

Internal Reflection Sensor for the Cone Penetrometer

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ABSTRACT

The objectives of this project are to design, assemble, test, and demonstrate a prototype *Internal Reflection Sensor (IRS)* for the cone penetrometer. The sensor will ultimately be deployed during site characterization with the goal of providing real-time, *in situ* detection of NonAqueous Phase Liquids (NAPLs) in the subsurface. In the first phase of this program, we have designed and assembled an *IRS* module that interfaces directly to a standard cone penetrometer system. Laboratory tests demonstrated that the sensor responds in real-time to a wide variety of "free phase" NAPLs without interference from natural materials such as water and soil of various types or dissolved contaminants. In a preliminary field test, the sensor was able to locate NAPLs at thin, discrete depths in a soil test pit when deployed with a cone penetrometer. Ruggedness of the device was tested with a series of penetrometer pushes to the depth of refusal at a clean location. There was no visible damage to the sensor and its performance did not change in the course of these experiments. Based on the successes of the Phase I program, it is recommended that the project proceed to full-scale demonstration in Phase II.

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INTRODUCTION

The presence of NonAqueous Phase Liquids (NAPLs) at U.S. Department of Energy (DOE) sites is cause for concern because these materials pose a long-term threat to drinking water supplies. By definition, NAPLs are free phase chemicals with low water solubilities, existing in soil and groundwater as undiluted "pools." These chemical pools are major contamination sources that are depleted only very slowly by dissolution into large volumes of water. The result is widespread pollution that can continue for many years if the NAPLs are not located and removed. Locating NAPLs is a challenging task, complicated by the fact that subsurface NAPLs are not stationary. Instead, larger pools can break up into much smaller ones that migrate (mostly through cracks and fissures) to other locations.

NAPLs fall into two categories based on their densities: Dense NAPLs (DNAPLs) are denser than water and sink in an aquifer, Light NAPLs (LNAPLs) are less dense than water and float. The most common DNAPLs are chlorinated hydrocarbon solvents such as trichloroethylene (TCE), tetrachloroethylene (perchloroethylene, PCE), carbon tetrachloride, and chloroform which have been found in many locations such as Savannah River (TCE, PCE), Hanford (carbon tetrachloride), LLNL (TCE), and ORNL (1,1,1-trichloroethane). The most common LNAPLs are fuels such as gasoline, diesel, and heating oils. Fuel contamination is a major problem at numerous DOE sites, most notably LLNL (gasoline), INEL (20,000 gallons of Texas Regal Oil), and Savannah River (diesel fuel).

Because of the significant threat posed by NAPLs, it is important that they be located during site characterization and quickly immobilized or removed. Remote, non-intrusive techniques that "look" into the subsurface for NAPLs would be ideal for this application because intrusion can open up new pathways for NAPL migration. Unfortunately, the non-intrusive approach is technically unfeasible. Instead, devices such as the cone penetrometer, geoprobe, or hydropunch have been developed to probe the subsurface with minimal intrusion. These devices simply push soil aside during deployment, producing a hole about 2 inches in diameter, which can be filled with grout after measurements are performed. This approach disturbs the soil far less than conventional rotary drill boring and produces no waste. Cone penetrometers have received particular attention due to their deeper profiling capabilities. A variety of sensors, most of them geophysical, have been developed for the cone penetrometer but none of them meets DOE's need for NAPL detection. Geophysical techniques such as resistivity and conductivity have been investigated most for NAPL detection, but have been shown to be ambiguous when trying to locate NAPLs. In particular, many natural soil types produce a false indication of contamination. Another limitation of these methods is the need for an uncontaminated soil reference. Usually this means that data must be collected from other onsite locations assumed to be clean and extrapolated to the actual penetration location - a time-consuming and inexact procedure at best.

