Bioremediation of a Process Waste Lagoon at a Southern Polish Oil Refinery - DoE's First Demonstration Project in Poland

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Abstract Nearly a century of continued use of a sulfuric acid-based oil refining technology by the Czechowice Oil Refinery, located in southern Poland, has produced an estimated 120 thousand tons of acidic, highly weathered, petroleum sludges. This waste has been deposited into three unlined process waste lagoons, three meters deep, now covering 3.8 hectares. Initial analysis indicated that the sludges were composed mainly of high molecular weight paraffinic and polycyclic aromatic hydrocarbons (PAHs). The overall objective of this project is to provide a cost-effective bioremediation demonstration with petroleum-sludge contaminated soil for Poland. The specific goal of the remediation is to reduce the environmental risk from PAH compounds in soil and provide a green zone (grassy area) adjacent to the site boundary. A 0.3 hectare site, the smallest of the waste lagoons, was selected for remediation using a technology known as biopiling. The original lagoon sludge was amended and sold as a fuel to a local cement company thereby eliminating the contaminants while providing the refinery an additional revenue source. Approximately 3300 m^3 of contaminated soil with a mean total petroleum hydrocarbon (TPH) concentration of 27,000 ppm was targeted for treatment. The biopile was divided into two sections; an area of approximately 1610 m^2 passively aerated using Baroballs™ and an area of approximately 1390 m^2 actively aerated via air injection. Use of both passive and active aeration methods allows for an accurate assessment of cost and efficiency, with the most appropriate design to be deployed for future lagoon remediation at the refinery. Since the fall of 1997, approximately 80 tons of TPH have been removed from the biopile as a whole. The remediation strategies that have been applied at the Czechowice Oil Refinery waste lagoon in Czechowice-Dziedzice, Poland were designed, managed and implemented under direction of the Westinghouse Savannah River Company (WSRC) for the United States Department of Energy (DOE), the Institute for Ecology of Industrial Area (IETU), Ames Laboratory and Florida State University (FSU). FSU has the overall lead for the DOE EM-50 Polish Initiative Program. This collaboration between IETU, DOE and its partners, provides the basis for international technology transfer of new and innovative remediation technologies which can be applied in Poland and Eastern Europe as well.

Introduction Poland is one of five central and eastern European nations expected to be included in the next proposed expansion of the European Union. With this inclusion, Poland must abide by Organization of Economic Cooperation and Development (OECD) standards for the environment. Much effort is still needed in educating the public and private sector on the necessity to reduce environmental pollution. An ecological fund (Fundacija Ekologii) has been set aside by the government to aid in the cleanup of the environment. However, this amount is insufficient given the magnitude and sheer number of contaminated sites in Poland. Historically, Poland's wealth in natural resources has been exploited leading to this legacy of environmental neglect. Although laws were put into place to punish polluters during the communist regime, they were not readily enforced.

This international project had been set up with the intent for scientific exchange between the American and Polish scientists from the IETU. The project was divided into three stages which included site characterization - provided under supervision of Ames Laboratory; environmental and health risk assessment - provided under supervision of Florida State University (FSU); remediation technology description and implementation - provided under supervision of Westinghouse Savannah River Company (WSRC). FSU was chosen to be the project manager for the IETU side of the project. The site chosen for the proposed project, the Czechowice Oil Refinery (CZOR), located in southern Poland, had been identified by the State Environmental Protection Inspectorate (PIOS) as one on Poland's top eighty most contaminated areas. During the first years, a concerted effort between Institute of Ecology for Industrial Areas (IETU)/ United States Department of Energy (DoE) scientists was made to characterize the site (geological, hydrological, chemical and microbiological) and to evaluate the potential risks to local inhabitants affected by the location of the sludge lagoons. The purpose of all of these activities was to get a better idea of what problems exist, the extent of the problems, and to formulate possible remediation strategies. During the course of the site characterization phase, the focus of the project shifted from contaminated groundwater to that of the sludge contaminated soils. Laboratory results indicated that the use of bioremediation would be a cost-effective solution given the local economic situation in Poland.

