. This has

necessitated a different approach for surfactant-enhanced aquifer remediation. This alternative approach seeks to maintain the interfacial tensions above 1 dyne/cm to minimize the possibility vertical and horizontal mobilization while striving for maximum effective solubility. Fountain et al. (1991) demonstrate that dilute (1%) surfactant solutions may have interfacial tensions exceeding 1 dyne/cm with respect to perchloroethylene (PCE) with a solubilization capacity of 1 g PCE / g surfactant.

PROJECT DESCRIPTION

Laboratory Experimentation

The Statement of Work indicated that SUNY-Buffalo would screen surfactants for use in solubilizing multicomponent DNAPLs *in situ* and that Sandia National Laboratories would conduct laboratory tests to explore the process of solubilization with the preferred surfactant. This program of work was only partly achieved because of the regulatory and bureaucratic barriers imposed on our work (see section below). However, a total of 99 surfactants were screened for their ability to solubilize chlorinated solvents (see *Results* section).

Site Selection

The Statement of Work indicated that the field work would be conducted at a Government-owned plant. Early on it was concluded that it would be advantageous to conduct the field test at the Paducah Gaseous Diffusion Plant (PGDP) in Kentucky. This decision to work with Martin Marietta Energy Services, DOE's contractor at PGDP, was endorsed by EM-50.

The first site chosen by PGDP for possible use by INTERA was abandoned in December 1993, after one full year of field testing and test design by PGDP, because it had become obvious that the shallow "aquifer" was not the high permeability sand and gravel PGDP first thought it was. Using this site would have meant running a field test, which would have had to last for several months—not the week or two planned and budgeted for by INTERA.

A second site at PGDP was chosen, the C-400 site, on account of the fact that a particular well at the site (MW-156) had a sufficiently high hydraulic conductivity and had TCE concentrations > 100 mg/L which suggested a nearby TCE DNAPL zone in the Regional Gravel aquifer. The presence of this DNAPL zone had been postulated by PGDP hydrogeologists based on a review of the site by an external expert (Clausen et al., 1992; Keuper, 1991). Thus, as the Statement of Work indicated, an existing well could be employed for the field test.

Regulatory and Bureaucratic Barriers

A number of bureaucratic and regulatory constraints were imposed on INTERA and SUNY prior to the field test which adversely affected their capability to undertake the test in a completely successful manner.

The first of these issues involved the inability of Sandia National Laboratories to sign a subcontract with INTERA to test the effectiveness of the surfactant in the laboratory. The tests at Sandia concerned laboratory-scale and bench-scale solubilization experiments employing single- and multiple-component DNAPLs with the surfactant blend identified by Dr. Fountain at SUNY-Buffalo.

Unfortunately, DOE Albuquerque and METC were unable to reach agreement on the issue of the permissibility of Sandia National Laboratories to be a subcontractor to INTERA for this work (J.Harness, METC, personal communication). DOE Albuquerque denied Sandia permission to subcontract from INTERA and an important experimental component of the project was lost to the project.

The second of these issues involved INTERA's inability to have cores of aquifer materials sent to SUNY-Buffalo for testing with the surfactants deemed suitable for injection into the aquifer. The difficulty in transferring core materials appears to have arisen from the presence of alpha and beta emitters in the aquifer samples (gross alpha = 3-5 pCi/g; gross beta = 6-10 pCi/g). The alpha emitters might include U, Pu, or other actinides, while the beta emitter would likely be ⁹⁹Tc. Lawyers for Martin at Oak Ridge wrote SUNY-Buffalo requesting changes to SUNY's Radioactive Materials License to allow for (1) the presence of tritium in these samples, (2) an extension of the License to include elements with atomic numbers 84 through 98 (i.e., the actinide series, radium etc.), and (3) concentrations of up to 100 mCi for isotopes with atomic numbers 84 to 98. Unfortunately, these changes could not be agreed upon and implemented before the test was undertaken in August 1994.

PGDP assisted in determining the nature of the aquifer materials by submitting a sample to the Oak Ridge National Laboratory for x-ray diffraction analysis. However, while this was a helpful step, it did not substitute for the detailed testing that was to occur at both SUNY and Sandia.

