2003 NASA/ASEE SUMMER FACULTY FELLOWSHIP PROGRAM

JOHN F. KENNEDY SPACE CENTER
UNIVERSITY OF CENTRAL FLORIDA

LEARNING NEW TECHNIQUES FOR REMEDIATION OF CONTAMINATED SITES

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ABSTRACT

The project emphasizes NASA's Missions of understanding and protecting our home planet as well as of inspiring the next generation of explorers. The project fellow worked as part of a team on the development of new emulsion-based technologies for the removal of contaminants from soil, sediment, and groundwater media with the scientists in charge of the emulsion-based technologies. Hands-on chemistry formulation and analyses using a GC/MS, as well as field sampling was done. The fellow was fully immersed in lab and fieldwork, as well as, training sessions to qualify her to do the required work. The principal outcome of the project is the motivation to create collaboration links between major research university (UCF) and an emerging research university (UT).

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1. INTRODUCTION

The Strategic Plan proposed by NASA in 2003 establishes three missions with its respective goals and objectives. The first and third missions are related with this project. The first mission in the plan is to understand and protect our home planet. One of the goals to reach that mission is to create a more secure world and improve the quality of life by investing in technologies and collaborating with other agencies, industry, and the academia. At the same time an objective to reach the goal is to eliminate environmental incidents, toxic chemical use, hazardous waste, and environmental liability at all NASA sites.

The third NASA mission is to inspire the next generations of explorers. The education component might be considered if our younger generations are to be motivated to pursue careers in science and technology. Education was added as a new NASA Enterprise in 2002 with the goal of inspire more students to pursue the study of science and engineering (Strategic Plan, 2003). One of it objectives is to improve higher education capacity to provide for NASA's and the Nations future science and technology workforce requirements. Students and educators will be able to work with NASA and university scientists to use real data to study the Earth, explore Mars, and conduct other scientific investigations. The Education enterprise will permeate and be embedded within all Agency activities.

This summer project involved the two missions. First it covered research related to the development and use of new technologies for the removal of contaminants to soil, sediment, and groundwater. The new emulsified-palladized-iron (EPI) technology is in an experimental phase. Emphasis had been put in hands-on chemistry formulation and analyses using GC-MS, as well as field sampling. In terms of the third mission it models collaboration between a research university and an emerging research university, Universidad del Turabo (UT). In accordance with NASA's missions this project has as main goals to:

- Understand science solutions to environmental problems
- Immerse science students at the fellow institution, graduate and undergraduate, in different research projects related to the environment
- Attract students to pursue careers in Science
- Work at the fellow institution to achieve and sustain national competitiveness in determined areas of science and/or engineering.

Universidad del Turabo is a private, non - profit institution in Puerto Rico with more than 10,000 regular Hispanic students. The Institution offers Baccalaureate degrees in Biology, Chemistry and Environmental Chemistry with 500 regular students. UT also offers a Masters degree in Environmental Science and recently submitted a proposal for a Ph D degree in Environmental Science to the Council of Higher Education in Puerto Rico. Students admitted to the Program will be involved in research related to: Innovative Clean-up Technologies, Environmental Chemical Analyses, Environmental Biology Analyses, and Environmental Management.

Over the last 6 years, UT has been building a research infrastructure in Science. The School has been working towards the establishment of Biology, Chemistry, Materials, and Environmental Science research niches. The creation of a masters' degree in environmental science was the first step. The next step is to build and improve the institution's research infrastructure. Collaborations and partnerships between agencies, industry, and well-known research institutions have been encouraged.

NASA and University of Central Florida (Geiger et al, 2001) have been working in the development of new emulsified technologies for environmental clean up of TCE, VOC, and PCBs. The fellow was interested in learning and understanding the techniques with the goal of motivating graduate students in UT to apply those remediation techniques in contaminated sites in Puerto Rico. Introducing students to these new methodologies will enhance their research capabilities. Also this is a way of developing new research and determining how successful can be the emulsion-based technologies to treat different kind of soils. Also graduate students will obtain clean up data that will be valuable to treat different polluted sites in Puerto Rico. At the moment the Emulsified Zero Valent Iron (EZVI) had been used at Launch Complex 34 (LC34) mostly in sandy soil.

