

## Oily Soil Clean Up Project – MSGP-AZ05-04

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### **Project Summary**

Historically the first full-scaled industrial oil-field development across the Absheron Peninsula of Azerbaijan was launched over 130 years ago. More than 1 billion tons of “black gold” has been extracted in this region since that time. However, the improper technology of oil production, transportation and refinery resulted in uncontrolled contamination of ground and water ecosystems. In particular, the topsoil within the adjacent to the Baku administration area is featured by formation of a man-caused desert without any vegetation. The area polluted by oil and oil products has a strong impact on all the elements of ecosystems including ground water that ultimately brings pollutants into the coastal water of the Caspian, air and surface water. The artificial oil-saturated lakes has been arisen in the vicinity of these old on-land oil fields (Binagadi, Surahany, Bibi-Eeybat) where the former fertile land once was covered by numerous vineyards and fig tree orchards. In view of this, the oil clean up of man-caused ecosystems and particularly, topsoil clean up appears to be one of the most important problems to be solved.

The target of this project is focused on elimination of pollutants across about 1 he site(s) on the Absheron Peninsula. The major objectives fixed in the framework of project implementation are focused on the use of a state-of-the-art technologies and bio-products for cleaning up oil contaminated soils and the final results will serve to predetermine the environmental and technological feasibility of the technology in question.

### **Background and Problem Statement**

It is well known that there exists today a great mass of oil-polluted soil in Azerbaijan, especially on the Absheron Peninsula and on some of the on-shore oil fields not far from the Caspian shore. In fact, thousands of hectares of soil across the Absheron Peninsula are contaminated by oil and oil products. Soils polluted with heavy metals and other contaminants are also widespread in the Caspian region, and oil polluted soil is a serious problem not only in Azerbaijan, but in Russia, Kazakhstan, Turkmenistan and Iran as well. Although there have been a number of initiatives to deal with the oily soil problem here in Azerbaijan, to date no concrete operational measures have been undertaken to actually clean these soils in an environmentally friendly and economical manner.

This pilot project will develop a strategy for and demonstrate the feasibility of cleaning up territories contaminated by hydrocarbons, heavy metals and other hazardous substances. The sites in Buzovna and Mashtagi districts at the Absheron peninsula will be investigated and samples of soil, water and air analyzed. Based on an assessment of available technologies and products for cleaning up contaminated soil, several pilot clean-up operations will be performed. The effect of the clean-up operations will be monitored and trees will be planted on some of the cleaned site. The economic potential of alternative option for sustainable use of cleaned territory will also be assessed.

The identified major objectives for implementation of the proposed project include the use of state-of-the-art technologies for cleaning up oil-contaminated soils. Final results will help to assess environmental and technological aspects as well as economical efficiency of the technology applied. All the clean up activities will be carried out under regulated physic-chemical parameters. The clean up process will be checked up through continuous monitoring, both chemical and biological. The efficiency index for the clean up process will be determined by degradation of 95-98% hydrocarbons comparing to its background content in the soil. The project results may be used in the framework of large-scaled pilot projects not only in Azerbaijan but also in other arid zones of all the Caspian countries.

### **Goal and Objectives**

The main goal of this pilot project is to demonstrate the feasibility of and evaluate remediation technologies for cleaning up and rehabilitate contaminated site(s) on the Absheron peninsula in an environmentally friendly and economical manner.

Within the framework of this environmental assessment and pilot clean up project we will:

- Describe the actual ecological situation on a number of contaminated sites in Absheron and assess the technical, operational and economical aspects of appropriate clean-up technologies;
- Perform a qualitative and quantitative assessment of the contaminants in soil, water and the atmosphere of the project site(s);
- Demonstrate the feasibility by performing a small-scale pilot clean up of the contaminated site(s) and measure the effect;
- Establish a strategy to clean and rehabilitate the site to a defined level of contaminants;
- Contribute to enhancement of environmental management within the framework of the policies of the Ministry of Ecology and Natural Resources;
- Increase the ecological awareness in the population.

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# MPPA REPORT ON OILY SOIL CLEAN UP PROJECT (MSGP-AZ05-04)

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The target of the “Oily Soil Clean up Project” is achieved by clean up of 1 he oily polluted site on the Absheron peninsula through effective application of state-of-the-art technologies and bio-products. Within the framework of this environmental assessment and pilot clean up project, the grantee has made the following issues:

- Described the actual ecological situation on a number of contaminated sites in Absheron and assess the technical, operational and economical aspects of appropriate clean-up technologies;
- Performed a qualitative and quantitative assessment of the contaminants in soil;
- Demonstrated the feasibility by performing a small-scale pilot clean up of the contaminated sites and measured the effect;
- Established a strategy to clean and rehabilitate the site to a defined level of contaminants;
- Contributed to enhancement of environmental management within the framework of the policies of the Ministry of Ecology and Natural Resources;
- Increased the ecological awareness in the population.

On January 12, 2005, I participated in a workshop the grantee organized to local experts and specialists dealing with oily soil clean up technologies. The first half of day was dedicated to presentation of the project results and exchange of ideas on oil waste utilization technologies. The second one was made to visit the project site and to show case of the project outcome. I visited to the project site which is nearly Buzovna area at territory of oil gas production unit named after H.Z. Tagiev. The grantee demonstrated a clean up area and told about each stage of project activities. He said that the level of pollution - mosaic and there were both strongly polluted and weakly polluted areas. The depth of pollution varied 0,2 m to 1,5 m. The operational part of the project that included: site state visual inspections; sampling programs; laboratory works; and use of remeiation technologies were made within 6-8 month period. Clean up operations (approx. 6 months) were done by a contractor selected as a result of tender made the grantee. Based on the UNDP procurement guideline, there were done the purchases of supplies and remediation materials under the project.

Based on the project reports and visual observations, all the project tasks and activities were done in a good manner. The only problems faced the grantee during the project execution was planting trees in the cleaned territory, although some natural growth of plants was observed in area of clean up. The grantee explained that it was impossible to make after October because of weather conditions. The most favourable period for planting is a second half March.

Under the project, over 1 he of polluted territory was cleaned up by use of the most advanced bioremediation, chemical oxidation, and solidification/stabilization technologies. The level of pollution was not exceeding 1%. The clean up operations were applied for both heavily and slightly contaminated sites. An economical potential of the reclaimed wastes as well as available waste clean up and utilization technologies were assessed. Please see below a list of remediation technologies used during the project implementation, their impact on clean up process and economical effectiveness.

Technologies	Advantages	Disadvantages	Economical Effectiveness to	Comments
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			1 m3 area clean up	
CHEMICAL OXIDATION	- fast treatment (weeks to months) - temporary facilities - treatment to low levels - effective on some hard-to-treat compounds	- requires spending "today's" money to get fast cleanup - involves handling powerful oxidants, and carries special safety requirements	USD 15 - 50	materials required for using this method is available in a limited quantity in Azerbaijan
IN-SITU BIOREMEDIATION	- low cost - very effective for cleaning soil polluted with oil of middle fraction - very natural method of clean up	- exits no equipment which could clean up oil polluted sites with depth of > 1m. - requires more water - not quite effective for cleaning soil polluted with oil fractions - long period required for clean up - not effective for cleaning heavily polluted sites	USD 05 - 25	materials required for using this method is completely available in Azerbaijan
STABILIZATION/SOLIDIFICATION	- hazardous components like PAH and olefins are corked up and waste is converted into not hazardous one - short period of cleaning - more CaO required	- more water required	USD 25 - 50	materials required for using this method is completely available in Azerbaijan

The project results were shared with governmental (SOCAR, MENR), NGO and private companies as well as released through mass media and specialized environmental workshop. So, I confirm that an operational part of the project is fully completed and project's outcome – achieved.

Re the latest Actual Expenditure List of project submitted on 23<sup>rd</sup> Nov05, please note that the grantee made mistyping with indicating number of months for expenses. I attach herewith the revised version of Annex 5A-5B.