The third issue involved the inability of INTERA to employ the preferred surfactant for the field test due to the denial of its use by the Division of Waste Management of the Environmental Protection Cabinet of the Commonwealth of Kentucky. The Division of Waste Management requested that a surfactant other than the first-choice surfactant be used because of the possibility that it might contain unreacted reagent chemicals which are prohibited in Kentucky ground waters.

RESULTS

Surfactant Screening

The objective of the SUNY program was to screen surfactants in the laboratory and to identify those that will efficiently extract PCE, carbon tetrachloride and TCE from sand aquifers by micellar solubilization, and then to investigate the physical-chemical properties of the best surfactants.

Ninety-nine surfactants (25 nonionics and 74 anionics) were screened for their ability to solubilize TCE, PCE, and carbon tetrachloride (CTET). Ten of these surfactants were able to solubilize TCE to concentrations greater than 15,000 mg/L. Four surfactants were identified as good solubilizers of all three solvents: a sorbitan monooleate (T-MAZ-80), an alkylaryl sulfonate isopropylamine, an alcohol ethoxylate (Tergitol 15-S-12), and a polyoxyethylene oleamide.

Tergitol was the first choice because of its excellent solubilizing ability and its low propensity to sorb. However, as noted above, this secondary alcohol ethoxylate was rejected by the Commonwealth of Kentucky because of the potential presence in the surfactant of

unreacted reagents which are banned for injection into ground waters in Kentucky. This regulatory action was particularly unfortunate in that this surfactant had been demonstrated to perform excellently during the *in situ* solubilization of carbon tetrachloride at the DuPont chlorocarbon facility near Corpus Christi, Texas (Fountain, 1993). Tergitol was replaced with a sorbitan monooleate surfactant (T-MAZ 80K) which had sorbed appreciably during the Corpus Christi test but was chosen on the basis of (1) the expected low clay content of the aquifer, and (2) its FDA-approved status as a food-grade additive with good biodegradation properties and very low toxicity.

Examination of the solubilization, adsorption, and toxicity data suggested that a sorbitan monooleate surfactant would be a good choice for the PGDP field test. It combines excellent solubilization ability with extremely low toxicity. Sorbitan monooleate increases TCE solubility to approximately 16,000 ppm in a 1% surfactant solution from an aqueous solubility of 1,100 ppm (Table 1). The interfacial tension also remains high, that is, above 10 dynes/cm (Table 2). Measurements indicated that the viscosity of 1% and 2% solutions of the surfactant are similar to that of water (Table 3) and thus the solutions should move at approximately the same rate as ground water. Sorbitan monooleate is a better performer than Tergitol 15-S-12 in these respects and is also tolerant of a wide range of water chemistries ranging from brines to fresh water.

Sorbitan monooleate was not initially recommended because its sorption is higher than Tergitol. However, studies of aquifer materials similar to those at PGDP indicated that the sorption remains low on sediments if

clay and organic contents remain low (see Table 4). If the mineralogical characterization data supplied to SUNY and INTERA are representative of the aquifer to be tested and the clay content of the aquifer is indeed below 1%, sorption should be minimal. Also, analysis of sorbitan monooleate is easy since it may be measured directly by UV adsorption. Finally, in view of the objections raised to Tergitol, sorbitan monooleates are food grade additives with low toxicity and high biodegradability.

Pilot Field-Scale Testing at PGDP

The second objective of this first phase of the project was to test, *in situ*, the efficacy of a micellar-surfactant solution to solubilize a TCE DNAPL (with minor amounts of PCE) by injection and then extraction of the surfactant solution through an existing well set within a sand and gravel aquifer at PGDP known as the Regional Gravel Aquifer or RGA.

The field test of the efficacy of sorbitan monooleate in solubilizing TCE DNAPL was conducted in August 1994. The injection phase lasted 96 hours, during which time a 1% surfactant solution was injected at the rate of 1 gpm. The extraction phase lasted 16 days at a rate of 1 gpm. Only one third of the injected surfactant was recovered during the extraction period, and consequently there was no enhancement in the concentrations of TCE recovered from the well. It is believed that the remainder of the surfactant became sorbed to the aquifer materials or underwent precipitation or liquid crystal formation, or some combination of the above. Therefore, the test has demonstrated that sorbitan monooleate is unsuitable for use *in situ* as a solubilizer in this aquifer.