Site History The original refinery, Schodnica, started operations in 1896 and processed less than 1000 tons of paraffinic crude a year. In 1902, an American firm, Socony Vacuum Oil Inc., New York, built a larger, state of the art facility capable of producing in excess of 3500 tons of paraffinic crude per year. In 1931, the first Foster Wheeler distillation unit of its kind in Poland was installed at the site. During the Second World War, the Allies bombed and partially destroyed the refinery. Limited production was restored by the Germans during the war. Restoration and construction of a cresol production unit was completed by Polish engineers after the war. Between 1959 and 1962, capacity of the CZOR was increased to 50000 tons per year. Although fire, caused by lightning, damaged a portion of the refinery in 1971, the CZOR was quickly rebuilt.

Initially built on the outskirts of the village of Czechowice, the refinery is now located in the middle of the town of Czechowice-Dziedzice, surrounded by businesses, residential areas and a town park. The current population of this town is approximately 36,000 with a population density of about 1080 persons / km^2. The CZOR covers an area of approximately 75 ha. The refinery presently produces gasoline, special lubricants, engine and fuel oils, paraffin and paraffinic products, and asphalts. The by-products from the various refining processes, collectively known as sludge, are disposed of in three lagoons, each about three meters deep, covering an area of 3.8ha. It is estimated that over 120 thousand tons of sludge have been deposited during the 70 years the sulfuric acid process was utilized (acid treatment was discontinued in 1984).

Potential Health Risks and Site Characterization Due to the proximity of the refinery to residential and recreational areas, clean up levels were set to PIOS multiple use values. During the risk assessment phase of the project, dermal exposure to PAH containing surface soil from the refinery was identified by the IETU as a potential carcinogenic risk. Therefore, protective clothing was required during construction phase and during soil sampling campaigns. Guidelines for allowable pollution levels in soil have been published by the State Environmental Protection Inspectorate (PIOS). Table 1. summarizes allowable soil contaminant levels for lands set aside for multiple use (residential, agricultural, recreational) and for industrial use (industrial sites, waste disposal sites, non-foodstuff agricultural sites).

Mean values for contaminants of concern are presented for three separate baseline studies and are also shown in Table 1. The baseline studies for comparison were; Refinery site characterization (1996), Lagoon bottom (1996) and Biopile (1997). Additional data obtained during site characterization phase (Ames Laboratory, 1996) of the project concluded that that sludge lagoons were not a source of detected groundwater contamination due to its separation from the aquifer by an impermeable underlying clay layer.

Remediation Strategies Until recently, the state-of-the-art approach to soil remediation was excavation and/or incineration followed by disposal at a secure landfill. Changes in liability concerns, increasing costs, and regulatory constraints have decreased the popularity of these methods as a soil cleanup alternative. Landfill disposal of contaminated soil does not remove the future liability of its generator, who will be held jointly liable with the landfill operator for any future associated contamination. As Poland strives to be incorporated within the EU, adaptation of similar regulatory and liability concerns are foreseeable. Thus, on-site permanent solutions must be sought whenever possible.

For fresh fuel spill sites, the following on-site *in situ* technologies have been used: Bioventing, the process of aerating soils to stimulate *in situ* biological activity and promote bioremediation; Nitrate addition, the process of adding nitrate which can act as an alternate electron acceptor under low or negligible oxygen concentrations to promote bioremediation; and Hydrogen Peroxide addition, the process of injecting hydrogen peroxide to serve as an oxygen source to overcome anaerobic conditions and stimulate *in* *situ* biological activity and promote bioremediation. Of the three aforementioned methods, Leeson and Hinchee (1997) suggest that bioventing is more cost-effective at approximately $73 per m^3 for treating fresh vadose zone fuel spills. Nitrate and Hydrogen peroxide addition are relatively more expensive to implement at $256 and $641 per m^3, respectively.

Biodegradation of heavily weathered petroleum contaminated soils, such as those encountered at the CZOR, often proceeds at very low rates. This is often due to problems with mass transfer of oxygen, water or other limiting nutrients. Soil structure and the amount of petroleum and petroleum waste present can further inhibit the transfer of essential nutrients to indigenous microbial communities capable of degrading these pollutants. Additionally, sorption of PAHs to soil organic matter and or clays can further hamper the bioavailability of these compounds. In such cases, *ex-situ* bioremediation methods may be more applicable. A technology known as Biopiling was selected to treat the contaminated soils on the site of the refinery process lagoon. The sludge contaminated soils were excavated and placed on an impermeable base (the natural clay layer forming the lagoon bottom) to form a soil pile constructed to allow aerobic bioremediation by aeration via perforated piping connected to an air blower, vacuum pump or barometric pump. Often biopiles are constructed with a leachate collection system for moisture addition. Nutrients can be added directly to the leachate for uniform distribution.

