Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy

Volume 16 Article 2

2011

Development of a Mobile Laboratory System for Site Characterization and Analysis of Subsurface Oil Contaminants

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Cover Page Footnote

The authors would like to recognize the fundamental contributions made by the research assistant of the team, Ms. Lincy Abraham and Mr. Anselm Pereira, the groups technician. We are indebted to their diligent and unremitting efforts. Also, we wish to express the deepest appreciation to the Kuwait Foundation for the Advancement of Sciences (KFAS) for the financial support of the project. In addition, the team would like to thank Kuwait Oil Company (KOC) for their support to implement the field-testing of the system at the company's sites.

PART I: Fate and Transport

Chapter 1

DEVELOPMENT OF A MOBILE LABORATORY SYSTEM FOR SITE CHARACTERIZATION AND ANALYSIS OF SUBSURFACE OIL CONTAMINANTS

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ABSTRACT

A mobile laboratory incorporating the techniques of laser-induced fluorescence (LIF) and cone penetration test (CPT) has been successfully developed and field-tested by members of Kuwait Institute for Scientific Research (KISR).

The LIF/CPT system consists of a custom designed stainless steel probe assembly incorporating a bundle of fiber optics with low absorption in the ultraviolet range. A pulsed 266nm laser source is coupled into one of the optical fibers and is utilized for exciting fluorescence in soil targets. The excitation laser pulse carried through the fiber optics interacts with the soil through a sapphire window placed on the probe head; the emitted fluorescence is collected and channeled back to a detection system through a separate fiber. The probe is capable of reaching a potential maximum depth of 50m. Among the detection systems that have been used for the system were a single and a multi-channel array photomultiplier tube based systems. The entire lab facility is installed inside a CPT 20-ton vehicle.

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The mobile laboratory is referred to as the Environmental Unit for Measuring Subsurface Oil Contaminants (EUMSOC), and it has undergone an extensive series of field tests at different sites in the oil-contaminated areas of north Kuwait.

Keywords: Laser induced fluorescence (LIF), soil, pollution, screening method.

1. INTRODUCTION

In the aftermath of the 1990-1 Gulf War, the environmental status of Kuwait was left in a state of severe damage. Principally, this devastation was due to the destruction of over 700 oil wells by the retreating invading Iraqi military forces. Almost 20 years after the end of the war, signs of the petroleum based environmental damage is seen in many parts of the Kuwaiti deserts. It is estimated that an equivalent of 10% of the country's area (about 18,000 km^2) remain under various states of contamination.

A massive series of cleanup operations became imperative to rectify this environmental calamity. Such an endeavor would require measuring types and levels of pollution in the environment and the extent of the damage. Such processes involve the collection of field samples and subsequently subjecting them to a series of lab measurements involving a variety of chemical extractions based on established procedures (e.g.; FTIR, GC/MS, GC/FID).

Given the massive spread of the contamination and the vast scope of the cleanup operations, such methods would pose a prolonged series of time-consuming processes. The need to develop a fast screening; semi-quantitative procedure that may provide in-situ pollutant profiles instantaneously became vital. Such a method should entail an acceptable level of correlation with established traditional lab methods in offering a viable semi-quantitative / qualitative results.

The method of choice that was chosen for this effort is based on prior work conducted at KISR over an extended period that dates back to the early 1980's, and it involves the technique of Laser Induced Fluorescence (LIF). The method involves the measurement and analysis of the optical emission from molecules that have been excited to higher energy levels by the absorption of electromagnetic radiation. The source of this excitation is a monochromatic UV laser source. In conjunction with the stand-alone LIF measurements, it was found that such measurements could be improved upon by augmenting them with diffuse reflectance (DR) measurements from a standard light source (a high pressure xenon lamp).

Over several years, KISRs previous efforts in the LIF field were documented in numerous project reports, as well as several publications. Detailed comprehensive descriptions of the lab-based LIF system developed by the team at KISR appeared in: (Qabazard et al., 2002), and (Quinn et al., 2002). What follows in this article is a description of the extension of the lab-based assembly and work, which has culminated in the development of a mobile laboratory capable of performing the same types of LIF measurements in-situ, hence providing timely results in the field (KISR, 2008).