It is particularly unfortunate that regulatory and bureaucratic matters prevented the laboratory testing of sorbitan monooleate with core from the aquifer prior to field testing, because it is probable that this result could have been identified in the laboratory beforehand and an alternative surfactant could have been chosen and tested. Paradoxically, these same results demonstrate that the single-well test is a useful method for the *in situ* testing of surfactants or cosolvents before proceeding to larger-scale field testing or remediation.

In analyzing the results of the field test with UTCHEM, a multiphase, multicomponent simulation model developed at the University of Texas, it became increasingly clear that PGDP's conceptual model of DNAPL migration and distribution at the C-400 site is questionable. This conceptual model, which is based on the work of Keuper (1991) and supported by the numerical simulations of McConnell et al. (1994), has been tested by using UTCHEM and found to be inconsistent with the aqueous TCE concentrations beneath the site. PGDP's conceptual model, which indicated very heavy saturation of the sand and gravel aquifer with DNAPL, played a significant role in choosing the C-400 site for this test and in designing the injection-extraction test conducted in August. INTERA has developed a revised model that is consistent with the aqueous TCE data.

FUTURE WORK

While it has been shown that the micellar surfactant solution did not perform as intended, the single-well test demonstrated its utility for testing surfactants prior to full-scale SEAR. It is probable that the loss of surfactant could have been identified in laboratory tests,

had it been possible to ship core from PGDP to SUNY Buffalo for testing beforehand and had it been possible for Sandia to have conducted its bench-scale tests with sorbitan monooleate.

Therefore we urge that the restrictions placed on the testing of the surfactants with aquifer materials from the RGA be swiftly resolved so that aquifer materials from the RGA can be shipped to SUNY Buffalo and to Sandia National Laboratories. Failing this, it will be necessary to set up a laboratory at PGDP to conduct the necessary tests. The expense of such a solution strongly recommends the resolution of the restrictions.

Recommendation 1: *That DOE seek to resolve the bureaucratic and regulatory restrictions which have limited the ability of INTERA to undertake the work contracted for.*

The understanding of the distribution of DNAPL in the aquifer beneath C-400 at PGDP is limited. This is quite typical of DNAPL sites, because of their complexity. The anticipated program of drilling and coring planned at C-400 for the spring of 1995 should be devised to help test divergent hypotheses of the geometry of the DNAPL zone. The application of NAPL partitioning tracer tests and multiphase, multicomponent simulators permit an integrated approach to the characterization of DNAPL zones.

Recommendation 2: *The program of drilling and aquifer coring planned by PGDP for the Spring of 1995 should be complemented by field and computational studies to develop a better understanding of the geometry of the DNAPL zones in the Regional Gravel Aquifer and the nature of DNAPL migration at PGDP.*

Because of this limited understanding of the DNAPL zone and the loss of the surfactant *in situ*, it would be advisable to repeat this test as an interwell test rather than a single-well test, so that a larger volume of the RGA can be tested for the presence and composition of the DNAPL.

Recommendation 3: *After re-evaluating the appropriate surfactants for use in the RGA at Paducah and installing an additional well at the C-400 site, an interwell DNAPL solubilization test should be undertaken over a distance of at least 30 feet to test the efficacy of DNAPL solubilization by micellar surfactant solutions.*

REFERENCES

- Clausen, J.L., J.W. Douthitt, K.R. Davis, and B.E. Phillips, 1992. Report of the Paducah Gaseous Diffusion Plant, Groundwater Investigation, Phase III. KY/E-150. Martin Marietta Energy Systems Inc., Paducah, KY.
- Fountain, J.C., A. Klimek, M. Beikirch, and T. Middleton, 1991. The use of surfactants for in-situ extraction of organic chemicals from a contaminated aquifer, *J. Hazard. Mater.*, 28: 295-311.
- Fountain, J.C., 1993. Extraction of organic pollutants using enhanced surfactant flushing - Part II. Pilot Scale Field Trial at Corpus Christi, Texas. Project Summary. New York State Center for Hazardous Waste Management, SUNY Buffalo, 9 pp.
- Jackson, R.E., 1993. Surfactant-enhanced remediation of DNAPL zones in granular aquifer systems. *Remediation*, 4(1):77-91.
- Johnson, R.L. and J.F. Pankow, 1992. Dissolution of dense chlorinated solvents into groundwater. 2: Source functions for pools of solvents. *Environmental Science and Technology*, 26(5):896-901.
- Keuper, B.H., 1991. The occurrence of dense, non-aqueous phase liquids in the subsurface at the Paducah Gaseous Diffusion Plant. KY/ER/Sub/0815-1015/91/2. Martin Marietta Energy Systems Inc., Paducah, KY, 26 pp.
- Lake, L., 1989. *Enhanced Oil Recovery*. Prentice Hall, Englewood Cliffs, New Jersey.
- Mackay, D.M. and J.A. Cherry, 1989. Groundwater Contamination: Pump-and-treat Remediation. *Environmental Science and Technology*, 23(6):630-636.
- McConnell, C.L., D. Numbere, E. Wahidiyat, and A. Erkal, 1994. Determining TCE distribution and mobility at the DOE Paducah Gaseous Diffusion Plant without direct tracing. Abstract, NGWA Conference on Petroleum Hydrocarbons and Organic Chemicals, Houston, Texas.
- Rosen, M.J., 1989. *Surfactants and Interfacial Phenomena*. 2nd Edition, John Wiley & Sons, New York.