DOE clearly has a need for a reliable (*better*) NAPL sensor that can be deployed in a cone penetrometer or similar subsurface delivery system for *safer, in situ* characterization. The primary requirements of the sensor are that it detect NAPLs in real time (*faster*) without responding to water, soil, or other natural subsurface constituents. Real-time response capability is essential

because data is collected "on-the-fly" at cone delivery speeds of 2 cm/sec or faster. Sensors that respond slowly or require long measurement times to achieve adequate sensitivity could easily miss a thin NAPL plume. A related issue is spatial resolution - the sensor must also be able to locate NAPLs on the centimeter scale, or less. The ability to distinguish between "free phase" NAPL and dissolved contaminants is also important because regulations governing the two are different. Additional requirements are that the sensor be of compact size and low cost, meeting DOE objectives for more fieldworthy, *cheaper* characterization.

The objective of this project is to design, construct and deploy an *Internal Reflection Sensor (IRS)* for the cone penetrometer that locates DNAPLs and LNAPLs of interest to DOE in real time. The *IRS* will meet the performance requirements outlined above in a relatively inexpensive device small enough to be fully housed in a standard penetrometer cone.

The project is divided into two phases, reaching the preliminary field testing stage in less than 1 year, during the first phase of the project. The second, 6-month phase of the program will be devoted to field demonstration of the technique at a NAPL contaminated DOE site and delivery of a working sensor to DOE personnel.

Specific goals of the Phase I program are to:

1. Design and fabricate a prototype *IRS* for the cone penetrometer.
2. Test the *IRS* in the laboratory and in a cone penetrometer under controlled field conditions.

RESULTS AND DISCUSSION

Task 1. Prototype Design and Fabrication

An *IRS* system compatible with a cone penetrometer has been designed and fabricated. A schematic of the down-hole sensor module is shown in Figure 1 and appended engineering drawings. The outer housing of the module is constructed of hardened steel, and all internal pieces are manufactured of stainless steel. Key sensing elements include a microlaser source, sapphire prism, and photodiode detector. The microlaser is a low power device (<120 mA @ 5V, battery compatible) and the photodiode requires no power for operation. The microlaser beam establishes the sensing area at 10 mm², which provides for high spatial resolution when the sensor performs measurements in the subsurface. Only four electrical conductors (two for laser power and two for detector signal) are needed for the device. Each optical element is preassembled into a mount that can then be securely inserted, yet be easily removed from the housing if replacement is necessary. The removable mount also contains a 0.25 inch diameter channel through which a standard cone penetrometer cable can pass (not shown in the figure, see discussion below).

Once the mounted optical elements are assembled and aligned in the housing, all components are fixed rigidly in place with a combination of locking screws and epoxy. There is no requirement for moving parts in the system, which renders it an extremely rugged and stable device. End caps, one of which is equipped with a strain relief assembly for the electrical cable, provide protection from dirt, water, etc. A hollow tube connects the two end caps and runs through the removable laser/detector unit, providing a pass-through channel for the cone penetrometer electrical cable. The overall diameter of the 13-inch long down-hole sensor module is 1.75 in, a standard cone penetrometer rod diameter. For preliminary field testing, both ends of the housing were threaded for compatibility with Applied Research Associates' cone penetrometer rods.

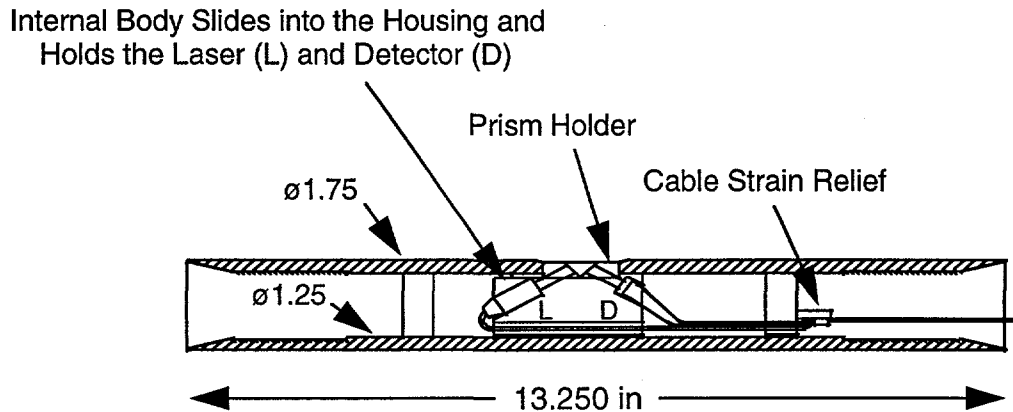


Figure 1. Schematic representation of the down-hole *IRS* module.