2. DESCRIPTION OF PREVIOUS WORK

Trichloroethylene (TCE), Volatile Organic Compounds (VOC), and Polychlorinated biphenyls (PCBs) are among toxic compounds that have high persistence in the body and the environment. Most have been proven to be carcinogenic, teratogenic, or mutagenic. Removal of these man-made pollutants is a significant problem. Once the heavy metals have been introduced to a body of water, they are extremely difficult to remove. When they mix with sediment in the bottom of a river, lake, or ocean it becomes even more difficult to remove them from the contaminated site. PCBs high toxicity results from their resistance to degradation and their propensity to bioaccumulation in living organisms. Numerous treatment technologies have been considered for soils and contaminated groundwater remediation.

Incineration is the recommended technology for destruction of PCBs. Incineration requires up to 1200°C achieving 99.999% destruction and removal efficiency necessary for discharging products into the air (De Filippis, P. et al, 1999). However this is an expensive process, unpopular with the public because of the potential for emissions of dioxins and other products of incomplete combustion. This technology is limited to pure PCBs mixtures.

Other technologies are emerging. Biological and chemical treatments are in experimental phases. The biological treatment requires conditions to be controlled over a four weeks or longer period and in some cases this is still ineffective. Chemical treatments such as Base-catalyzed decomposition - hydrogen transfer agents and catalysts improve the base-catalyzed decomposition of PCBs (Kawahara & Michalakos, 1997). It had been applied *ex situ.*

TCE degradation is increased by deliberately treat iron with chloride ions (Gotpagar J, 1999). Chloride ions are responsible for the crevice corrosion observed. Gotpagar hypothesized that increasing that kind of corrosion; TCE degradation rates should increase too. He found that TCE degradation is most prominent in the reaction at early times. At later times, the effect of chloride pre-treatment provides little improvement.

In situ techniques would be much simpler to implement and more cost effective than many of the techniques in use today. A methodology for groundwater *in situ* remediation is the use of permeable iron barriers. These have become a popular choice as a passive, cost-effective *in situ* remediation. Economic considerations and the concern about effective long-term disposal are contributing to a shift towards methods that specifically enhanced biodegradation or abiotic transformation (Ruiz et al, 2000). In biotic environments, microorganisms attach to metal surfaces and change the surface chemistry via biofilm formation. Such metals present a unique opportunity to provide passive *in situ* treatment to degrade chlorinated organics. Iron provides an opportunity to degrade chlorinated organics under reducing conditions, rather than simply transfer them to the subsurface to another medium. Loss of reactivity over time, due to corrosion products on the iron surface is a great concern. As a result of their study, Ruiz et al concluded that acid washed iron presents more reactive surface, with a high first-order rate constant in TCE disappearance.

Treatment of the source of contamination in the subsurface is essential to lowering the overall cost and time required for complete remediation of affected aquifers. Emulsified zero-valent iron (EZVI) has been shown to be a useful technique in the *in situ* remediation of Dense Non-Aqueous Phase Liquids (DNAPL) such as TCE. EZVI is composed of surfactant, biodegradable oil, water and zero-valent iron particles (either nano or micro-scale iron), which form emulsion particles that contain the iron particles in water surrounded by an oil-liquid membrane. It has been demonstrated in laboratory experiments conducted at UCF that DNAPL compounds diffuse through the oil membrane of the emulsion particle and undergo reductive dechlorination facilitated by the zero-valent iron particles in the interior aqueous phase.

3. NEW EMULSIFIED TECHNOLOGIES

A field-scale technology demonstration of the use of EZVI to degrade TCE DNAPL was conducted in the summer of 2002 at the LC34 Site at Cape Canaveral Air Force Station, FL. DNAPL, consisting primarily of TCE, is present in the subsurface at the Site as a result of historical releases from operations at the Site. The technology demonstration involved the injection of EZVI, an emulsion containing nano-scale zero-valent iron, vegetable oil and surfactant. Significant reductions in TCE concentrations were observed at all soil boring locations with the exception of two locations where the EZVI migrated up from the injection interval. For those two locations the observations suggested that most if not all of the EZVI migrated up above the target treatment depth. There was a significant reduction in the concentrations of TCE in groundwater samples following treatment with EZVI. The significant reduction in concentrations of TCE in samples following treatment demonstrates that a significant change has occurred in the treatment zone. It is believed that the reduction in dissolved phase concentrations is due to the destruction/degradation of residual and pooled TCE DNAPL by the EZVI. EZVI is a very promising technique for removal of DNAPL in subsurface environments. Soil coring from the LC 34 demonstration confirmed that where EZVI reached, the soil was cleaned.