2. MATERIALS AND PROCEDURE

2.1 Mobile System Requirements and Development

Leading to the actual construction of the mobile laboratory facility, several steps were taken in order to test the concept. This procedure took the shape of packaging the existing lab-based LIF facility in a sports utility vehicle. With the aid of a custom made probe head and segment; experimental pushes were attempted utilizing the weight of the vehicle to drive down the probe to acquire LIF measurements at subsurface depths. While this procedure failed to drive the probe to any appreciable depths, yet the concept was clearly demonstrated and the decision was made to proceed with the full-scale development of a dedicated mobile system that relied on cone-penetrometer techniques (CPT).

The mobile LIF laboratory system design called for the following main components:

- An optical assembly, incorporating a pulsed Nd/YAG Laser with second and fourth harmonic generating crystals, harmonic separation module, a bundle of fiber optical cables, and fluorescence / diffuse reflectance (DR) detection systems.
- LIF subsurface probe with optics incorporated to direct the excitation light to the soil target through a sapphire window.
- 20-ton truck, equipped with a hydraulic mechanism capable of achieving a force of 200kN.

2.1.1 Optical Assembly

The choice to extend the functionality of the LIF system from the lab to the field entailed the same requirements that were needed in terms of optics and the involved excitation sources. While the lab based system enclosed of two laser sources: a 266 nm and a 366 nm sources (both Nd:YAG laser sources based on the Minilite series from Continuum, Inc.), for the mobile system the choice was made to rely exclusively on the 266nm source, operating at 10Hz to deliver ~1mJ pulses. Furthermore, while a streak camera was used in the laboratory system as a detector, for the mobile field laboratory two photomultiplier tube (PMT) sub-systems are utilized: The first detector consists of a custom-built single channel photomultiplier system for profiling both total integrated fluorescence (300nm to 600nm) and diffuses reflectance (532nm). The second detector is comprised of a 32-channel PMT array (made by Hamamatsu: Model H7260-04) photomultiplier detector for measuring fluorescence spectra at the range spanning: 300 to 600nm. Signals measured by this detector first pass through a polychromator for spectral differentiation (Shamrock 163i, made by Andor Technology). For DR measurements, and rather than only relying on a xenon lamp as a light source, a special setup of optical wedge prism and dichroic mirrors, along with physical blocking apertures are used to separate the second harmonic component of the 266nm laser, equivalent to 532nm. This portion of the pulse is used for DR, and it is delivered ahead of the 266nm pulse by approximately 20ns.

A special bundle of fiber optical cable was utilized to deliver the excitation laser source and to receive the resultant collected fluorescence emissions. The fiber bundle, which was designed by the team and manufactured by Fiberguide Industries Ltd., is comprised of four 600µm quartz fibers each with a numerical aperture of 0.22. The 25 meter long bundle is ruggedized with a jacket made of interlocking PVC-covered segments. One fiber is used to channel the 266nm excitation laser pulse to the target. A second fiber is used to channel the 532nm laser pulse for DR measurements purposes. Each one of the remaining two fibers is used for the collection of the emitted responses for LIF and DR measurements, respectively.

2.1.2 The LIF Probe

The conical probe head was designed by the team and fabricated by a specialized precision workshop. The main probe head is 200mm in height and 36mm in diameter. The probe head functions as a conduit for the various pulses from the fiber bundle to the spot of soil under examination behind a synthetic sapphire crystal window, and vise versa for the emissions that are channeled to the detection systems by the fiber bundle. This action would require a 90° diversion in the paths of excitation / emissions from the orientation of the fiber bundle, and this is achieved by an optically coated aluminum finger reflector, situated in front of the sapphire window which is located on the flush surface of the probe. The choice for the sapphire window stems mainly from its extreme hardness (exceeding grade 9 on the Mohs scale), making it extremely rugged and scratch proof in repeated field usage.

The probe head is threaded on its top other end; an arrangement that facilitates the attachment of the conical probe head to the probe segments. Each one of these hollow segments is 1-meter in length, and the fiber bundle is threaded into each one from the head to the labs optical assembly.

2.1.3 The Vehicle and the Laboratory Compartment

The mobile laboratory utilizes its own weight to drive the probe to subsurface levels. To that end, requirements called for a truck equipped with self-lifting jacks mechanism equipped with a hydraulic pushing device based on cone penetration test (CPT). Once lifted on its own jacks, the truck's CPT press directed the equivalent of 200kN pressure to the LIF/CPT probe and its attached segments through the ground. Operators inside the lab compartment attach the probe segments to one another manually, incrementally adding each one as the need arises to push the probe deeper.