ACKNOWLEDGEMENT

This study could not have been undertaken without the active collaboration of Martin Marietta Energy Systems. The staff of Martin's Environmental Restoration Division provided substantial and tireless help with permitting, site characterization, waste-water treatment, and field testing.

Table 1. Solubilization Data for Three Sorbitan Monooleate Surfactants

| Surfactant Number* | TCE (ppm) | PCE (ppm) | CTET (ppm) |
|--------------------|-----------|-----------|------------|
| 18 | 16157 | 6023 | 12509 |
| 60 | 16338 | 6734 | 10595 |
| 64 | 15407 | 5161 | |

* Identification numbers of SUNY-Buffalo.

Table 2. Interfacial Tension Measurements Between Two Sorbitan Monooleate Surfactants and TCE, PCE, or CTET

| Surfactant No. and Standards | TCE IFT (dynes/cm) | PCE IFT (dynes/cm) | CTET IFT (dynes/cm) |
|----------------------------------|--------------------|--------------------|---------------------|
| Referenced value with D.I. water | 34.50 | 44.40 | 45.00 |
| Measured value with D.I. water | 27.49 | 44.43 | 43.48 |
| 18 | 11.67 | 11.08 | 11.10 |
| 60 | 11.26 | 10.72 | 10.72 |

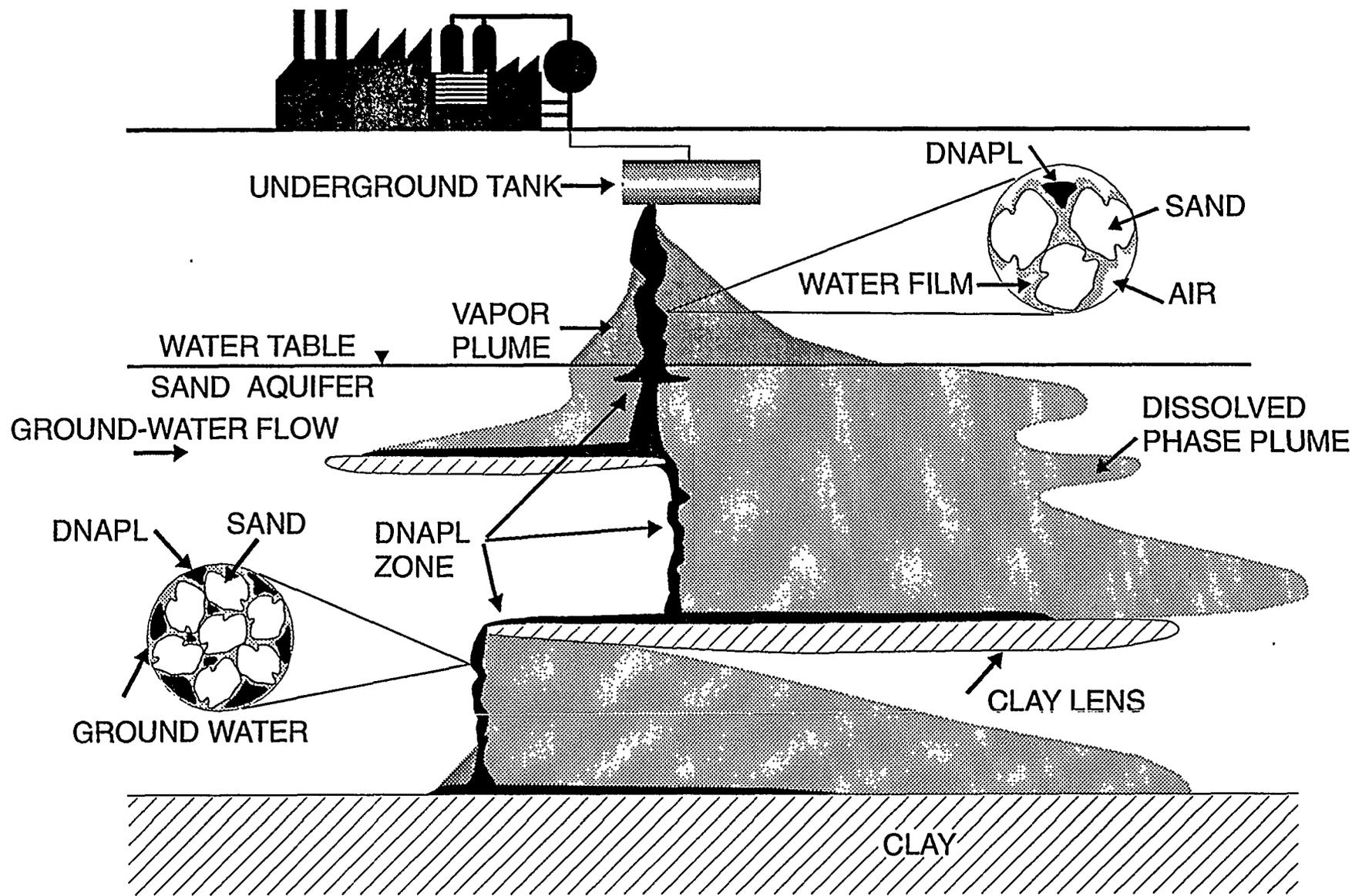
Table 3. Viscosity of Sorbitan Monooleate Surfactant (No. 18)