For stand-alone laboratory testing, the sensor module was interfaced to a portable computer data acquisition system. Although the *IRS* signals are large enough that electrical noise should not

become a problem even at the greatest measurement depths (150-200 ft), we decided to employ a new down-hole, 8-channel analog-to-digital (A/D) system developed for DOE by UTD, Incorporated (Newington, VA) for data acquisition. The UTD system is uniquely configured to fit inside a cone penetrometer rod and performs both signal amplification and A/D conversion down-hole. This approach has the advantage of minimizing noise and loss of signal in deep pushes. The A/D system was connected through a small (6in x 6in x 2in), up-hole power box to the serial port of a laptop computer. The software available from UTD was rudimentary; therefore, we wrote our own routines for data acquisition, display, and storage. The A/D system worked well in all subsequent experiments and was used to collect the data in Task 2.

Task 2. Prototype Testing

The prototype, stand-alone *IRS* system was tested in our laboratory to validate its performance for NAPL characterization. To evaluate any potential interference from naturally occurring materials, a series of soil and water samples was tested first. Water samples ranged from clean distilled water to murky stream and pond waters. Soils included organic rich topsoil, sand, and several uncontaminated clays obtained from the Savannah River Site (SRS), where it is proposed to conduct the field evaluation as discussed later in this report. The clays were collected from depths where NAPL contamination has been found and therefore represent a likely background matrix for NAPL detection at SRS. The soils were tested both wet (saturated with water) and dry.

The tests were performed by placing each material firmly in contact with the sensing prism face. Any response was measured as a decrease in laser light internally reflected by the prism; hence, a decrease in the voltage measured from the photodiode detector. Table 1 summarizes the results of the background tests, which clearly validate that the system does not respond to naturally occurring materials found in the subsurface under the test conditions. For the soils, response was unaffected by moisture content - only the dry soil results are included in the table. Neither dense clays nor loose, gravelly materials posed an interference to the sensor. Because the prism is made of sapphire, none of the materials scratched or damaged the face.

Next, the response of the system was characterized with a series of 23 "pure" test samples selected to cover a wide range of refractive indices (n_D). Many of the samples were chosen in part due to their lower volatility, which ensured that they remained as a thin layer on the sensing surface while the measurement was being made. Figure 2 is a plot of percent reflectivity vs. refractive index for the test compounds included in Table 2. As expected, the internal reflectance decreases with increasing refractive index. All of the compounds, with the exception of acetone, gave strong, easily measured responses. Although the instrument can be configured to respond strongly to acetone, some natural waters have a comparable refractive index (1.36) and would produce a false positive response. We have chosen to configure the device conservatively, so that only materials of refractive index about 1.38 and higher produce strong responses. However, this refractive index cutoff is sufficiently low such that virtually all the common NAPLs will produce a response. The most likely NAPLs to be encountered at DOE sites are chlorinated solvents and hydrocarbon fuels, which have relatively high refractive indexes as listed in Tables 2 and 3, and will produce strong responses.

Table 1. Water and Soil Background Test Results.

Sample	Starting mV	Final mV	Δ mV	% Reflectivity
Distilled Water	203	202	1	99.5
Tap Water	204	204	0	100
Stream Water	204	204	0	100
Pond Water	206	205	1	99.5
Topsoil Outside EIC	206	204	2	99.0
Saudi Arabian Sand	204	204	0	100
SRS Gray/Brown Clay	205	204	1	99.5
SRS Red Clay	205	204	1	99.5

