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ENVIRONMENTAL SERVICES FOR CLEANUP OF HAZARDOUS WASTE SITES

Remediation of polluted sites may be achieved by either removal (cleanup) of contaminants or preventing them from being spread (by isolation or immobilisation). The most frequent cleanup techniques currently available for practical application to contaminated soils are biological, chemical and thermal conversion or (physical) separation from the soil followed by concentrating them within a small volume. Managing sites polluted with heavy metals requires the assessment of the various remediation alternatives which may be applied, i.e. electroreclamation, bioleaching, phytoremediation, immobilisation. There is a strong challenge for the future, further to develop new and cheap remediation techniques for soil cleanup.

LIST OF SYMBOLS

TCE – trichloroethylene,
PCE – perchloroethylene,
PCB – polychlorinated biphenyls,
PE – polyethylene,
PH – petroleum hydrocarbons,
TPH – total petroleum hydrocarbons
PAH – polycyclic aromatic hydrocarbons.

1. INTRODUCTION

Hazardous waste disposal today is a worldwide environmental problem. During the last decade great efforts have been made to develop techniques for remediation of contaminated soil [1]–[3]. Techniques successfully applied in practice for the cleanup of excavated soil are thermal treatment, extraction/classification and bioremediation [4]–[6].

During the past years the approach of soil remediation has been shifted more and more from complete cleanup after excavation to complete or partial in situ cleanup

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(i.e. biorestoration, extraction, soil venting). It is a technological challenge to improve techniques and to develop treatment systems for the cleanup of soil in temporary disposal sites and of very large, diffusely polluted areas which were the subject of Comco Martech activities on the territory of Central Europe as well [7], [8]. Comco Martech is a full-service environmental firm, committed to providing innovative, practical and affordable technological solutions to Central Europe's environmental problems. The state-of-the art services include soil remediation and water treatment, preparation of waste management strategies, environmental risk appraisal and assessment [9], [10]. Martech USA Inc. provided the technologies and field experience instrumental in the Alaskan Valdez oil spill cleanup effort and in the post-Gulf War cleanup in Saudi Arabia and Kuwait. Comco Holding AG provides substantial financial assistance for Comco Martech endeavours.

The scope of this paper is to discuss briefly several principles and relevant factors technologies of cleanup as well as to survey the most important techniques for cleanup of excavated soil and in situ treatment. Company's experience observed during the practical application and project's operation will be mentioned, too.

2. BIOREMEDIATION OF EXCAVATED SOIL ON BIOPAD AND IN CONJUNCTION WITH SOIL WASHING TECHNIQUE

Due to the fact that soil pollution has been caused mainly by industrial activities, the types of pollutants observed in different countries look very similar (volatile and non-volatile aliphatic and aromatic hydrocarbons such as petrol, benzene and polycyclic aromatic hydrocarbons, halogenated organic compounds, i.e. TCE, PCE, PCB and pesticides, heavy metal compounds, free or complex cyanides and the others).

Regarding the history of the polluted site, three factors have relevance for soil cleanup, especially for in situ cleanup: the way the site has been polluted, the way the site has been used after it has been polluted and the time interval inbetween.

Basically, there are four different principles for their removal, i.e. molecular and phase separations, chemical destruction and biodegradation. All types of cleanup methods make use of the specific differences in properties between the pollutants (or polluted particles) and the soil particles.

The main properties, which may be the basis for a cleaning technique, are volatility, solubility, chemical and thermal instability, biodegradability of pollutants, adsorption or absorption behaviours, magnetic properties, size, shape or density of particle pollutants [11], [12].

In ex situ biodegradation processes, microorganisms are used for conversion of contaminants into water, carbon dioxide and residual bacterial biomass. Natural conditions for biodegradation are not favourable for achieving a progressive cleanup. Currently, there are several biological techniques available for ex situ soil treatment, i.e. land farming, sludge farming, bioreactors, natural lagoons, composting, biostimulation on biopad with and without covering (glass, PE).