Re the verification of all financial documents, the grantee has invested \$20,000 in cash and \$20,000 as in-kind for implementation of this project. Also, they did spend \$39,900 from grant funds -- even if only \$30,035 was transferred to the grantee's bank account by this -- for clean up operational works, supplies and other activities. Thus, the grantee will reimburse itself and its contractors for the remaining balance from grant: \$9,865 as soon as it is released. I have reviewed all financial documents (invoices, bills, bank transfer receipts, procurement records, etc.) made for project expenses and can confirm their originality and accuracy. All the documentation is filled in the grantee's office and always available for review.

Attachments: Annex 6A - Project Final Report  
Annex 5A - Last Financial Report (revised)  
Annex 5B - List of Actual Expenditure  
Annex 8A - Inventory of Equipment  
Bank document verifying the deposit for remaining balance from matching  
Project Photos

- In dependence of level and depth of pollution

**Site Visit Report**  
**Oily Soil Clean Up Project – MSGP-AZ05-04**  
**26<sup>th</sup> February 2006**

A site visit was conducted by the Grants and Public Participation Manager on 26<sup>th</sup> February 2006 with participation of the MPPA-Azerbaijan, the Executive Director and Technical Advisor of the CASAM Butan Tex Company to the MSGP-AZ05-04 project. The project aimed to eliminate the pollutants in the target oil contaminated area of Absheron Peninsula – Azerbaijan.

The observation was as follow:

- The targeted polluted area, 1 hectare, was cleaned and stabilized utilizing three advanced technologies of bioremediation, chemical oxidation, and solidification/stabilization. Detailed technical reports are available at the project office, CEP/PCU and CEP Website;
- The area was too polluted than what was expected prior the project implementation which caused a bit longer duration of the project implementation;
- Planting the trees in the cleaned areas was delayed to March 06, due to weather condition;
- Some grass has already been grown in the land as the indicator for the success of project. The successful result of the project also determined the environmental and technological feasibility of using above technologies;
- The technologies being used for the clean up has also been shared through workshops, mass media, ... with relevant authorities such as SOCAR, BP, Salyan Oil, to be considered and utilization of the successful methods for further clean projects. Local people of the area were also informed of the project results.
- Successful result of the project made the Grantee to start another clean up project using the same methodologies in other lands;
- The cleaned land will be given back to government (SOCAR) and national oil company will be responsible to take care of the project after the project termination;
- The project is successfully operationally completed, with only remained activity of planting trees in the land which will be done during March.

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# OILY SOIL CLEAN UP PROJECT (MSGP-AZ05-04)

*CASAM Butan Tex Company*

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## Technical Progress Report on Phase II (April-November 2005)

### **SUMMARY**

In order to select a subcontractor to conduct the clean up works, several experienced companies were invited to submit their proposals. As a result of tender conducted, an ETS was selected as a winner based on cost and service offered. However, this company withdrew the proposal with doing service works on some reasons. In this regard, CASAM contracted another company, ranged next to ETS as per the tender results, to perform clean up operations. After signing an agreement clean up operations on the project site were launched. All the info and detail of laboratory analyses will be shared with the company before the clean up works. During 4-6 month period about 1 he of polluted territory was cleaned up by use of the most advanced bioremediation, chemical oxidation, and solidification/stabilization technologies. The clean up operations were applied for both heavily and slightly contaminated sites. An economical potential of the reclaimed wastes as well as available waste clean up and utilization technologies were assessed by CASAM under phase II.

In period of April to November 2005, some purchases of supplies such as mineral fertilizers; chemicals; and bioremediation products were procured by CASAM and some parts of Butan Injector 2000™ technology used as in-kind contribution. In addition, preparation for 1-day workshop with participation of environmental experts and specialists was started in October. The purpose of this seminar is to share project results with local colleagues and exchange each other on the most perspective and effective oily clean up technologies and products.

All the project targets are made as per workplan and an operational part is completed. CASAM considers implementation of the project successful. The last grant tranche in amount of USD 9,865 is requested by CASAM to complete the project activities as stated in the original workplan. In the frame of the last phase, there will be made the workshop and summarized the project results. The final progress report is expected to submit until end this year.

## STABILITY AND REPLICABILITY OF THE PROJECT

According to the State Oil Company of Azerbaijan Republic (SOCAR), there are 30,000 ha of oily polluted sites in Azerbaijan of which about 2,700 ha are contaminated by oil-slimes and drill cuttings. Most of pollutions are happened because of oil spills. Various methods of clean up can be applied for different type of pollutions and for that a few billion dollars can be needed.

Our company is ready to give information on practical and theoretical experience to organizations of four countries of the Caspian region within the framework of the realized ecological project in view of the obtained results and learned lessons. The development of the project has shown that all necessary equipment and raw materials are available at local market and so the similar projects in the Caspian Sea region seems to be economically profitable. The CASAM Butan Tex Company is ready to render the scientific-technological and technical help in implementation of the similar projects in all the Caspian countries.

## LOCATION OF THE PROJECT SITE

The project site is situated nearby Buzovna area at territory of oil gas production unit named after H.Z. Tagiev. Exact coordinates of the site were fixed by GPS equipment:

1.  $40^{\circ}30'36,1''$
2.  $40^{\circ}30'37,0''$
3.  $40^{\circ}30'36,4''$
4.  $40^{\circ}30'37,4''$

Size of the site is: Width –95 m and Length – 105 m. The level of pollution is mosaic and has both strongly polluted and weakly polluted areas. The depth of pollution is from 0.2 m to 1.8 m.