The laboratory's floor plan called for a compartment that is about 4.2 by 1.5 meters. Furthermore, the compartment required a special lift mechanism arrangement to hoist heavy masses (<200kg) such as equipment from the ground up to the labs entrance. The compartment facilitates the three main types of activities encompassed by the relevant nature of the fieldwork activities: the optics (both operating the laser source and the various detectors), the CPT activities and feeding the probe segments. Among the other necessities called for in the design of the compartment was the need to provide measures for environmental control. This was a vital requirement given the often harsh local weather conditions; and not only did it provide for a comfortable working environment for the operators inside the lab, but it also guaranteed a temperature range for the proper operation of the laser sources and optical detectors.

Geomil Equipment, B.V. of the Netherlands, was selected to build the laboratory compartment according to the required specifications. The company also supplied the laboratory's 20-ton MAN truck. Upon its completion the mobile lab became designated as the Environmental Unit for Measuring Subsurface Oil Contaminants (EUMSOC).

2.2 Case Study: Field-Testing the EUMSOC

2.2.1 Analytical Methods

In order to correlate LIF measurements with established laboratory methods, a series of control spiked soil sample were prepared. Various batches of spikes were prepared using a variety of fuels, but mostly concentrating on spikes made with crude oil. The spiking process involves the selection of a representative soil sample from the field, generally from the vicinity of the area under examination. The specimen was chosen to epitomize the type of soil in the area under

Figure 1. The mobile LIF/CPT lab developed at KISR and identified as the Environmental Unit for Measuring Subsurface Oil Contaminants (EUMSOC). In this view the vehicle is raised on the self-lifting jacks, and the lowered LIF probe is seen in between the vehicle's front-rear wheel and the front lifting jack.

Figure 2. View inside of EUMSOC showing the laboratory's main components. From the right: the optical bench incorporating the laser source, detectors and optics. The CPT control, output displays and the main press mechanism are at the center. On the left is the carriage-holder of the probe segments.

observation in terms of the particle size distribution and the amount of background hydrocarbon residue. As such, the representative soil is examined to ascertain the low amount of extractable material within it, as well as establishing particle sand-silt-clay distribution. The physical characteristics of subsurface samples obtained from the test boreholes in that area were equally tested and compared to the representative test soil.

The spikes were then tested both with the LIF process as well as subjected to an extraction laboratory method (e.g., EPA 418.1). Results from the two outcomes are compared and the linearity between the two methods is examined. The LIF results are further refined by applying diffuse reflectance (DR) measurement corrections to account for the variation in the absorbed emissions due to the change in the tested samples opacity with increased levels of contamination. An outline of a typical spiking procedure and the obtained results appeared in (Quinn et al., 2004). For classification purposes, results from the multi-channel detectors are subjected to a series of high-level statistical methods, namely utilizing principal component and discriminant component analysis. The framework of this method in our deployment of LIF measurements appeared in (Alemeddine et al., 2004).

2.2.2 Choice of a Test Location

The laboratory was field-tested at an area in northern Kuwait known as Um Al-Aish. In particular, the spot that was chosen for the field test involved the massive remains of an oil lake that is approximately 0.5km^2 in area, centered at the geographical location: 29° 48.89’ N, 47° 48.02’E. The spot resembles a natural basin in comparison with the adjacent terrain, for the general elevation at the location of interest drops to approximately 30m above sea level, down from a maximum of about 70m in the surrounding location. The aim of the tests centered on the ability of EUMSOCs two detectors: namely the single channel and the 32-channel PMT detectors in identifying traces of pollution at various subsurface levels, and how the results from the two detectors compare to one another.

A series of test boreholes surrounding that location helped to establish the nature of the subsurface soil strata, along with the expected levels of contamination. The area is located inside the compounds of Kuwait Oil Company; it is closed to the public with minimal subsurface infrastructure installations, hence facilitating the subsurface test pushes of the LIF probe.