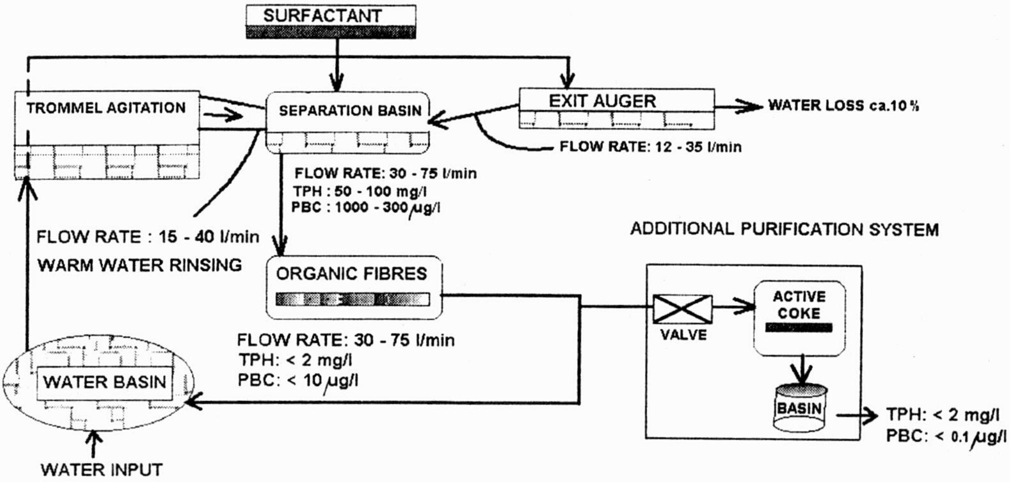

Figure. Flow diagram of the soil washing process

The practical application of bioremediation is limited to the removal of easily biodegradable compounds such as petrol and low-molecular aromatic hydrocarbons [8], [13]. The main reason may be in low bioavailability of contaminants determined by the desorption from the soil particles. Therefore several prospects for improving the above process used to be applied, i.e. inoculation of cultivated microorganisms, especially for the sites contaminated with chlorinated compounds and for reducing mass transfer limitations separation of the soil into an easily biodegradable fraction using the physical method.

Extraction/classification or soil washing is a treatment method in which the pollutants are removed from the soil by means of an extracting agent. Basically, the extraction process consists therefore in an intensive mixing of contaminated soil and extracting agent, separation of both – the used agent and soil particles, as well as in the treatment of extracting agent. The process may be intensified by the addition of chemicals such as inorganic and organic acids, complexing agents, sodium hydroxide, detergents or surfactants [6], [7].

Several physical and chemical wastewater treatment systems are available for cleaning the separated extracting agent (i.e. active coke, fibroil, vapex adsorption). Generally, extraction/classification of excavated soil is a cleanup process suited to treat sandy soils or sandy soils with clay and humic content of less than 10 to 15%.

2.1. CASE HISTORIES

Comco Martech performed field biodegradation and has completed preliminary site assessments at eleven former Soviet military bases throughout Hungary and Czechoslovakia. Remedial services based on soil and groundwater sampling, a review of historical documents and physical site inspections were provided at four of the eleven bases.

Following the site assessments, which included determining the location and detection of the presence of remaining munitions, company completed the demolition of remained weapons, the excavation and preparation of contaminated soils, treatment of contaminated soils and the final site restoration.

The Comco Martech was contracted to assess the extent and magnitude of environmental problems caused by lagoons of mixed refinery and coal gasification waste products in the northeastern Bohemia. Company's experts determined that due to the relatively low levels of hazardous chemicals, the waste could be recovered as a low-grade industrial fuel. Some treatment methods have been developed to dewater the waste, so that the waste could be converted into a fuel meeting European specifications. The end result was an effective remediation plan with costs defrayed by the sale of the waste as fuel.

Regarding another project, two green houses (biopads of 12×45 m) were constructed at a selected site for treatment of about 1000 tons of soil contaminated with gasoline and other light fractions of petroleum hydrocarbons (PH). The storage area (used Asphalt Recycling facility in Austria) was lined with a sealed watertight asphalt and a collection system for rainwater runoff. Eluate analyses of the initial preatreatment samples showed that the highest concentration of PH in the soil eluate was 4 mg/dm^3 and an average concentration – 1.8 mg/dm^3. About two months lasting enzymatically enhanced biotreatment was realized to suppress the total PH concentration to a sufficiently low level [8], [14], [15].