## Design of Polluted Site

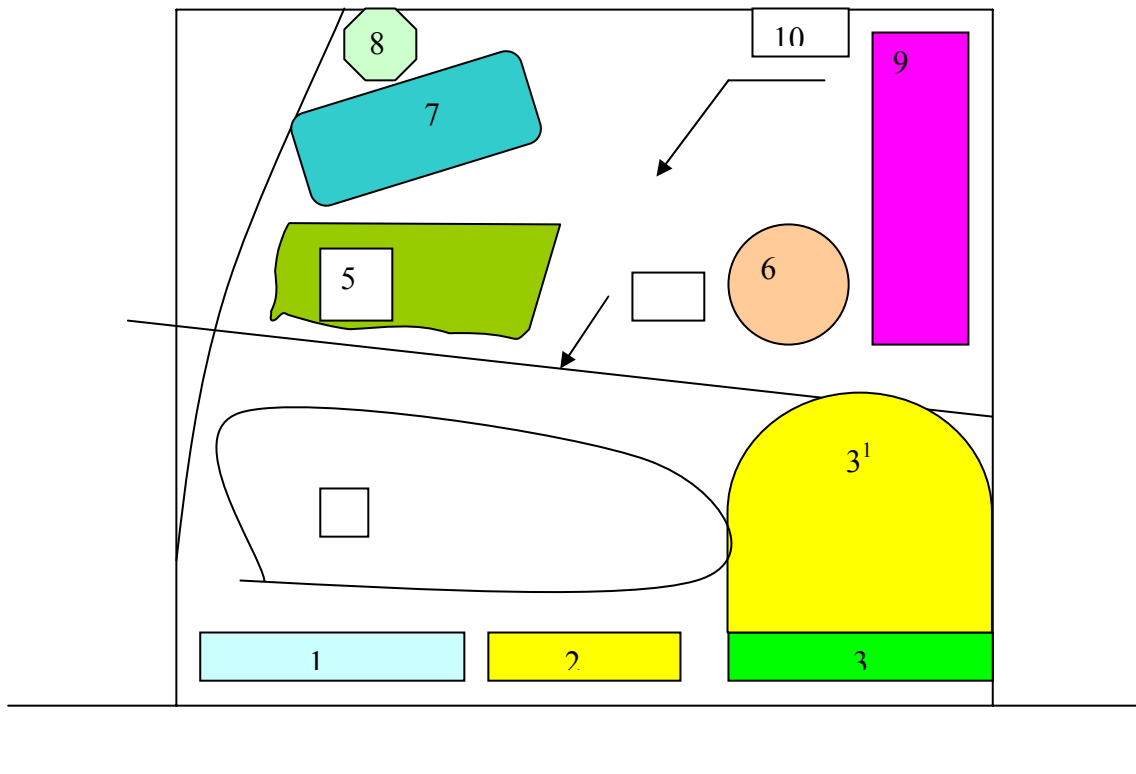


Table N1: Site characteristic

Points	Pollution nature	Volume, m <sup>3</sup>	Sizes	Depth, m
1	Oil spills	105	5mX35m	0,6
2	Oil spills	45	5mX20m	0,45
3	Oil spills	140	5mX35m	0,8
3 <sup>1</sup>	Oil spills	178	17mX35m	0,3
4	Oil spills	280,3	55mX17m	0,3
4 <sup>1</sup>	Oil duct	2,2	0,15mX97m	0,15
5	Oil spills	90	10 mX30m	0,3
6	Oil earth storage	589	circle d=25m	1,2
7	Oil spills	245	35mX20m	0,35
8	Oil spills	28,3	circle d=6m	1
9	Oil spills	60	40mX10m	0,15
10	Slightly polluted	1200	4000m <sup>2</sup>	0,3

LABORATORY ANALYSES									
Client-Field	Ref.#	1	2	3	4	5	6	7	8
Analyses									
TPH	g/kg	55,11	44,14	117,2	81,18	43,24	143,6	75,55	33,58

#### Volume of Oil Products Contained in a Treated Soil

Sampling was realized in those sub sites. Total hydrocarbons were investigated in the samples in laboratory conditions (tab. 2). The site was investigated during implementation of phase 1, but some more samplings and analyses were done from sub-sites 9 and 10. Special sampling procedures were used.

**Table N2: Pollution characteristic**

Points №	Average degree of pollution	Volume, m <sup>3</sup>	Content of oil products (m <sup>3</sup> )
1	5,5%	105	5,77
2	4,4 %	45	1,98
3	11,7%	140	16,78
3 <sup>1</sup>	11,7%	178	20,83
4	8,1%	280,3	22,68
4 <sup>1</sup>	8,1%	2,2	0,18
5	4,3%	90	3,87
6	14,4%	589	84,82
7	7,6%	245	18,62
8	3,3%	28,3	0,94
9	3,4%	60	2,04
10	2,6%	1200	31,2
<b>Total volume of oil products</b>			<b>209,71</b>

Results of research show that volume of oil products on the site at beginning of remediation process was 209.71 m<sup>3</sup>. As it can be seen from the above design, the pollution is matrix and heterogeneous.



## RESULTS OF RESEARCH

### Chemical Oxidation Method

Chemical oxidation technology is based on the oxidative power of specific chemicals. Through the process of oxidation, groundwater contaminants are ultimately broken down into carbon dioxide and water. Some oxidants are stronger than others, and it is common to calculate a relative strength for all oxidants using chlorine as a reference. Table 3 lists the relative strengths of common oxidants.

**Table N3:: Oxidant strengths**

Chemical species	Standard oxidation potential (volts)	Relative strength (chlorine = 1)
Hydroxyl radical	2.8	2.0
Sulfate radical	2.5	1.8
Ozone	2.1	1.5
Sodium persulfate	2.0	1.5
Hydrogen peroxide	1.8	1.3
Permanganate (Na/K)	1.7	1.2
Chlorine	1.4	1.0
Oxygen	1.2	0.9
Superoxide ion	-2.4	-1.8

All the oxidants shown in Table 3 have enough oxidative power to remediate most organic contaminants. The standard potentials are a useful general reference of the strength of an oxidant, but these values do not indicate how they will perform under field conditions. Four major factors play a role in determining whether an oxidant will react with a certain contaminant in the field, three of which are illustrated in Figure 3. On a microscale, kinetics or reaction rates are perhaps the most important. In fact, reactions that would be considered thermodynamically favorable based on  $E^0$  values may be impractical under field conditions. The rates of oxidation reactions are dependent on many variables that must be considered simultaneously, including temperature, pH, concentration of the reactants, catalysts, reaction by-products, and system impurities (e.g., natural organic matter [NOM], oxidant scavengers, etc.).

There are two common forms of permanganate—potassium permanganate ( $\text{KMnO}_4$ ) and sodium permanganate ( $\text{NaMnO}_4$ ). Both are available in a range of purities and have similar chemical reactivities.  $\text{KMnO}_4$  is a crystalline solid from which aqueous solutions of a desired concentration (up to 4%) can be prepared on site using ground- or tap water. Because it is a solid, transportation hazards are minimized.  $\text{NaMnO}_4$  is usually supplied as a concentrated liquid (40%) but is usually diluted on site and applied at lower concentrations. The potential for higher concentrations of sodium permanganate solutions gives more flexibility in the design of the injection volume and, because it is in liquid form, the dusting hazards associated with dry  $\text{KMnO}_4$  solids are eliminated. However,  $\text{NaMnO}_4$  has the additional hazard of being more highly reactive, with potential exothermic release if neutralized with concentrated reductants. Both forms of permanganate are strong oxidizing agents with a unique affinity for oxidizing organic compounds containing carbon-carbon double bonds, aldehyde groups, or hydroxyl groups. The stoichiometry and kinetics of permanganate oxidation at contaminated sites can be quite complex as there are numerous reactions in which manganese can participate due to its multiple valence states and mineral forms. The primary redox reactions for permanganate are given in Equations 1–3. These half-cell reactions are useful for two purposes to :

- evaluate stoichiometric requirements of the oxidant for complete mineralization of contaminants via electron transfer balances; and
- determine potential environmentally significant reaction products.

Typical of all oxidants, permanganate can also react with water, but at very slow rates, resulting in nonproductive depletion of permanganate and further generation of  $\text{MnO}_2$

solids. When reduced species (contaminant or natural) are no longer available to react with permanganate, this slow decomposition process eventually results in depletion of excess permanganate that may remain in the subsurface after treatment. Permanganate decomposition reactions can also occur, but at appreciable rates only under extremely high pH. Permanganate is a stable oxidant and can persist in the subsurface for months. Table 4 presents a comparison of the stoichiometric requirements for mineralization of several organic compounds with permanganate.

**Table N4:. Stoichiometric requirements for complete mineralization by permanganate\***

Target compound	Compound molecular weight (g/mol)	Oxidant demand (g MnO4 <sup>-</sup> /g of target)	MnO2 produced (g MnO2/g target)
Tetrachloroethene	165.6	0.96	0.70
Trichloroethene	131.2	1.81	1.32
Dichloroethene	96.8	3.28	2.39
Vinyl chloride	62.4	6.35	4.64
Phenol	94.1	11.8	8.62
Naphthalene	128.2	14.8	10.8
Phenanthrene	178.2	14.7	10.7
Pyrene	202.3	14.5	10.6

\*Molecular weight: MnO4<sup>-</sup> (118.9 g/mol), KMnO4 (158 g/mol), NaMnO4 (141.9 g/mol).

Oxidation of sorbed and nonaqueous-phase liquid chlorinated ethenes has been demonstrated with permanganate at various sites. These oxidation reactions occur in the dissolved aqueous phase after the contaminants desorb from the media and/or dissolve from the free phase.

Because permanganate, like all oxidants, is nonselective, it also oxidizes NOM present in the soil. Since organic contaminants sorb to NOM in the soil matrix, they can be released as the NOM is oxidized by the permanganate. After this initial contaminant release, the rate of continued desorption should be increased due to the shift in equilibrium partitioning that results as the aqueous-phase concentration of the target organic is depleted.