3. RESULTS AND ANALYSIS

3.1.1 The Nature of Soil at the Test Sites

In comparison with the range of spiking levels applied uniformly for the batches of spiked soil samples (ranging from 250-20,000 ppm) used in the calibration procedures, the amount of total extractable material within the representative test soil selected for the various spiking batches turned out to be low (>56ppm, petroleum hydrocarbons constituted about 70% of that amount). The test soil turned out to be very sandy; it resembled soils extracted at different depths from the test borehole at the site.

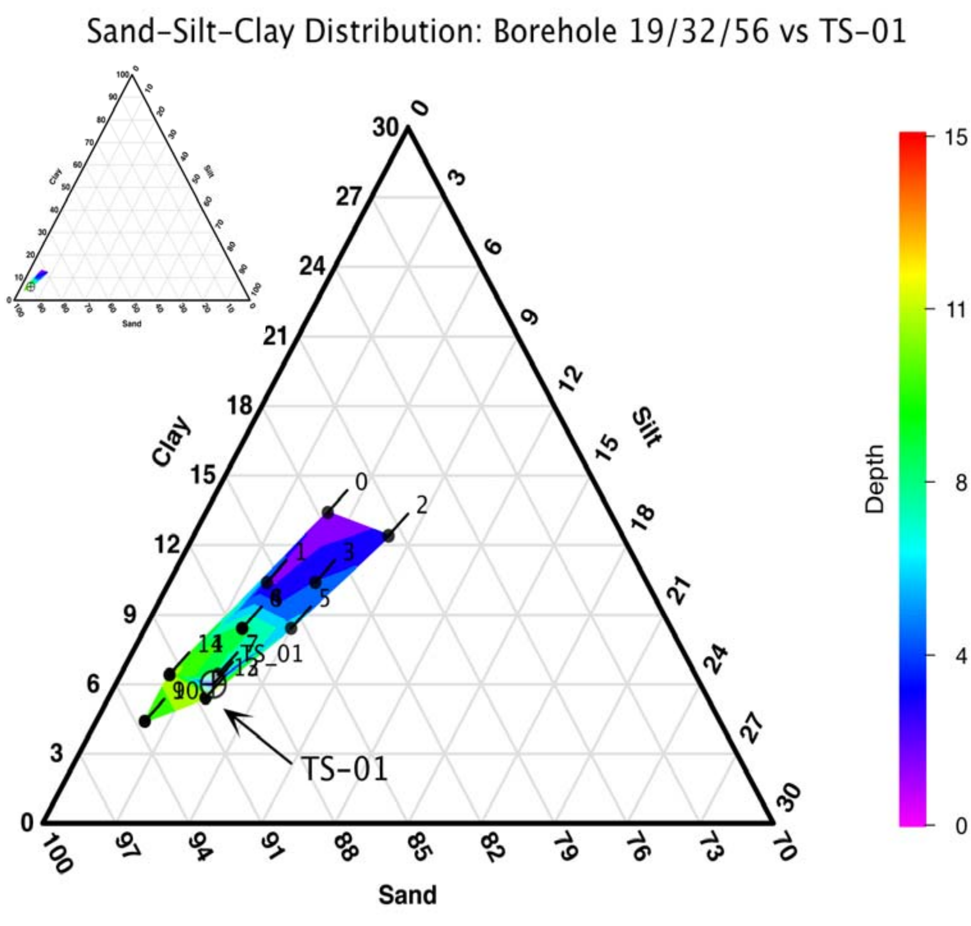

Figure 3. A ternary plot demonstrating a typical sand-silt-clay particle distribution for soil samples obtained from various depths at the site of test borehole: 19/32/56 vs. the test soil (TS-01) used in the various spiking procedures. The inset graph shows the plot in its entirety, with the portion in

the lower left enlarged to show detail. The borehole results verify an increase in the sandy nature of the soil with depth.

3.1.2 Corroborating the LIF Results with Established Techniques

When the batches of laboratory prepared spiked soil samples were tested, the results of the tests (based on the EPA 418.1 method) proved to offer a reasonable linear response when compared with both the single-channel and the multi-channel detectors.

Both the physical nature of the soil used in the spiking procedure, as well as the level of correlation between lab-based and the LIF results led to conclude that EUMSOC could be utilized for field screening purposes. This conclusion stems from the original assumption that LIF measurements conducted on batches of laboratory prepared crude oil-spike soils would constructively correlate with field-based LIF results.