Process Verification and Testing Based upon preliminary biodegradability tests on surface soils at the CZOR (> 200,000 mg/kg TPH in litter) reported by Ulfig, et al. (1996), the rates of removal should range between 10 to 80 mg/kg of soil per day for TPH and could exceed 120 mg/kg of soil per day, based on similar work by Reisinger, et al. (1996). Soil column studies were employed to test passive versus active aeration, and differing nutrient amendments on TPH removal in order to optimize the bioremediation process. Data suggests that the addition of wood chips improve hydraulic conductivity of the clayey soils, use of dolomite for soil pH maintenance, commercial fertilizers to replenish depleted soil nutrients, recirculation of leachate - as a source of induced microbial inoculum and readily available nutrients, and ventilation will stimulate biological activity and promote increased bioremediation of contaminated soils that would be used to construct the Biopile at the CZOR.

Biopile A 0.3 hectare site, the smallest of the waste lagoons, was selected for remediation using a technology known as biopiling. The final biopile design consisted of 1) dewatering and clearing the targeted lagoon to the clean clay layer, 2) adding a 20 cm layer of dolomite with pipes for drainage, leachate collection, air injection, and pH adjustment, 3) adding a 1.1 m layer of contaminated soil mixed with wood chips to improve permeability, and 4) completing the surface with 20 cm of top soil planted with grass. Approximately 3300 m^3 of contaminated soil with a mean total petroleum hydrocarbon (TPH) concentration of 27,000 ppm was targeted for treatment. The biopile was divided into two sections; an area of approximately 1610 m^2 passively aerated using Baroballs^{TM} and an area of approximately 1390 m^2 actively aerated via air injection. Use of both passive and active aeration methods allows for an accurate assessment of cost and efficiency, with the most appropriate design to be deployed for future lagoon remediation at the refinery. A combination of microbial and chemical determinations were used to track the bioremediation process in the biopile (please refer to the Technical Test Plan by Altman et al. 1996). The influence of different aeration schemes (passive vs. active) on TPH removal are exemplified by Figure 1. during a four month period. Since the fall of 1997, approximately 80 tons of TPH have been removed from the biopile as a whole. For a total summary of the project, please refer to Table 2.

Conclusions The Biopile project was the first bioremediation technology demonstration of its kind in Poland. Understanding the economic situation of a country is necessary before trying to apply new technologies for environmental clean-up. Often, cheaper, simpler solutions will satisfy local expectations. This is the case with using passive ventilation (Baroballs^{TM}) to provide air for the Biopile method of soil remediation. It is effective with recalcitrant materials such as the sludge contaminated lagoon soils of the CZOR as shown by the decrease in baseline values of PAH and TPH. If there will be no regulatory pressure to speed up closure of the CZOR lagoon site, use of biopiling and Baroballs^{TM} can be used to treat the rest of the contaminated lagoon soils. However, if compliance with regulatory bodies are time dependent, use of active ventilation and biopiling is cost and time effective. Data obtained from experiments carried out at the Biopile site enable refinement of the technology making it more user-friendly and cost-effective. Additionally, this improved technology can be transferred back to the USA for deployment to similar sites across the DOE complex. Furthermore, implementation of technologies such as Biopiling will enable countries like Poland to help itself with past, present and future environmental problems caused by petroleum or petroleum wastes.