Sampling of the material to determine the concentration of contaminants took place on a monthly schedule. Samples were analysed for soil nutrients, total petroleum hydrocarbons (TPH) and on microorganism count (by classical plate count method).

Each week a strict regime was followed to ensure the optimum process (tillage, fertilizing, moisturing, pH adjusting, etc.). As soon as the data indicated that the cleanup objectives had been reached, the soil was removed from the treatment cells and used in the asphalt recycling production.

An asphalt production plant in former Czechoslovakia contaminated by PH as well as by PCB (production of asphalt was stopped in 1986 when the contamination was identified) has been planned for cleanup using the Comco Martech soil washer [6], [7], [14].

Commercial product of PCB Delor 103 produced in Czechoslovakia till 1984 was used in heat-exchanger medium by the processing of asphalt. On the base of insufficiently protected concrete and asphalt surface area, the leachate of heating medium caused the pollution with PCB. Since 1986 the site has been continuously analysed. The main zone of contamination (PCB higher than 6 mg/kg) estimated by the volume of 2500 cubic meters was excavated and temporarily placed at the protected deposit for the planned soil washing. Structure of this material was appropriate to undergo the soil washing process on the base of approximately 60% content of sandy particles of the size higher than 3 mm.

Bench-scale treatability study was performed before the field pilot treatment was accomplished. Three types of surfactants were tested at laboratory (DetClean, Universal Acies, and EarthWash Detergent) for enhancing the wash treatment in separator – screw units in real conditions.

Some progress in laboratory bench-scale studies which demonstrated approximately 60% efficiency of PCBs and PH washout from the asphalt plant samples caused that at the asphalt plant the coarse material washing process was simultaneously started to examine the treatment efficiency in pilot scale. A simplified flow diagram of the soil washing process is sketched in the figure.

However, on the base of insufficient time-table managing and organization and due to excessive machinery assembling, financial deficiency and generally some fears to use a new, unconventional soil treatment, the soil washing technology in the selected locality failured in the end. A secure landfill, excavation of soil and incineration as well as partial immobilization of soil have been chosen to solve the above problems, finally.

3. CLEANUP OF LARGE AREAS DIFFUSELY POLLUTED WITH ORGANIC OR/AND INORGANIC COMPOUNDS

In highly industrial regions of Central Europe, there are large areas at which the top layer of the soil is diffusely polluted with inorganic and/or organic pollutants. For the cleanup of such areas several principles derived from the experiences in the foregoing projects could be applied. Basically, they have to be relatively simple, cheap and treatment time has to be in contradiction with ex situ methods sufficiently long. The process has not to exhibit any negative environmental impact and the results of such cleanup may not always achieve the necessary clean soil standards. Though the principles of these methods are known, there is still a long way to apply them in real conditions.

Several methods of such a process are: utilization of green plants which posses the capability to accumulate the pollutants [16], [17], addition of the small amounts of chemicals into soils to promote microbiological degradation or cultivating the top layer of the soil to promote natural photochemical conversion or biodegradation [18]–[20].

Potential alternatives to predominantly inorganically polluted sites, especially with heavy metals, are electroreclamation, bioleaching, heperaccumulation of heavy metals in green plants (phytoremediation) and soil remediation by isolation or immobilisation.

By electroreclamation method an electric current is generated between a cathode and anode horizontally or vertically installed in the soil. Mostly metals adsorbed onto the clay soil particles or bound as oxides, hydroxides, carbonates will dissolve and thus be separated from the soil.

By bioleaching process the heavy metals in soil can be mobilized by several types of acidophilic, aerobic and autotrophic bacteria (*Thiobacillus* genus), which oxidize reduced sulphur compounds to sulphuric acid. If no sulphides are present in the soil, an external reduced sulphur source may be added. Bioleaching can be performed either in more reliably controlled soil–slurry systems or by heap-leaching. However, no practical application of bioleaching processes in the treatment of contaminated soils has been reported so far.