The following additional issues must be considered during the evaluation, design, and implementation of permanganate oxidation, regardless of the delivery system being employed:

- Permanganate is not effective at oxidizing benzene, chlorinated benzenes, MTBE, carbon tetrachloride, or chlorinated ethanes (1,1,1-TCA, etc.).
- As with all oxidants, the optimal oxidant loading, including both target and nontarget compounds, should be determined before injection.
- MnO2 precipitates in the soil can reduce subsurface permeability.
- As with all oxidants, metals can be mobilized within the treatment zone due to a change in oxidation states and/or pH.
- There is a dust hazard to consider when handling potassium permanganate.
- Aggressive reactions are possible when concentrations of sodium permanganate greater than 10% are mixed with incompatible materials (reductant solutions, hydrogen peroxide, petroleum compounds, glycol, etc.).

We have used KMnO4 in this project. According to our workplan, we should use each method to both slightly and heavily polluted sites.

### Results of Works in Slightly Polluted Sites

The sub-site N2 was used for experimental clean up works. 45 m<sup>3</sup> of oily polluted land was there. A full content of oil products was 1.98 m<sup>3</sup>.

Finish Date: 10.08.2005	Station		Start results	Finish results	Change (%)
TPH GC-frac-comp.					
C10-C20	%		8,88	14,21	
C21-C36	%		89,41	85,27	
>C36	%		1,71	0,51	
TPH(Aliphatics)	mg/kg	10	4834	651	86,5
PAH					
Naphthalene	ug/kg	1,1	69,6	44,1	36,6
Acenaphthene+Fluorene	ug/kg	0,6	977,0	4,1	99,6
Phenanthrene	ug/kg	0,6	46,9	20,1	57,1
Anthracene	ug/kg	0,1	649,1	0,4	99,6
Fluoranthene	ug/kg	0,4	646,0	62,7	90,2
Pyrene	ug/kg	0,6	1407,4	47,3	96,6
Benzo(a)anthracene	ug/kg	0,4	1213,7	64,6	94,6
Chrysene	ug/kg	0,9	3482,8	232,5	93,3
Benzo(b)fluoranthene	ug/kg	0,5	1305,9	98,8	92,4
Benzo(k)fluoranthene	ug/kg	0,4	33,6	4,3	87,2
Benzo(a)pyrene	ug/kg	0,3	401,0	20,2	94,5
Dibenzo(a,h)anthracene	ug/kg	0,3	261,2	25,0	90,4
Benzo(ghi)perylene	ug/kg	0,6	<0,6	<0,6	
Indeno(1,2,3-cd)pyrene	ug/kg	0,4	6,8	<0,4	
Total PAH	ug/kg		10501,0	1375,09	87
Total organic	g/kg	10	102,10	12,21	88
pH		0,5	7,50	7,50	

As it can be seen from the above table, not bad results were achieved by means of chemical oxidation method for slightly polluted sites. Total PAH was reduced to 87% and total organic to 88%.

### Results of Works in Heavily Polluted Sites

The sub-site №4<sup>1</sup> was used for experimental clean up works. 2.2 m<sup>3</sup> of oily polluted land was there. A full content of oil products was 0.18 m<sup>3</sup>.

Finish Date: 10.08.2005	Station		Start results	Finish results	Change (%)
TPH GC-frac-comp.					
C10-C20	%		4,88	8,31	
C21-C36	%		93,61	90,64	
>C36	%		1,51	1,04	
TPH(Aliphatics)	mg/kg	10	12958	1014	92,1
PAH					
Naphthalene	ug/kg	1,1	56,2	6,3	88,7
Acenaphthene+Fluorene	ug/kg	0,6	<0,6	<0,6	
Phenanthrene	ug/kg	0,6	115,5	5,9	94,9
Anthracene	ug/kg	0,1	0,3	<0,1	
Fluoranthene	ug/kg	0,4	167,7	4,0	97,6
Pyrene	ug/kg	0,6	372,8	28,5	92,4
Benzo(a)anthracene	ug/kg	0,4	558,8	9,1	98,4
Chrysene	ug/kg	0,9	1310,5	152,8	88,3
Benzo(b)fluoranthene	ug/kg	0,5	255,5	52,8	79,3
Benzo(k)fluoranthene	ug/kg	0,4	2,7	0,9	66,6
Benzo(a)pyrene	ug/kg	0,3	0,3	<0,3	
Dibenzo(a,h)anthracene	ug/kg	0,3	1458,1	54,1	96,3
Benzo(ghi)perylene	ug/kg	0,6	<0,6	<0,6	
Indeno(1,2,3-cd)pyrene	ug/kg	0,4	15,1	1,9	87,4
Total PAH	ug/kg		4313,6	441,32	97,4
Total organic	g/kg	10	199,27	11,5	94,2
pH		0,5	7,0	7,0	

As it is seen from the above table, better results were achieved for heavily polluted sites by chemical oxidation method. Total PAH is reduced to 97,4% and total organic to 94,2%. Chemical oxidation method cleans up organic pollutions only.

### **In Situ Bioremediation**

Generally stated, the phrase "in situ bioremediation" refers to a broad spectrum of bioremediation techniques and technologies that rely on the capabilities of indigenous or introduced micro-organisms to degrade, destroy or otherwise alter objectionable chemicals in soil and ground water. Three factors affect the success of ISB. These are (1) the type of organisms, (2) the type of contaminant, and (3) the geological or chemical conditions at the contaminated site. The key players in ISB are bacteria. ISB is an extension of the natural function of existing microorganisms to break down human, animal and plant wastes. Typically, ISB systems rely on microorganisms indigenous to the contaminated site. An emergent technology involves injection of microbes to augment biodegradation at contaminated sites. A critical factor in determining whether ISB is appropriate at a site is whether the contaminants are susceptible to biodegradation. ISB is well established for certain types of petroleum hydrocarbons and their derivatives, including gasoline, fuel oil, alcohols, ketones, and esters. For other types of organic contaminants, such as solvents, ISB has been successfully tested in the laboratory and at a limited number of field sites. The amenability of the subsurface environment to ISB depends, in part, on whether the bioremediation will be intrinsic or engineered. Intrinsic bioremediation utilizes the innate capabilities of naturally-occurring microbes without any enhancements. Engineered bioremediation accelerates microbial activity by site-modification procedures, such as by introduction of microbes or the installation of wells to circulate fluids and nutrients that stimulate microbial growth. The case studies in this report focus only on engineered bioremediation. Proponents of ISB say it is a less costly, faster, and safer method for the cleanup of contaminated soil than more conventional cleanup methods. Likewise, they assert that conventional methods of soil cleanup involve excavation and treatment or disposal elsewhere with increased exposure to contaminants for both workers and neighbors.

### ***Selection of In Situ Bioremediation***

In situ bioremediation was selected by the Task Group as the innovative technology that would be the subject of the case studies. ISB has the potential of providing cost-effective, safe, and successful cleanups for a variety of waste sites, but that the technology was not being widely implemented.

### ***Institutional/Regulatory Barriers to In Situ Bioremediation***

The barriers to deployment of innovative technologies can be technical, institutional, and/or regulatory. This report focuses on the institutional and regulatory barriers. This subsection addresses institutional and regulatory barriers to innovative technologies, generally, and to ISB, specifically. Institutional/Regulatory Barriers to Innovative Technologies – Generally The major incentives for use of innovative technologies for environmental restoration include their promise of faster, better, safer, and cheaper cleanups. Yet, institutional/regulatory barriers to the use of innovative technologies often arise by virtue of (1) the lack of cost and performance data and (2) an inflexible institutional/regulatory framework.

At the beginning and end of treatment process, soil samples were selected from the parts of site according to the developed methodology. The biological analysis of the samples was carried out. The intensity of carbonic gas production as a parameter of intensity of hydrocarbon pollutions was identified. Monitoring of soil humidity and pH was realized at the same time. One of bioremediation parameters is presence of microorganisms capable to decompose oil hydrocarbons. The preliminary researches on pilot site have shown the presence of own indigenous microflora capable to decompose oil hydrocarbons in soil.