In Puerto Rico as in all parts of the world exists contamination of soil, water, and air. USEPA has identified eleven superfund sites. Among the sampled chemicals and other contaminants found in them are TCE, VOC, and PCBs. Vega Alta Public Supply Wells Site is an example of groundwater and soil contamination with TCE and VOC. After different studies it was found that groundwater poses an unacceptable carcinogenic risk to human health for the ingestion and inhalation routes of exposure for sites residents and workers. Two long-term remedial phases were designed and approved by USEPA. Soil Vapor Extraction System was selected as the remedial alternative for the cleanup of the contaminated soil to avoid further migration of contaminants to the groundwater. To treat groundwater they constructed a Source Area Wells System. *In situ* treatment like injecting the EZVI to the soil could be tried as a cleanup alternative in this case. EZVI is cost effective, takes less time to decontaminate, and no residue goes to the air.

The Island-town of Vieques is part of the Commonwealth of Puerto Rico. It is located about seven miles southeast of the main island of Puerto Rico. The United States Navy owns approximately one-third of the island and conducts military training exercises that, until recently, included live bombing. The Agency for Toxic Substances and Disease Registry (ATSDR), USEPA, Puerto Rico Department of Health

(PRDOH), USGS and a Navy contractor conducted sampling studies of the different wells at Vieques from 1995 to 2000. No action has been taken at the moment. Vieques represent another possibility to use the EZVI injection *in situ* remediation.

4. EXPERIMENTAL METHODS

During this summer the team (colleague, two fellows and two students) have been experimenting with a matrix for emulsion formulation for PCBs cleanup. First the emulsions were prepared using the designated formulation. The emulsion was prepared in the following way: first iron and d-water were mixed together in a blender. Oil, d-limonene and surfactant were mixed together in a beaker and added slowly to the aqueous mixture in the blender during two minutes. After two days volume of d-limonene and/or oil that crashed out of the emulsion was measured using a graduate cylinder to see what emulsion configuration was the most stable. Then the top layer was decanted off and the emulsions were re-emulsified in the blenders. Later studies and comparison with lab results at UCF suggested that iron had to be acid washed.

Figure 1: MATRIX FOR EMULSION FORMULATION EXPERIMENTS

Formulation designation (ml-ml-g-g)w/o d-limonene (ml-ml-ml-g-g) w/ d-limonene	d-limonene as % of oil mass	Oil in g (ml)	d-limonene g(ml)	Water (ml)	Metal (g)	Surfactant-Spam 85(g)
80-100-20-3	0	73.44(80)	0	100	20	3
64-17.5-100-20-3	20	58.75(64)	14.69 (17.5)	100	20	3
60-100-20-3	0	55.08(60)	0	100	20	3
48-13-100-20-3	20	44 (47.9)	11 (13)	100	20	3
16-70-100-20-3	80	14.69 (16)	58.75 (69.9)	100	20	3
12-35-100-20-3	80	11 (12)	44 (52)	100	20	3
48-35-100-20-3	40	44 (47.9)	29.4 (35)	100	20	3
32-52.4-100-20-3	60	29.4 (32)	44 (52.4)	100	20	3
56-26-100-20-3	30	51.4 (56)	22 (26.2)	100	20	3
42.4-19.6-100-20-3	30	38.6 (42.4)	16.5 (19.6)	100	20	3
24-61.2-100-20-3	70	22 (24)	51.4 (61.2)	100	20	3
18-46-100-20-3	70	16.5 (18)	38.6 (46)	100	20	3
40.3-43.7-100-20-3	50	36.7 (40.3)	36.7 (43.7)	100	20	3
30-32.7-100-20-3	50	27.5 (30)	27.5 (32.7)	100	20	3