The removal rate with phytoremediation may be lower by several orders of magnitude compared to intensive, ex situ process. Several plant species growing in a moderate European climate, such as *Polygonum sachalinese*, *Thlaspi*, *Alyssum*, *Urtica*, *Chenopodium*, are usually cultivated on the soil under optimal conditions, so that the highest possible quantities of metals will accumulate in their shoots or other harvestable parts. The opinions voiced on this technique are rather controversial [16], [18], [21]. When vegetative uptake of heavy metals is considered, special measures should be taken to reduce the risks connected with the spreading of contaminated biomass over the environment, which may endanger wildlife or agriculture production. The other aspect of phytoremediation is the treatment technique employed to remove the heavy metals from the contaminated biomass [17].

Techniques not intended to remove heavy metals but focused on the isolation of a site or immobilisation of heavy metals are usually applied, when cleanup of the soil is unfeasible [22], [23].

3.1. CASE HISTORY

The objective of the Comco Martech project directed towards chemical factory in Slovakia was to submit preliminary analytical data beneath the enterprise impacted by mercury releases. The main impacted areas in this facility were acetaldehyde production, mercury cell production and mercury distillation plants.

Soil samples collected outside these three areas contained mercury at average concentrations of 0.374 mg/kg. Reportedly mercury contamination of soil is primarily elemental (metallic) in form [22], [23]. Groundwater samples collected from several places within the enterprise contained mercury at the concentrations ranging from 0.006 to 0.01 mg/dm^3. These samples were collected from maximum depths of 10 meters. Soil samples were collected at discreet intervals, using hand auger and a diesel powered drill rig. Samples were transported to laboratory in glass containers with air-tight Teflon lined lids, stored in an insulated chest at a constant temperature of 4° C under chain of custody. Typical soil analyses included pH, porosity, density, particle size, dissolved solids, moisture content and total mercury content.

In Slovakia, the standard for total mercury in soil characterized as hazardous waste is 10 mg/kg and the criteria for the soluble component of the total mercury as related to the weight of the soil tested is 1 mg/kg. The underground water limit necessary to be decontaminated is for mercury 0.005 mg/dm^3. In California, USA, the standard for total mercury in soil is 20 mg/kg and for soluble mercury is 1 mg/kg [24].

As a result of investigation the cost effective technology for mercury recovery was recommended (i.e. roasting, soil washing, solidification of the hazardous waste for storage at an encapsulated landfill equipped with a leachate collection system). A review of in situ remediation techniques was prepared to address the mercury contamination at this enterprise. There are: slurry wall technology, interceptor trench and recovery, grout walls and curtains, sheet piling, removal of elemental mercury, passivation or insolubilization of elemental mercury [22].

4. CONCLUSIONS

Future development of soil cleanup may be directed partly to the application of extensive treatment, because soil contamination is nowadays very serious and widespread problem. The treatment time will not be longer a limiting factor and the future technologies will probably be focused on creating mild treatment conditions as well as keeping the cost low.

It should be clear that for financial, technological, environmental, geographical or social reasons, it is mostly unfeasible to cleanup soil or soil sites contaminated with heavy metals or other hardly biodegradable pollutants. In order to prevent such pollutants from spreading, various combination techniques with in situ soil site isolation are expected to be improved perspectivelly.

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SŁUŻBY ŚRODOWISKOWE OCZYSZCZAJĄCE MIEJSCA SKAŻONE NIEBEZPIECZNYMI ODPADAMI

Skażone miejsca można przywrócić do pierwotnego stanu albo usuwając zanieczyszczenia, albo zapobiegając ich rozprzestrzenianiu się (przez izolację lub unieruchomienie). Obecnie w przypadku skażenia gleb najczęściej stosuje się metody biologiczne, chemiczne oraz termicznej konwersji lub separacji. Są one poprzedzone zagęszczaniem zanieczyszczeń do małej objętości. Zarządzanie miejscami skażonymi metalami ciężkimi wymaga oceny, które z różnych metod można zastosować, np. biologiczne wymywanie, użycie prądu, roślin (akumulujących zanieczyszczenia) lub unieruchomienie zanieczyszczeń. Oczyszczanie środowiska jest wyzwaniem, które każe rozwijać nowe i tanie techniki oczyszczania gleby.