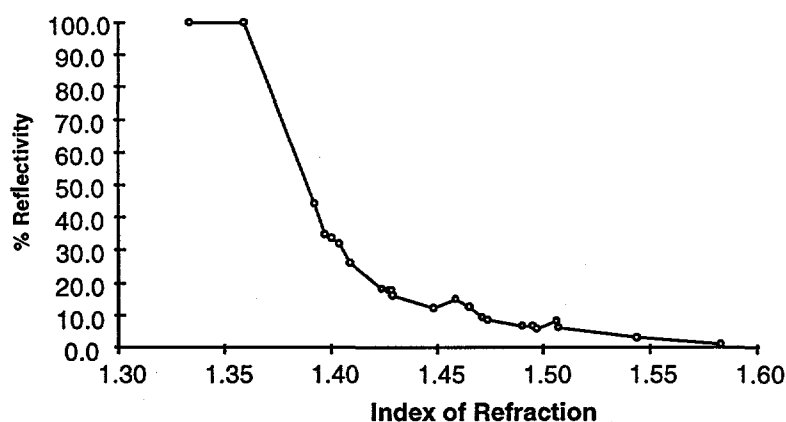


Figure 2. *IRS* response to various NAPLs before preliminary field testing.

In a third series of experiments, NAPLs were spiked into soil and water and the responses of the mixtures were measured with the *IRS* system. The water samples were prepared by adding an excess of each NAPL to tap water in a closed vial to produce the maximum aqueous concentration possible. The vial was shaken and allowed to equilibrate for several hours (to ensure saturation of the water layer) before a sample was pipetted from the water layer and placed on the *IRS* sensing face for measurement. Soil samples were prepared by adding 1 mL of NAPL to 2 g of a topsoil collected from outside our research facility, either dry or wet, in a vial and mixing with a spatula. In some cases, it was difficult to prepare a homogeneous sample with the wet soils due to the immiscibility of the NAPLs with water.

Table 2. "Pure" NAPL Test Results.

NAPL	n_D	Starting mV	Final mV	ΔmV	% Reflectivity
Tap Water	1.333	311	311	0	100
Acetone	1.359	311	311	0	100
Isooctane	1.392	310	138	172	44.5
1-Butanol	1.397	310	108	202	34.8
Amyl Acetate	1.400	310	105	205	33.9
3-Methyl-1-Butanol	1.404	310	100	210	32.3
Decane	1.409	310	81	229	26.1
Cyclohexane	1.424	311	57	254	18.3
N,N-Dimethylformamide	1.427	311	55	256	17.7
Dimethyl Adipate	1.428	310	55	255	17.7
Ethylene Glycol	1.429	309	50	259	16.2
Cyclohexanone	1.448	311	38	273	12.2
Carbon Tetrachloride	1.459	310	47	263	15.2
α -Pinene	1.465	310	39	271	12.6
Limonene	1.471	309	29	280	9.4
Glycerol	1.474	311	27	284	8.7
Dibutylphthalate	1.490	310	21	289	6.8
ASE30 Motor Oil	1.495	310	21	289	6.8
Toluene	1.497	310	19	291	6.1
Tetrachloroethylene	1.506	310	26	284	8.4
Pyridine	1.507	310	20	290	6.5
Benzaldehyde	1.544	310	10	300	3.2
Aniline	1.583	309	4	305	1.3

The results for the saturated water samples are presented in Table 3. Clearly, the NAPLs do not produce an appreciable *IRS* response when dissolved at maximum concentration in water. This is not surprising as the solubilities of the NAPLs are less than 1% in water and therefore change the refractive index of water by less than 0.01 units. The *IRS* has been configured so that a refractive index shift of this magnitude from water goes undetected. This provides the necessary discrimination between "free phase" NAPLs and dissolved contaminants.

Table 3. Test Results for NAPLs Dissolved at Maximum Concentration in Water.

NAPL	n_D	Starting mV	Final mV	ΔmV	% Reflectivity
Trichloroethylene	1.476	210	209	1	99.5
Tetrachloroethylene	1.506	210	209	1	99.5
Toluene	1.497	211	211	0	100
Gasoline	-----	210	209	1	99.5
10W-40 Motor Oil	1.495	209	206	3	98.5

The spiked soil sample results are summarized in Table 4. The overriding trend in the data is that the response increased (% reflectivity decreased) as the refractive index of the test compound increased. This is the same trend as for the "pure" NAPLs and confirms that the sensor was responding only to the NAPL. The wet and dry soil results were comparable; the wet soil gave a slightly lower response in nearly all cases. This is presumably due to part of the sensing region being occupied by water, rather than NAPL. The largest difference was for 1-butanol. We found it especially difficult to determine if the butanol was mixed uniformly with the wet soil. The variance is accentuated by the fact that 1-butanol falls on the steep portion of the % reflectivity vs. refractive index curve (see Figure 2). Trichloroethylene, one of the most prevalent NAPLs at DOE facilities, gave a strong response in soil.