### ***Stages of treatment (field works):***

- Ripping on depth of pollution with the purpose of improvement of ground structure and its airing by atmospheric air (for this purpose a wheeled tractor with shed plough will be used);
- *Fungoid compost*, which carries out a number of functions: a) a source of microorganisms – destructors of hydrocarbons; б) ripper, improves physical and chemical and agrochemical properties of the polluted ground (increases capacity of absorption and water-holding capacity; c) source of biogenic elements - nitrogen, phosphorus etc.
- *Mineral fertilizers*. As mineral fertilizers ammophos will be used, containing in its structure all three biogenic elements in the ratio necessary for microorganisms. The quantity of applied mineral fertilizers will be calculated on the basis of given chemical analysis of the initial hydrocarbons content in soil. In a basis of calculations the rule about an optimum ratio of C: N in soil 25-30:5 is used. The mineral fertilizers will be applied as water solutions with the help of 10 t. water carriers, supplied by pumps - sprays. At the first stage 1/3 of whole quantity of fertilizers calculated for application for the whole period of carrying out of clearing will be applied into soil.

### Results of Works in Heavily Polluted Sites

The sub-site №4 and №7 was used for experimental clean up works. 525.3 m<sup>3</sup> of oily polluted land was there. A full content of oil products was 41.3 m<sup>3</sup>.

Client-Field	St N	#4	#7
TPH	g/kg	1,01	0,93
Total Organic	mg/kg	1,25	1,35
S	mg/kg	0,21	0,18
As	mg/kg	12,1	2,6
Ba	mg/kg	81,2	85,1
Cd	mg/kg	0,12	0,48
Cr	mg/kg	22,21	23,75
Co	mg/kg	3,15	4,03
Cu	mg/kg	13,8	9,65
Fe	mg/kg	467	945
Pb	mg/kg	8,74	6,93
V	mg/kg	18,89	17,87
Zn	mg/kg	16,67	15,76

### Results of Works in Slightly Polluted Sites

The sub-site №5; №9 and №10 were used for experimental clean up works. 1350 m<sup>3</sup> of oily polluted land was there. A full content of oil products was 37.11 m<sup>3</sup>.

Client-Field	St N	#5	#9	#10
TPH	g/kg	0,49	0,73	0,26
Total Organic	mg/kg	0,65	0,89	0,30
S	mg/kg	0,21	0,19	0,19
As	mg/kg	10,5	4,8	6,9
Ba	mg/kg	95,5	78,5	83,7
Cd	mg/kg	1,13	0,80	0,64
Cr	mg/kg	7,04	11,05	14,45
Co	mg/kg	3,11	4,18	3,21
Cu	mg/kg	11,9	8,43	8,81
Fe	mg/kg	482	571	722
Pb	mg/kg	4,32	3,21	5,23
V	mg/kg	20,1	18,0	17,9
Zn	mg/kg	18,8	19,1	19,1

## **Solidification and Stabilization Method**

Soil stabilization significantly changes the characteristics of a soil to produce long-term permanent strength and stability, particularly with respect to the action of water and frost. Lime, either alone or in combination with other materials, can be used to treat a range of soil types. The mineralogical properties of the soils will determine their degree of reactivity with lime and the ultimate strength that the stabilized layers will develop. In general, fine-grained clay soils (with a minimum of 25 percent passing the #200 sieve (74mm) and a Plasticity Index greater than 10) are considered to be good candidates for stabilization. Soils containing significant amounts of organic material (greater than about 1 percent) or sulfates (greater than 0.3 percent) may require additional lime and/or special construction procedures.

Subgrades (or Subbases): Lime can permanently stabilize fine-grained soil employed as a subgrade or subbase to create a layer with structural value in the pavement system. The treated soils may be in-place (subgrade) or borrow materials. Subgrade stabilization usually involves in-place "road mixing," and generally requires adding 3 to 6 percent lime by weight of the dry soil.

Bases: Lime can permanently stabilize submarginal base materials (such as clay-gravel, "dirty" gravels, limestones, caliche) that contain at least 50 percent coarse material retained on a #4 screen. Base stabilization is used for new road construction and reconstruction of worn-out roads, and generally requires adding 2 to 4 percent lime by weight of the dry soil. In-situ "road mixing" is most commonly used for base stabilization, although off-site "central mixing" can also be used. Lime is also used to improve the properties of soil/aggregate mixtures in "full depth recycling."

### Lime Modification & Soil Drying

There are two other important types of lime treatment used in construction operations: First, because quicklime chemically combines with water, it can be used very effectively to dry wet soils. Heat from this reaction further dries wet soils. The reaction with water occurs even if the soils do not contain significant clay fractions. When clays are present, lime's chemical reaction with clays causes further drying. The net effect is that drying occurs quickly, within a matter of hours, enabling the grading contractor to compact the soil much more rapidly than by waiting for the soil to dry through natural evaporation.

"Dry-up" of wet soil at construction sites is one of the widest uses of lime for soil treatment. Lime may be used for one or more of the following: to aid compaction by drying out wet areas; to help bridge across underlying spongy subsoil; to provide a working table for subsequent construction; and to condition the soil (make it workable) for further stabilization with Portland cement or asphalt. Generally, between 1 and 4 percent lime will dry a wet site sufficiently to allow construction activities to proceed.

Second, lime treatment can significantly improve soil workability and short-term strength to enable projects to be completed more easily. Examples include treating fine-grained soils or granular base materials to construct temporary haul roads or other construction platforms. Typically, 1 to 4 percent lime by weight is used for modification, which is generally less than the amount used to permanently stabilize the soil. The changes made to lime-modified soil may or may not be permanent. The main distinction between modification and stabilization is that generally no structural credit is accorded the lime-modified layer in pavement design. Lime modification works best in clay soils.

### The Chemistry of Lime Treatment

When lime and water are added to a clay soil, chemical reactions begin to occur almost immediately.

1. Drying: If quicklime is used, it immediately hydrates (i.e., chemically combines with water) and releases heat. Soils are dried, because water present in the soil participates in this reaction, and because the heat generated can evaporate additional moisture. The hydrated lime produced by these initial reactions will

subsequently react with clay particles (discussed below). These subsequent reactions will slowly produce additional drying because they reduce the soil's moisture holding capacity. If hydrated lime or hydrated lime slurry is used instead of quicklime, drying occurs only through the chemical changes in the soil that reduce its capacity to hold water and increase its stability.

2. **Modification:** After initial mixing, the calcium ions ( $\text{Ca}^{++}$ ) from hydrated lime migrate to the surface of the clay particles and displace water and other ions. The soil becomes friable and granular, making it easier to work and compact. At this stage the Plasticity Index of the soil decreases dramatically, as does its tendency to swell and shrink. The process, which is called "flocculation and agglomeration," generally occurs in a matter of hours.
3. **Stabilization:** When adequate quantities of lime and water are added, the pH of the soil quickly increases to above 10.5, which enables the clay particles to break down. Determining the amount of lime necessary is part of the design process and is approximated by tests such as the Eades and Grim test (ASTM D6276). Silica and alumina are released and react with calcium from the lime to form calcium-silicate-hydrates (CSH) and calcium-aluminate-hydrates (CAH). CSH and CAH are cementitious products similar to those formed in Portland cement. They form the matrix that contributes to the strength of lime-stabilized soil layers. As this matrix forms, the soil is transformed from a sandy, granular material to a hard, relatively impermeable layer with significant load bearing capacity. The process begins within hours and can continue for years in a properly designed system. The matrix formed is permanent, durable, and significantly impermeable, producing a structural layer that is both strong and flexible.