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Table 1. PIOS Recommended Soil Contaminant Levels, Actual Refinery, Lagoon Soil and Biopile Levels

Contaminants of Concern	MCL (MU)[1]	MCL (Ind)[1]	ESC Refinery (mean)	Lagoon soil (mean)	Biopile (mean)
BTEX COMPOUNDS					
Benzene	0.2	100	0.12	27.4	0.17
Ethylbenzene	1.0	200	0.04	3.3	0.0035
Toluene	1.0	200	0.38	14.6	0.011
Xylenes	1.0	100	0.11	7.3	0.008
PAH COMPOUNDS					
Fluoranthene	0.2	50	19.7	6.54	1.47
Benzo(b)fluoranthene	5	50	4.25	1.8	0.22
Benzo(k)fluoranthene	5	50	1.21	1.3	0.11
Benzo(a)pyrene	5	50	3.7	2.29	0.34
Benzo(g,h,i)perylene	10	50	1.1	0.624	0.11
Indeno(1,2,3-cd)pyrene	NR[2]	NR[2]	1.1	6.16	0.38

1 - All values in mg/kg, Polish Maximum Contaminant Level (MCL) guidelines
(Ind - Industrial Use, 0-2 M depth), (MU - Multiple Use, 0.3-15 M depth)
2 - NR = No Recommendation
(IETU Risk Assessment Report, 1997)

Figure 1. Comparison of Aeration on TPH removal during a four month period. Passive section of the Biopile is aerated using barometric pumps known as Baroballs^{TM}. Aeration to the active section of the Biopile was provided by an air blower. S2 represents baseline TPH values while S1 represents final TPH values during the experimental campaign.

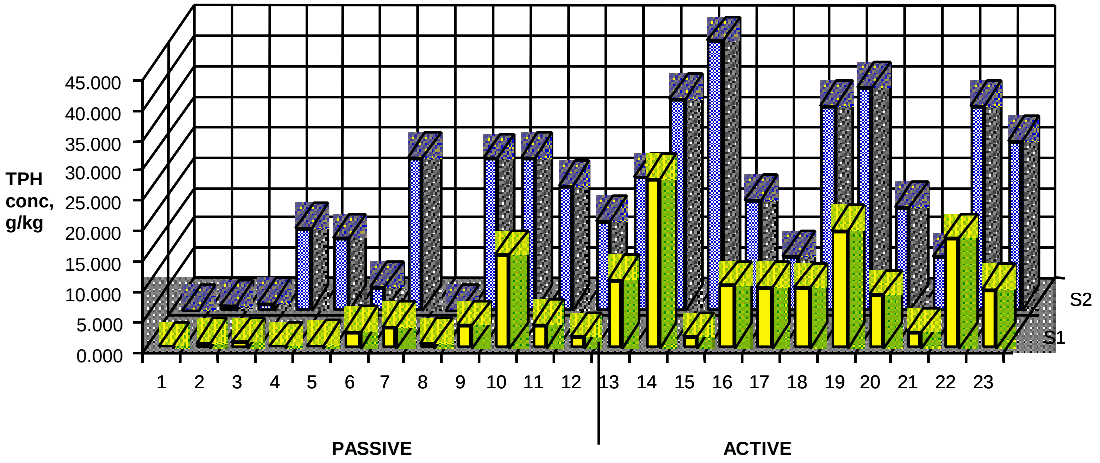

Table 2. Project Summary

Cleanup Authority: State Environmental Protection Inspectorate (PIOS), Poland.

Contaminants: Total Petroleum Hydrocarbons (TPH) and Polycyclical Aromatic Hydrocarbons (PAH).
- Initial mean TPH levels were 27,000 ppm.
- Benzo(a) pyrene concentrations ranged from 0.059 ppm -1.73 ppm

Technology: Biopiling
- Passive versus Active Aeration
- Leachate recirculation
- Fertilizer addition as required
- Seasonal operational constraints

Type/Quantity of Media Treated: Clayey Soils
- 3300 m^3 sludge contaminated soils
- 30% porosity after amendment with wood chips

Period of Operation: 9-97 to 9-98

Results: As of September 1998, 50% TPH removal (nearly 80 metric tons), BTEX and PAH levels are near PIOS guidelines for residential areas. Degradation rates greater in active portion when air blower is operational. Aeration by Baroballs ^{TM} adequate except during winter months when valve can freeze shut. Slightly lower degradation rates in passive portion.

Total Costs : $322,070 * or $98 per m^3 of contaminated soil

Original Cost Estimate : $300,000 to $500,000 (1996)

*Costs do not include costs involved with teaching IETU staff ES&H, GLP, Standard Methods for Chemical and Microbiological Monitoring of Biopiles, use and maintenance of Monitoring equipment, Statistical Analysis techniques and report writing. Furthermore, transportation of equipment, and personnel to Poland has not been included.