Table 4. Test Results for NAPLs Mixed With Dry and Wet Soils.

Sample	n_D	Starting mV	Final mV	ΔmV	% Reflectivity
Acetone in Dry Soil	1.359	204	201	3	98.5
Acetone in Wet Soil	1.359	204	200	4	98.0
1-Butanol in Dry Soil	1.397	203	68	135	33.5
1-Butanol in Wet Soil	1.397	203	110	93	54.2
Gasoline in Dry Soil	-----	204	29	175	14.2
Gasoline in Wet Soil	-----	204	40	166	19.4
Trichloroethylene in Dry Soil	1.476	205	18	187	8.8
Trichloroethylene in Wet Soil	1.476	206	20	186	9.7
ASE30 Motor Oil in Dry Soil	1.495	203	9	194	4.4
ASE30 Motor Oil in Wet Soil	1.495	207	14	193	6.8
Aniline in Dry Soil	1.583	203	1	202	0.5
Aniline in Wet Soil	1.583	204	2	202	1.0

Task 3. Preliminary Field Tests

Field testing of the *IRS* was conducted the week of June 8, 1997 in collaboration with Applied Research Associates at their New England Division Headquarters in South Royalton, Vermont. The two major objectives of the preliminary tests were to: (1) test *IRS* durability during a real penetration and (2) evaluate the system's ability to detect and locate NAPLs in a controlled test pit. Detection entails responding to NAPLs contacting the face of the internal reflection element. A measured response indicates only the presence of NAPL and does not identify the contaminant. Location of NAPLs refers to establishing the vertical extent of contamination by following sensor response as a function of depth. As with all optical techniques deployed in a cone penetrometer, there is no provision for providing measurements at any appreciable lateral distance from the cone.

The test pit experiments were conducted first using ARA's cone penetrometer "skid" rig. The skid consisted of a cone penetrometer mounted on a trailer with lead weights added for ballast. A portable data system was set up in the back of a pickup truck parked nearby and was connected to the rig through an electrical cable. In order to maximize the depth of each push for the *IRS* within the constraints of a 55-gallon drum (about 3 ft deep), a short uninstrumented cone tip was configured ahead of the *IRS* for these tests. This resulted in the sensing element being 12 inches behind the cone tip. The four-conductor *IRS* cable was connected to the cone penetrometer data system cable, which had been pre-strung through the penetrometer rods. The data system supplied +4dcV to power the laser and 10X amplification of the detector signal. It also provided real-time readout and display of both depth and *IRS* response during each push.

The test pit consisted of a cemented hole in the ground slightly larger than the 55-gallon drum "sample." A forklift was used to place the drum in the pit and position the skid over the drum. Figure 3 shows the test sample prepared by Applied Research Associates. First, clean sand was placed in the drum to a depth of about 15 in. Then a black plastic bag containing some of the same sand wetted with weathered motor oil was placed in the drum. The oil sample was about 3-4 in thick and covered most of the cross-sectional area of the drum. Approximately 5 in of clean sand was then used to cover the sample. A second, smaller and thinner (about 1 in thick) sample of tetrachloroethylene (perchloroethylene) saturated sand in a plastic bag was placed in the center of the drum and covered with 1-2 in of a different, local sandy loam soil. A final sample of gasoline in the sandy loam (not contained in a plastic bag) was placed in the drum as a small, 1 in thick patch centered in the drum (see Figure 3). The remainder of the drum was filled with moist sandy loam.

Three pushes were made into the drum. The first, slightly off-center push hooked the edge of the tetrachloroethylene bag and dragged a portion of the sample down the hole. This smeared the contamination and produced a real, but invalid response over a depth of about a foot. The other two pushes went "cleanly" through the samples, providing accurate profiles of the contamination. The results are presented in Figure 4.