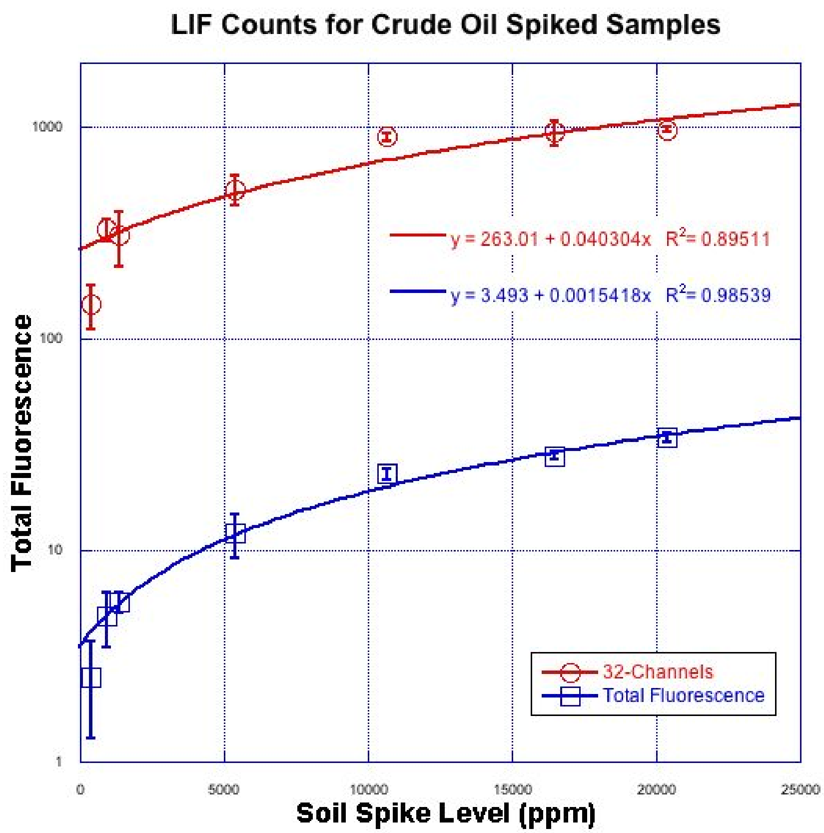

Figure 4. Linearity fits demonstrating high levels of correlation between spiking levels (in part-per-million as verified by EPA 418.1 method) versus the total fluorescence (single channel) and 32-channel LIF detectors used at EUMSOC.

3.2 Probe Tests at Various Depths

The facility was extensively field tested at the oil lake employing the two detectors on board. Tests were conducted over a variety of different terrains, from areas where the topsoil was virtually loose sand, to areas where the ground was covered by a layer of hardened thick dry oil. In general EUMSOC proved to be