The emulsion matrix was prepared in the glove box using bimetal (Pd/Fe). A total of 80 ml of PCB was added and six vials were prepared. After three days, biphenyl extraction in two samples was done. For the extraction a Dismembrator and EPA SW 846 Method 3550 was followed. The aqueous layer was decanted off and the remaining Methylene chloride and nanoiron were passed through a column of granular anhydrous sodium sulfate. The dried Methylene chloride extract was exchanged into hexane prior to Florisil cleanup and reduced it volume using EPA SW 846 Method 3620 reduced version for cleanup of PCBs and organochlorine pesticides. After reduction to a volume of 5 ml, the mix was ready GC/MS analysis. The final emulsion has not been found yet. Replications of the experiment, during the summer are taking place and will keep until the right emulsion is found. Changing the percent of palladized iron had been one way of experiment with the emulsion. Also new studies using magnesium instead of iron had begun.

5. RESULTS AND DISCUSSION

The experimental results for the emulsion at the moment are not final. The main focus during this summer was on attaining a stable emulsion containing both d-limonene and oil. Stability of the emulsion was achieved with the percent of d-limonene being about twenty percent by mass. Readings from the GC/MS reveal that the production of biphenyl is rather low and that the production is not mass dependent. The importance of Pd on iron for best results is evident. It seems that for a fixed total PCB concentration, the rate of the reaction depends on the amount of Pd/Fe used. For about 40ppm of PCBs, only 1ppm of biphenyl is recovered through the extraction process (16ppm is expected), regardless of the amount of iron or emulsion that is being extracted. Stability and transport are limitations to be considered in the experimental phase. The transport limitation is caused by the inability of PCBs to dissolve fast enough in the water. PCBs may be getting trapped in the oil layer and not transferred over to the water and bimetal layer where dechlorination takes place. Presently, the use of methanol is being tested to see if the solubility of the PCBs can be increased. New experiments with magnesium are being tried.

Soil coring from the LC34 demonstration confirmed that where EZVI reached, the soil was cleaned of TCE. Demonstrations of the EZVI should be replicated at other sites. Puerto Rico has contaminated sites with urgent needs of remediation. The EZVI represents an alternative. For NASA-KSC this implies assessment of the technology. Finding a funding source for field demonstration in Puerto Rico is an expected outcome.

6. EDUCATIONAL OPPORTUNITY

Academic institutions of higher education play a vital role in conducting research that contributes to our knowledge base in all disciplines, and in educating students who go on to careers in fields of science, technology, engineering and mathematics. A way of building and improving research infrastructure in academic institutions of higher education is by encouraging science and/or engineering faculty in general to compete and participate in fellowships and internships programs so they learn new technologies that could be demonstrated and teach to their undergraduate and graduate students. Hands on activities, learning by doing, are invaluable.

Faculty participation in this program contributes to build the research infrastructure of the faculty Institution by bringing students the tools and motivation necessary to be involved in research. This involvement will represent an increase of minority, graduate and undergraduate students participating in the national pool of scientists. Once the student learns and understands new research technologies the next step is to obtain data that could be use as a research basis to solve environmental problems.

Compromise with the education enterprise is outstanding. Networking between colleagues and faculty is strongly supported. The fellow participation is a form of encouraging the establishment of collaborations between recognized research universities, the agency, and emerging research universities: minority and non-minority. These collaborations will help in achieve and sustain national competitiveness in determined areas of science or engineering research.

For future selection of participating faculty it is suggested to invite science or engineering fellows from minority institutions along with a scientist from primarily researching universities. In doing so more students will be touched. The science fellow from the minority institution, especially those who attend freshmen and sophomore population, is in charge of maintaining the student motivation to keep in the science/math/ engineering fields. If this person has the knowledge about what is new, she/he will teach with a different view and conceptualization.

Funding fellow participation through other agencies, not NASA, have a positive impact in the Fellowship Program. This year few fellows were supported by other agencies. Puerto Rico Space Grant Consortium (PRSGC)was one of those agencies. This gave the opportunity to more faculty members to participate of a unique experience.

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