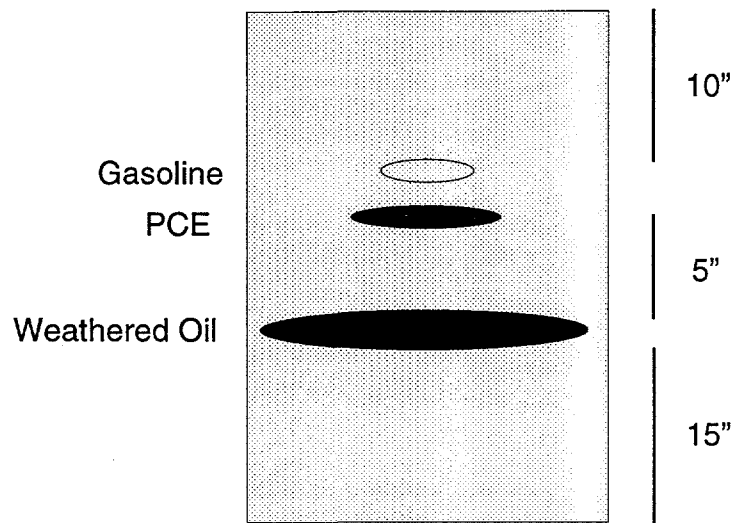


Figure 3. Cross-sectional view of NAPL test samples prepared in a 55-gallon drum.

The first of the two valid pushes (Push #2) was directed toward one edge of the drum. Therefore, it missed the two top contaminant layers, encountering just the lower weathered oil layer. The trace in Figure 4 indicates a strong *IRS* response to the weathered oil, beginning immediately at the depth at which the top of the material was buried (about 18 in = 32 in measured - 12 in tip-to-sensor distance - 2 in "offset" at top of hole). Note that the response persists about twice as long as expected based on the thickness of the sample placed in the drum. We attribute this to the loose packing of the freshly prepared soil sample. Loose packing may have allowed some of the contaminated sand to migrate with the cone tip and also provided less effective cleaning of the sensing surface than the more tightly packed soils of the real subsurface. Considering that motor oil is viscous and difficult to clean from glass surfaces, the results are excellent. Note also that the *IRS* gave no response to soils of different types or water contents, confirming again that the sensor does not respond falsely to natural subsurface constituents.

The second of the two valid pushes (Push #3) was positioned very close to the center of the drum. Therefore, the sensor encountered all three contaminants. Even at a much faster push rate (note the lower point density compared to the previous trace) approaching that normally used in the field, all three contaminants were easily detected. The gasoline and tetrachloroethylene layers were fully resolved from one another with only an inch or two of soil separating them. Although the layers of these contaminants were thinner, it is still evident that the response to those materials did not persist to the same extent as for the oil. This can be attributed to the lower viscosity of these compounds, allowing them to be more easily cleaned from the sensing surface during a push. It is also notable that the profile for the oil layer was the same as that observed in the previous push, demonstrating the reproducibility and reliability of the technique for locating NAPLs.