Lime by itself can react with soils containing as little as 7 percent clay and Plasticity Indices as low as 10. If the soil is not sufficiently reactive, lime can be combined with an additional source of silica and alumina. Such "pozzolans" include fly ash and ground blast furnace slag. The additional silica and alumina from the pozzolan react with the lime to form the strong cementitious matrix that characterizes a lime-stabilized layer. Properly proportioned mixtures of lime and pozzolans can modify or stabilize nearly any soil, but are typically used for soils with low to medium plasticity.

Fly ash is the most commonly used pozzolan. It is the finely divided residue that results from the combustion of pulverized coal in power plant boilers, which is transported from the combustion chamber by exhaust gases.

Solidification and/or stabilization are relatively simple processes. The treated material (soil, sludge, etc.) is mixed with a binder or mixture of binders and received mass is then cured to form a solid matrix that contains the contaminants.

#### *Stabilization*

This term refers generally to processes reducing the risk posed by a waste by converting the contaminants into a less soluble, less toxic, and immobile form. This state is usually achieved purposeful chemical reactions. The physical character of the treated material is not necessarily changed.

#### *Solidification*

This method refers to the processes that encapsulate the contaminants in a monolithic solid of high structural integrity. The encapsulation may be:

- of fine particles (micro-encapsulation);
- of a large block or container (macro-encapsulation);
- solidification resulting in a soil-like material.

Solidification does not necessarily involve a chemical interaction between the contaminants and solidifying agents. It may mechanically bind the treated material. Contaminant migration is restricted by vastly decreased the surface area that is exposed to leaching and/or by isolation the contaminants within an impervious capsule.

Most of the processes utilized in the application of S/S are modifications of proven processes and are directed at encapsulating or immobilizing the hazardous constituents and involve excavation + processing or in situ mixing.

### Results of Works in Slightly Polluted Sites

The sub-site №1 and №8 were used for experimental clean up works. 133.3 m<sup>3</sup> of oily polluted land was there. A full content of oil products was 6.71 m<sup>3</sup>.

#### Results

Sample	Mixture composition	TPH (mg/kg)	TPH-L (mg/l)	PAH (mg/kg)	PAH-L (M9/l)
#1	10% lime	127,320	0.18	97.27	6.26
#8		205,610	0.13	98.15	4.1

**Table 5: Heavy metals concentration**

Analyte	Unit	Sample	
		#1	#8
Ba	mq/kq d.w.	1701.35	1.460.00
Ba-L		134	110.00
Cd	mg/kg d.w.	0.035	0.07
Cd-L		<0.1	<0.1
Co	mq/kq d.w.	20.54	13.76
Co-L	Mmfl	0.52	<0.5
Cr <sup>+6</sup>	mg/kg d.w.	21.4	21,40
Cr <sup>+6</sup> -L		0.57	5.49
Cr <sub>6</sub> tai	mg/kg d.w.	79.46	118.00
Cr <sub>6</sub> tai - L		1834	410.00
Cu	mg/kg d.w.	90.85	49.40
Cu-L	WJ/l	32	28.00
Pb	mq/kq d.w.	65	54.12
Pb-L	MOfl	<0.4	<0.4
Zn	mq/kq d.w.	113.18	114.20
Zn-L	ng/l	<0.5	<0.5

### Results of Works in Heavily Polluted Sites

The sub-site №3; №3<sup>1</sup> and №6 was used for experimental clean up works. 907 m<sup>3</sup> of oily polluted land was there. A full content of oil products was 122.43 m<sup>3</sup>.

#### Results

Sample	Mixture composition	TPH (g/kg)	TPH-L (mg/l)	PAH (mg/kg)	PAH-L (M9/l)
#3	10% lime	3.160	0.16	842.11	2.18
#3 <sup>1</sup>	10% lime	2.452	0.14	715.48	3.18
#6	10% lime	5.478	0.15	973.18	6.35

**Table 6: Heavy metals concentration**



Analyte	Unit	Sample		
		#3	#3 <sup>1</sup>	#6
Ba	mq/kq d.w.	1846.35	1574.00	1735.00
Ba-L		118	121.00	185
Cd	mg/kg d.w.	0.041	0.083	0.065
Cd-L		<0.1	<0.1	<0.1
Co	mq/kq d.w.	23.67	21.42	20.12
Co-L	Mffl	0.52	<0.5	0.12
Cr <sup>+6</sup>	mg/kg d.w.	26.34	24,22	22.16
Cr <sup>+6</sup> -L		0.34	3.21	1.35
Cu	mg/kg d.w.	85.41	56.23	72.15
Cu-L	WJl	11	18.00	15.3
Pb	mq/kq d.w.	83	75.4	74.7
Pb-L	MOil	<0.2	<0.3	<0.2
Zn	mq/kq d.w.	132.2	141.5	136.3
Zn-L	ng/i	<0.5	<0.5	<0.5

## LESSON LEARNED

### Advantages and Disadvantages of Chemical Oxidation:

- *Advantages*
  - fast treatment (weeks to months)
  - temporary facilities
  - treatment to low levels
  - effective on some hard-to-treat compounds
- *Disadvantages*
  - requires spending "today's" money to get fast cleanup
  - involves handling powerful oxidants, and carries special safety requirements

### Advantages and Disadvantages of In Situ Bioremediation Method:

- *Advantages*
  - low cost
  - very effective for cleaning soil polluted with oil of middle fraction
  - very natural method of clean up
- *Disadvantages*
  - exists no equipment which could clean up oil polluted sites with depth of > 1m.
  - requires more water
  - not quite effective for cleaning soil polluted with oil fractions
  - long period required for clean up
  - not effective for cleaning heavily polluted sites

### Advantages and Disadvantages of Solidification and Stabilization Method:

- *Advantages*
  - hazardous components like PAH and olefins are corked up and waste is converted into not hazardous one
  - short period of cleaning
  - more CaO required
- *Disadvantages*
  - more water required

## CONCLUSION

### I. Economical Effectiveness

**Chemical Oxidation Method** – quite cheap method. The cost for clean up 1m<sup>3</sup> of polluted soil is from US\$15 to US\$50 in dependence of level/depth of pollution. Materials required for using this method is available in a limited quantity in Azerbaijan.

**In Situ Bioremediation Method** – the cheapest method. The cost for clean up 1m<sup>3</sup> of polluted soil is from US\$5 to US\$25 in dependence of level/depth of pollution. Materials required for using this method is completely available in Azerbaijan.

**Solidification and Stabilization Method.** The cost for clean up 1m<sup>3</sup> of polluted soil is from US\$25 to US\$50 in dependence of level/depth of pollution. Materials required for using this method is completely available in Azerbaijan.

### II. Treatment Effectiveness

**Chemical Oxidation Method.** Contaminants of concern commonly (COCs) remediated through oxidation technologies include chlorinated solvents, PAHs, and petroleum products. This includes PCE and daughter products, the BTEX compounds, as well as naphthalenes. Stronger oxidants have been proven to be effective with chlorinated alkanes (chloroform, carbon tetrachloride, etc.)

#### *Oxidant effectiveness for contaminants of concern*

Oxidant	Amenable COCs	Reluctant COCs	Recalcitrant COCs
Permanganate (K)	PCE, TCE, DCE, VC, BTEX, PAHs, phenols, high explosives	Benzene, pesticides	TCA, carbon tetrachloride, CHCl <sub>3</sub> , PCB

Chemical Oxidation Method can clean both strongly and weakly polluted sites. The depth of clean up can be up to 12 meters.

**In Situ Bioremediation Method.** The method of bioremediation is the most natural one for soil clean up. However, microbiological method better cleans oil products with medium fraction (C<sup>10</sup>-C<sup>18</sup>). These oil products do not influence on vital functions of oil-decomposed microbes. Light fraction (C<sup>4</sup>-C<sup>9</sup>) is very hard to be cleaned by microbiological method, and so these oil products negatively influence on vital functions of oil-decomposed microbes. Heavy fraction (C<sup>21</sup>-C<sup>40</sup>) of oil beginning since C<sup>21</sup> to C<sup>35</sup> is effectively cleaned up by microbiological method, but bitumen and asphaltens (C<sup>35</sup> до C<sup>40</sup>).