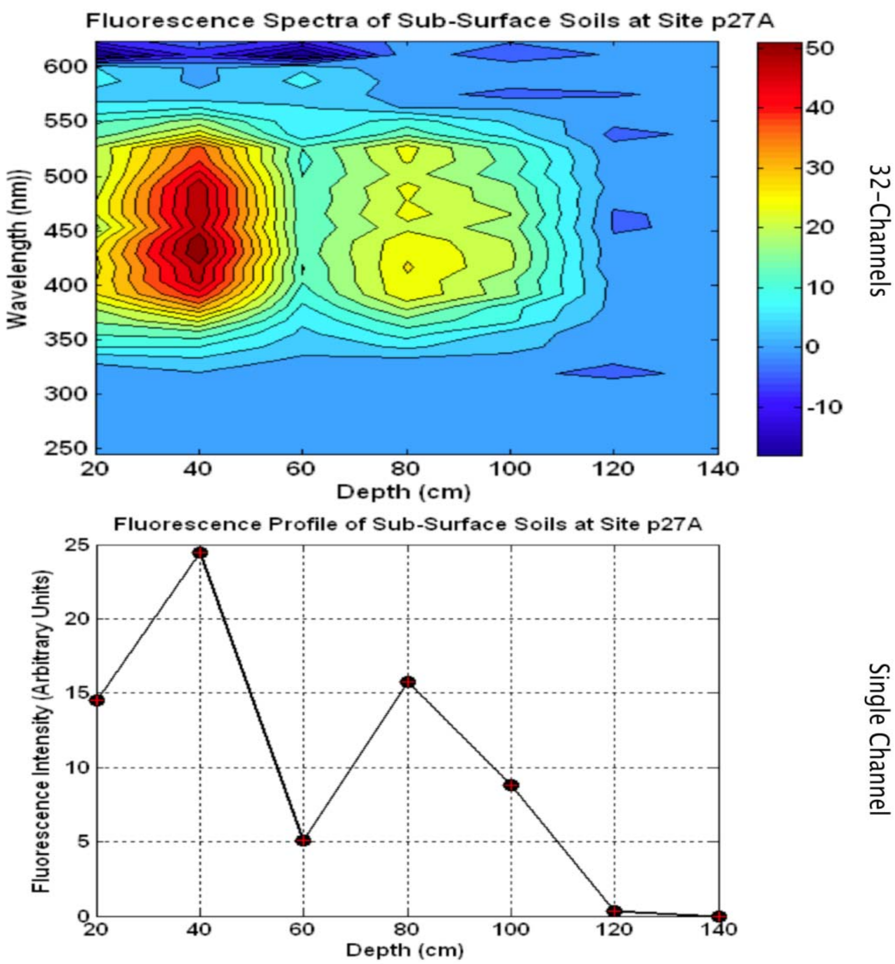

Figure 5. Comparison between the results obtained with the 32-Ch. and single channel PMT detectors at the same test point. The top portion showcases the wavelength vs. depth “fingerprint” obtained with the multi-channel detector. Both results demonstrate that for that particular location there is an increase in responses at a depth of 40-cm, which is followed by a decline in fluorescence at 60-cm. Another, though lower increase is observed at a depth of 80-cm.

both adaptable and highly mobilized. In certain instances, it was required to drive the probe for a test at a confined point. With a combination of hand gestures by members of the team observing from the front and the sides, the driver of the lab managed to precisely position the truck with a minimal amount of effort and time. Once a point is chosen for a subsurface series of measurements, a test – or “dummy” – probe is pushed before using the LIF probe. This practice is employed to guarantee that the actual probe will not be encounter a layer of hardened sand, subjecting it to an aggregated amount of pressure that might damage it. After the push process is completed, the geographic location of each test point was recorded with the aid of a DGPS. The terrain is observed and distinguishing features are noted and recorded. Any holes left from the push were grouted in a separate procedure.

Results from the two detectors generally agreed with one another, with the multi-channel detector yielding an extended insight into the tested spot when the results are combined with the depth to form a “fingerprint” for the range extending from the surface to the furthest point the probe was driven into. In several instances, such fingerprinting provided a perception on the mechanism with which petroleum hydrocarbon based pollutants infiltrated soil layers.

4. CONCLUSIONS

The mobile LIF/CPT laboratory (EUMSOC) was successfully developed and proved to be effective in the fast screening for pollutants in surface and subsurface layers of soil in various areas around Kuwait. It further confirmed the successful demonstration of contaminant classification with the aid of spectral measurement and advanced statistical methods This fast method to screen for the extent of contamination will offer an invaluable service to current and future cleanup operations in the country.

There are other systems built on the concept of LIF/CPT techniques. Chief among such systems is the US Department of Defense Tri-Services “Site Characterization and Analysis Penetrometer System” (SCAPS). The primary difference between these two systems is EUMSOCs implementation of DR corrections. Augmenting LIF results with DR measurements aid with the accuracy of the quantification of contaminant levels.

The lab functionality required supporting data about the nature of the soils being examined, as well as the availability of a database of pre-measured LIF calibration sets of various contaminant sources.

Among the considerations for further system optimization include the augmentation of a full CPT probe head attachment with dedicated strain gauge sensors. Furthermore, the addition of an optical aid to provide visual feed back to offer a real-time observation of the spot under examination. Such additions will aid in the categorization of soil types and site characteristics with less dependence on extra lab based tests of samples obtained by independent physical collection.

5. ACKNOWLEDGMENTS

The authors would like to recognize the fundamental contributions made by the research assistant of the team, Ms. Lincy Abraham and Mr. Anselm Pereira, the groups technician. We are indebted to their diligent and unremitting efforts. Also, we wish to express the deepest appreciation to the Kuwait Foundation for the Advancement of Sciences (KFAS) for the financial support of the project. In addition, the team would like to thank Kuwait Oil Company (KOC) for their support to implement the field-testing of the system at the company's sites.

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