| Solution | Viscosity (kg/m·s) |
|--------------------|-----------------------|
| Distilled Water | 8.95×10^{-4} |
| 1% Solution No. 18 | 9.38×10^{-4} |
| 2% Solution No. 18 | 1.01×10^{-3} |

Table 4. Retardation Factors for Sorbitan Monooleate Surfactant

| Surfactant Number | Natural soil with 10% smectite ⁽¹⁾ | Na smectite - sand mixtures ⁽¹⁾⁽²⁾ | Ca smectite - sand mixtures ⁽¹⁾⁽²⁾ | 3% illite/ smectite - sand mixture |
|-------------------|---|---|--|------------------------------------|
| 18 | 22.05 | 1% = 1.51 5% = 13.68 10% = 20.70 20% = 19.98 | 1% = 1.48 5% = 5.95 10% = 12.09 20% = 20.80 | |
| 60 | | | | 2.22 |
| 64 | 20.71 | | | |
| 161 | 21.68 | | | |

- (1) From studies other than DOE.
- (2) Percentages indicate fraction of clay in mixture.



-262-

Figure 1: Schematic showing the migration of DNAPL in a granular aquifer system and the development of both a DNAPL zone, comprising several vertical fingers and horizontal lenses, and two dissolved-phase plumes.

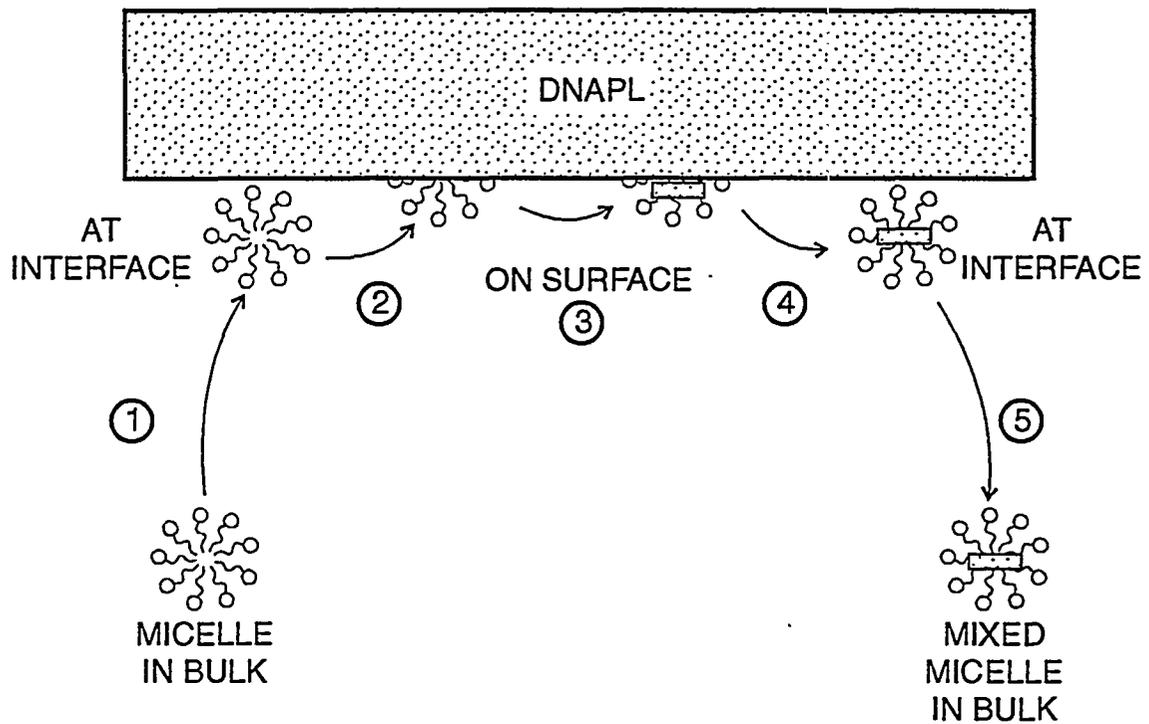


Figure 2: Schematic mechanism for initial solubilization. Mixed micelle desorption and diffusion [steps (4) to (5)] are assumed to control DNAPL solubilization (Modified after Chan, et al., 1976).

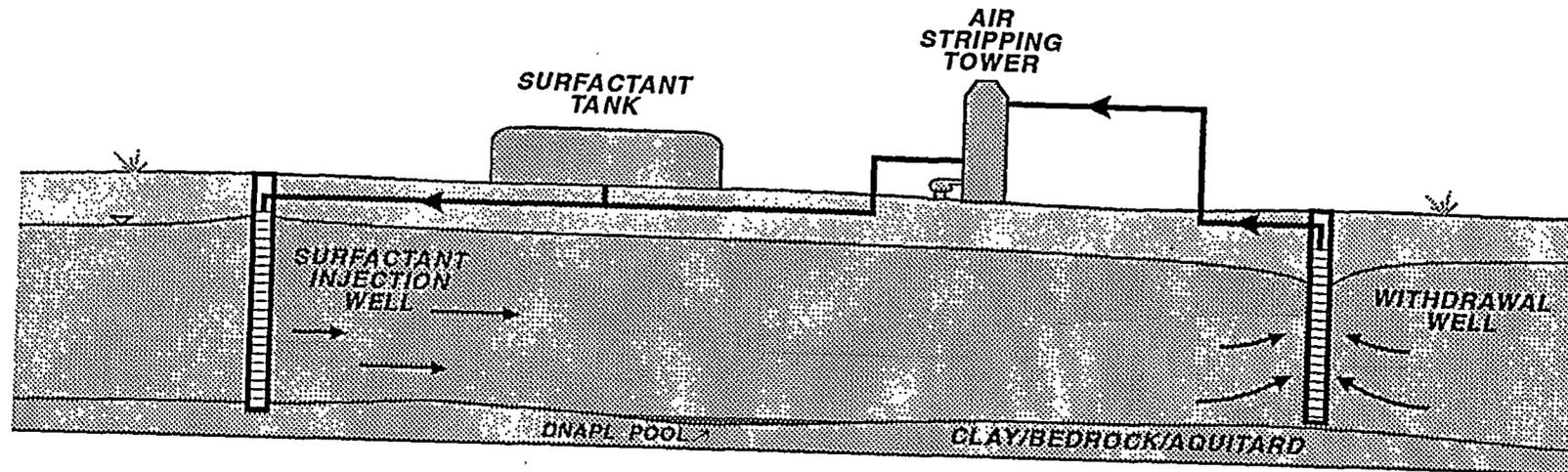


Figure 3: Schematic of a SEAR operation showing a single surfactant injection well and a single withdrawal well. For most operations, multiple injection wells will be necessary.