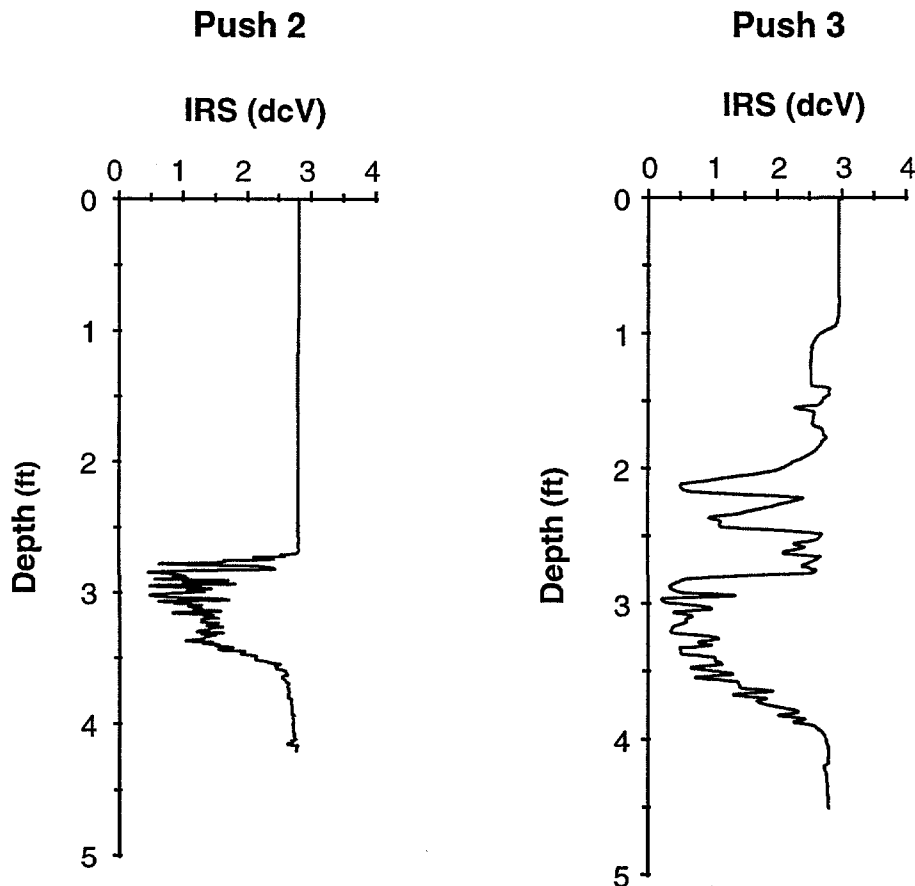


Figure 4. Cone penetrometer *IRS* results for the NAPL test pit sample.

As a test of sensor ruggedness, four pushes were conducted at a farm site near the Applied Research Associates facility. The penetrometer skid rig was towed to the site with a tractor and setup as for the test pit experiments. However, the cone tip was replaced with a fully instrumented cone for these tests. The longer, instrumented cone placed the *IRS* sensing element 33 inches from the tip. Standard cone parameters and *IRS* response were monitored in real-time during the pushes. The first push reached refusal at only 19 ft; however, we were able to eclipse thirty feet in each of the other three pushes for a total deployment of over 100 ft.

The results of the four pushes are presented in Figure 5. As expected, no *IRS* responses were measured at this clean site. The down-hole module performed well throughout the tests, with no equipment failure even at points of high resistance and "hard" refusal. At these positions, some minor baseline shifts were observed. These may be due in part to temperature changes as frictional forces vary. We have measured the temperature coefficient of the sensor to be approximately $1\text{mV}/^\circ\text{C}$ in the range $20\text{-}40^\circ\text{C}$. This temperature effect is clearly shown in Figure 5 for the first push, where the sensor baseline drifted upward as it went from the hot sun (where it had been for almost an hour) into the cool ground. Unfortunately, the cone penetrometer was not equipped with a temperature sensor to confirm this hypothesis. It is important to note, however, that the

magnitude of these effects is small when compared to the magnitude of the sensor response to NAPLs.

Upon completion of the preliminary field tests, we repeated the laboratory tests with the 23 NAPLs of varying refractive index. The results shown in Figure 6 are the same as those obtained prior to the field tests (see Figure 2). This demonstrated that there was no degradation in performance of the sensor as a result of the field testing. There was also no physical damage to the sensor that we could observe. The sensing prism face was unblemished.