**Solidification and Stabilization Method.** The Solidification and Stabilization Method was originally developed for the immobilization of heavily oiled sludges, water-in-oil emulsions, oil-contaminated wastes, and industrial wastes such as acid-tars. All of these wastes contain liquid hydrocarbons. The Solidification and Stabilization process caused a major decrease in many hydrocarbons. Both volatilization and Ca(OH)<sub>2</sub> encapsulation may have played a role in the disappearance of these organic constituents. Lower-molecular-weight volatile constituents, such as BTEX, are no doubt lost to volatilization; however, intermediate- and higher-molecular-weight petroleum hydrocarbons are probably largely sequestered into the newly formed Ca(OH)<sub>2</sub> matrix.

Heavy metal immobilization would seem a natural application of the Solidification and Stabilization technology because many heavy metals form insoluble hydroxides and carbonates. In fact, the Solidification and Stabilization treatment greatly reduced the mobility of Zn through greenhouse soil columns. Solidification and Stabilization process was successful in stabilizing liquid organics and heavy metals but not solid-phase organics.

This work also demonstrated a favorable influence on plant growth of the Solidification and Stabilization treatment of heavy metal contaminated soil. The high alkalinity of the Solidification and Stabilization product helped neutralize the heavy metal mobility, which led to improved plant growth. This work demonstrated that the Solidification and Stabilization product is compatible with revegetation of contaminated sites and can be used for the remediation of severely contaminated soils, where several technologies may be necessary to fully remediate a site.

## Oily Soil Clean Up Project (MSGP-AZ05-04)

*CASAM Butan Tex Company*

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### **Progress Technical Report (Phase I: Jan-Apr 2005)**

#### **SUMMARY**

CASAM Butan Tex Co staff participated in and made a presentation at the CEP UNDP MSGP Grantee Orientation Meeting in December 2005. The Memorandum of Agreement (MoA) was signed between United Nations Office for Project Services (UNOPs) and Mr. Nurlan Maharramov, Director of CASAM BUTAN Tex Co (GRANTEE) about fulfillment of the oily soil clean up project. An official letter of allocation of the site in Buzovna area belonging to oil and gas production unit was given by State Oil Company of Azerbaijan Republic to CASAM Butan Co to implementation of the Oily Soil Clean Up Project. A project team was established in order to manage and execute the project. In addition, two experts/specialists from the National Academy of Sciences were hired on consultative basis.

As per the project workplan, the team was collecting and assessing the existing background data regarding oily polluted sites on Absheron and undertaken measures towards cleaning up them. The project staff has informed local community about launching the oily soil clean up project in Buzovna settlement directly and through municipality and Binagadi executive power. The project implementation was very welcomed and encouraged by local population. The project team had over 20 visits to the project site (Buzovna settlement) to conduct pre-project activities and to assess a type and degree of contamination of soil. The specific sampling program was worked out at the site. A full quantitative analysis of chemical and radioactive elements in soil of the project territory was carried out. The results of laboratory analyses are shown below.

In order to select a subcontractor to conduct the clean up works, several experienced companies were invited to submit their proposals. As a result of tender conducted, an Eco Tech Services (ETS) was selected as a winner based on cost and service offered. Under phase I of the project, some purchases of supplies such as mineral fertilizers; chemicals; and bioremediation products were procured.

## I. Collection and Assessment of Existing Background Data

In the environmental safety risks system of modern Azerbaijan one resource-environmental component has been formed historically recently since pre-Soviet period. It can be shown mainly in intensive anthropogenic change of nature-resource potential of ecologically extremely sensitive territory of Absheron peninsula and adjacent Caspian water areas.

Total area of grounds and ponds polluted with oil and oil products makes more than 8-9% from Absheron territory. It's known that ecological-socio-economic effect in any region is achieved at different square ratio of transformed and natural ecosystems: appropriate ecological balance appears at the ratio 40% of the first ones to 60% of the second ones. However, for Absheron region deviation from normal status in ecosystem structure is 2 times more. The emissions density on 1 km<sup>2</sup> of peninsula territory makes more than 285t/year – i.e. 10 times more than in Japan. The average module of man-caused pressure of crude oil (14.0 million ton of oil was produced in 2000 year) is more than 5000 t/km<sup>2</sup>/year – i.e. 60 times more than in the average in Azerbaijan. Rather remarkable indicator of man's load is energetic load: energetic load for the given territory is 1140 Kvt/ km<sup>2</sup>, exceeding permissible one in 11.0 times. At steadiness index standard  $I_{sd} > 1$ , development steadiness index of given region is 2 times more, i.e.  $I_{sd} > 2$ , which is inadmissible.

Unit well-being index of any country with land resources is used while analyzing the state and perspective of socio-economic development of countries and separate regions owing to food and population problems. Predominance of oil producing, oil processing, chemical, energy, engineering, metallurgy, agro-industrial fields in economics structure has caused formation of a great deal of man-caused environmental systems and firstly on Absheron which led to wide landscape change spectrum. These systems cause some changes of geo-chemical, hydrological, geophysical and other parameters of ecosystems. Among all the measures on optimization of ecological-resource potential of the environment the main priority for ecocatastrophe prevention is given to pollution control.

Among polluted grounds, the first place takes soils polluted with oil and oil products. The most acute situation is taking place on Absheron peninsula where the antagonisms between nature and socio-economic activity of man for the recent 150 years are concentrated in most contrast form. The history of oil production on Absheron has influenced mostly on all the landscapes of Absheron peninsula. It's enough to mention that there are more than 10-15 thousands hectare of soil on peninsula, i.e. 7-10% of all territory, polluted with oil, oil products, drill cuttings and refinery wastes. So, at the moment more than 7,400 he of oil polluted soil, 2,800 of which must be cleaned in the first place, are on the balance of State Oil Company Azerbaijan Republic

(SOCAR). Self-regulation processes in oil polluted soils and ponds do not provide self-recovery of these ecosystems. Absheron industrial region is not completely sufficient. At the same time, reproductive potential of the given territory is not capable to “neutralize” effectively anthropogenic loads.

Besides the above, according to systematic regularity the territory of Azerbaijan, being the weak socio-economic and ecological system, can not exist for a long period in more primitive ecological state having an “ecological swelling” – Absheron peninsula. It’s impossible to get maximum socio-economical-ecological effect without fundamental change and recovery of ecological situation on Absheron peninsula. Since recently, the government of the country has taken measures on solution of ecological problems including clean up of oil-polluted soils. In particular, as a result of joint work of Azerbaijan Government and World Bank -- “the National Plan of Actions on Environmental Protection” was prepared (NPAEP) in 1998. Among basic ecological problems, NPAEP includes the point about great damage from environmental pollution, caused by industrial enterprises and oil production. Clean up of oil-polluted territories is one of the foreground tasks and includes purification measures of Apsheron territory, which is regarded as the territory of first urgency.

According to NPAEP (1998), most of the territory on Absheron peninsula may be interesting for house building both now and in the future. According to the estimations, the average cost of 1 he will be equal to US\$10,000. If 25-50% of polluted territory on Absheron peninsula were appropriate for house building, then the cost of the territory would be US\$25-50 million. However cost rate of this territory will commensurate with economic growth rate. In connection with the fact that economic growth rate in Azerbaijan for the recent 5 years made in the average 5-7% per year and this rate will be kept within the next few years, it’s possible to forecast the appropriate growth of territory cost. In accordance with the existent legislation, oil polluted territories being at the moment on SOCAR balance after clean up must be returned to local authorities. In that way, the potential customer of cleaned territories may be local city and/or municipal officials that will allot some territories under planting of greenery and house building based on long-term development plans. This is rather important problem for Azerbaijan as a whole and for Absheron peninsula especially where the territorial area per 1 person makes only 0.02 he, i.e. 20-30 times less than normal one.

Thus, development of clean up technologies of soils polluted with oil and oil products as well as ones for drill cuttings on hydrocarbon basis, their scale practical realization can be treated as priority ecological, socio-economic problem not only for Absheron peninsula, but also for the whole country. The definite activities concerning Absheron polluted soil clean up and reclamation problem solution were carried out for the last 3-4 years with the participation of international organizations and companies. In particular, some activities on selection of local technology (method of clean up with assistance of hydrocyclones was mainly examined) on clean up of oil-polluted soils was used in

republic in 2000 according to TESIS program. Bioremediation clean up technologies were used to removing small oil spills nearby Baku-Novorosisk oil pipeline in period of 1997- 2000. However, there was no any hectare of the territory cleaned from oil.

Moreover, some activities on Mashtagi area concerning the testing of bio-treatment methods were finished together with Czech company KAP with the cost of the project in US\$480,000. Azecolab Company cleaned up about 4 he of oil-polluted territory by remediation method in the framework of Matched Small Grants Program in period of 2003-2004. Since 2004, Aztrans Co. together with a US company has launched clean up works of 50 he of oil polluted site nearby Binagadi area.

## **II. Location of the Project Site**

The project site is situated nearby Buzovna area at territory of oil gas production unit named after H.Z. Tagiev. Exact coordinates of the site were fixed by GPS equipment:

4. 40°30'36,1"    2. 40°30'37,0"    3. 40°30'36,4"    4. 40°30'37,4"

Size of the site is: Width –70 m and Length – 143 m. The level of pollution is mosaic and has both strongly polluted and weakly polluted areas. The depth of pollution makes from 0,2 m to 1,5 m.

## **PHOTOGRAPHIC PICTURES OF THE SITE**

## **III. Examination of the Project Site Initial State**

To study an initial state of the site, the following activities were carried out:

- (1) Site state visual inspection
- (2) Pollution depth study
- (3) Sampling program
- (4) Chemical analyses
- (5) Radioactivity measurement

### *Site state visual inspection*

The level of pollution is mosaic and has both strongly polluted and weakly polluted areas. The main reasons for pollution is due to oil spills from nearby petroleum wells which are not functioning at the present time. The oil products are in both liquid and solid stage. It can be presumed that there are only heavy fractions of oil products as light and medium fractions are evaporated. Some photo pictures were done at the place.

## **Pollution depth study**

As a result of study, the depth of pollution was identified. Toward this end, the observed holes were made in some parts of the site and then sampling was done by special soil sampler. All the samples were analyzed then. It was fixed that the depth of pollution is variable of 0,2 m to 1,5 m.

## Sampling program

To make sampling procedures, a special program was prepared. For study of site state, the samples were taken from different parts that (as we seem) maximally characterize the site pollution. These samples were taken from different depths. The basic issues of the sampling program was carried out as follows:

- The project site was divided on several parts where the marked indicators (wood dibbles and columns) were set up to control the site parts for future samplings. Although the parts can be of any size, in our cases they were not exceeding 0,15 he what is more practicable. To take samples in area of 1 he, the project site was divided on 7 sampling parts. For this purpose, we used the marked indicators (wood dibbles and columns). At least one mixed sample was taken from sampling parts. Total number of samples was not less 7. In case we found the pollution of the parts variable, a number of mixed samples were increased.
- Two mixed samples were sent to laboratory analyses and one left in case of need to be analyzed in future.
- The results of analyses were reviewed and compared with control indicators which should be achieved on the site after clean up activities. The control indicators of clean up on the site parts made up 2% of oil products in the soil. The results of first and second samples were compared and their difference was not more than 10% of low level of concentration.

## Chemical analyses

LABORATORY ANALYSES									
Client-Field	Ref.#	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
Analyses									
<i>TPH</i>	g/kg	117,2	44,14	33,58	75,55	55,11	81,18	43,24	143,6
<b>pH</b>		8,04	7,15	7,22	7,54	7,22	7,85	7,17	8,11
<b>K</b>	mg/kg	4700,5	5925,9	5436,7	5143,7	6143,8	4984,6	6254,9	4374,8
<b>Total P</b>	mg/kg	10,1	49,6	54,9	12,7	45,7	10,8	60,6	9,7
<b>Total N</b>	mg/kg	911,5	743,1	742,4	845,5	744,4	856,6	742,1	885,7
<b>Humus</b>	%	0	0,06	0,05	0	0,05	0	0,06	0
<b>Total Organic</b>	g/kg	162,5	47,37	35,96	93,45	67,45	99,13	55,12	157,18
<b>Water</b>	%	39,3	16,1	19,5	27,3	22,5	31,5	27,4	30,4
<b>Soil</b>	%	43,83	78,1	79,23	63,13	70,21	57,6	66,5	52,89
<b>S</b>	mg/kg	0,15	0,22	0,19	0,11	0,10	0,096	0,046	0,075
<b>As</b>	mg/kg	11,12	2,18	3,87	8,67	2,89	3,42	3,48	7,65
<b>Ba</b>	mg/kg	98,81	132,32	156,2	176,8	112,2	78,9	99,4	135,2
<b>Cd</b>	mg/kg	0,173	0,442	0,113	0,356	0,164	0,123	0,167	0,195
<b>Cr</b>	mg/kg	31,41	22,13	19,75	45,84	22,11	23,41	23,18	35,12
<b>Co</b>	mg/kg	5,09	4,14	4,15	6,11	5,14	4,78	2,93	4,11
<b>Cu</b>	mg/kg	16,3	9,38	9,21	14,13	7,18	8,18	6,27	11,15
<b>Fe</b>	mg/kg	4373	6735	8834	11724	8356	10893	3678	9967
<b>Pb</b>	mg/kg	7,11	5,18	5,11	18,95	6,41	7,19	5,18	9,89



V	mg/kg	31,34	25,2	18,17	46,8	19,21	18,8	28,45	36,1
Zn	mg/kg	15,56	18,67	19,11	31,13	28,18	16,47	27,11	23,14

As per results of analyses, the pollution level in some parts of the site is > 6% and some others – < 6%.

## Radioactivity measurement

Medium level of radiation background on Azerbaijan is 18 micro roentgen/hour. The level of radiation background on the site is changed from 10 to 20 micro roentgen/h which is acceptable to conducting the works at the site.

## Plans for Phase II

Under the phase II, the CASAM BUTAN Tex Co plans to start pilot clean up operations. For this purpose, we will contract an ETS company which was selected as a result of the tender to clean up 1 ha of the polluted territory. All the info and detail of laboratory analyses will be shared with the ETS before the clean up works launch. Together with the ETS Co., we also plan to assess an economical potential of the reclaimed wastes and assess available waste clean up and utilization technologies. The period of clean up operations is about 6 months, including planting of trees on contaminated site. We intend to purchase the rest of supplies such as chemicals and bioremediation products to be used during the practical works as well as fully use our Butan Injector 2000 TM technology to clean the site. In addition, we will start preparation to the workshop where relevant specialists and experts can share each other their views, technologies and proposals how efficiently recultivate oil-polluted lands in Azerbaijan.

We assume the second project phase activities to cover the period of April through September (quarter 2 and 3 as per the workplan). As most part of the project is to be fulfilled under phase II, we will need for \$28,950 which is 72,5% of total grant. The last 12,5% of the grant funds is to requested after completion all the operation works. From our share, we already made \$11,950 of matching funds and \$17,000 of in-kind contribution for execution of the second project phase. Totally, the CASAM Butan has made \$15,300 as matching and \$20,000 as in-kind which is 88.25% of its own contribution for implementing the first two phases of oily soil clean up project.