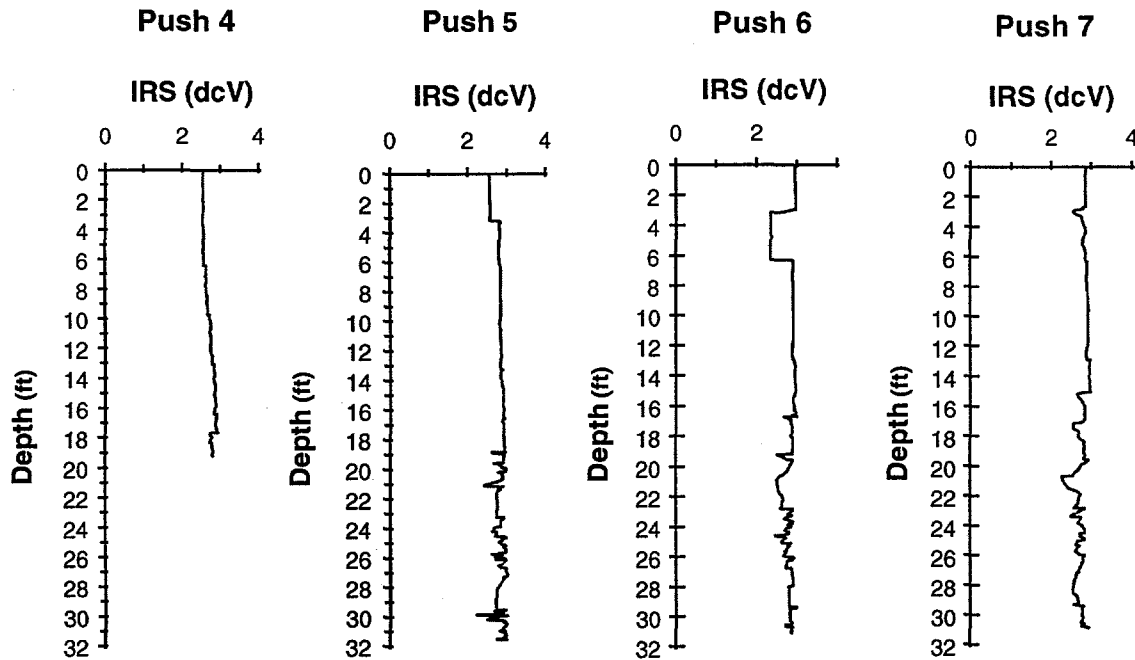


Figure 5. IRS response during cone penetrometer deployment.

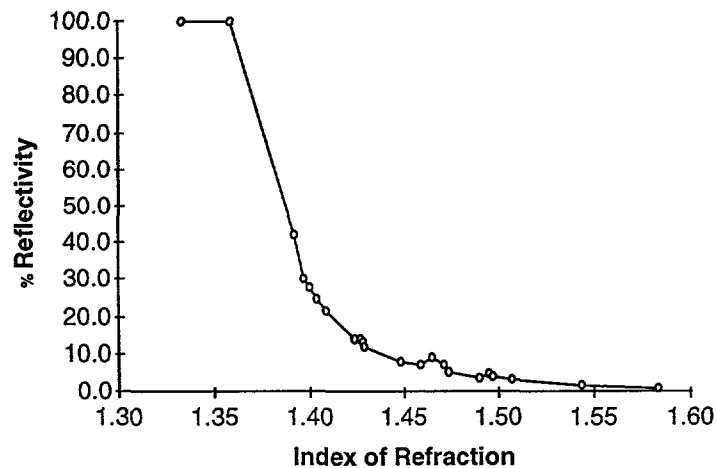


Figure 6. IRS response to NAPLs after preliminary field testing.

CONCLUSION

Each of the Phase I program objectives has been successfully met. We have assembled and tested a prototype *IRS* instrument compatible with operation in a standard cone penetrometer. The device performs measurements with high spatial resolution (10 mm²) in real-time. Extensive laboratory testing has shown that the sensor responds strongly to a wide range of NAPLs of concern to DOE without interference from natural subsurface materials comprising soil and groundwater. The device also differentiates "free phase" NAPLs from dissolved contaminants, even when the contaminants are present at their maximum solubility limit.

In a blind field test we were able to locate NAPLs at discrete depths in real-time during a cone penetrometer push into a soil test pit. The sensor was also integrated into a fully instrumented cone penetrometer and multiple pushes were performed to the depth of refusal. The sensor withstood this preliminary deployment well, demonstrating no change in performance from before the test.

Based on the successful results of the Phase I base program, we recommend that the optional Field Testing (Task 4, Phase II) phase of this program proceed as planned. It is recommended that the field testing take place at SRS where NAPLs are known to be present and a cone penetrometer truck is stationed for this type of testing. Prior to the final field test at SRS, we will be redesigning the probe to make it more fieldworthy (waterproof, etc.) Site contacts there (Mr. Joe Rossabi, Ms. Carol Eddy-Dilek) are interested in testing the technology. A preliminary Field Operations Plan for testing at SRS has been submitted separately from this report.