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REMEDIATION OF THE POLLUTED SOIL ON THE NIS-RNS LOCALITY

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ABSTRACT
NIS-RNS Oil Refinery in Novi Sad (NIS-RNS) is the only refinery in Serbia and Montenegro which produces both energy fuels and lubricants and has the annual capacity of 2.5 mil t. NIS –RNS is a complex of processing facilities and oil products, tankage, transport and manipulative, research and laboratory space, and other facility objects, covers an area of approximately 156 ha of the industrial area and is situated on the left river bank of the Danube. The main production program included production of: motor gasoline, diesel fuel, low sulfur fuel oil, lube oils, bitumen.
During NATO intervention in 1999, all processing units in Refinery were damaged. More than 51% of the available Refinery tankage for the storage of crude oil, oil products, utility components etc., were destroyed and more than 34% of tankage were severely damaged during bombing.
Contaminated area on the location of the 85,524m^2 i.e. 8,5ha (about 4,6%) and contaminated soil is around 40,000m^3.
This paper presents results of amogeochemical research on determination of concentrations of volatile organic compounds (VOC) in 17 identified contaminated areas, and describes methodology of identification of contaminated spots, quantification of toxicants (with oil and it's derivates) and gives summary of the recommended work process (type of contaminant, contaminated area, lithological profile, depth, excavation process, incineration of contaminated soil, ex situ bioremediation).
In this study, two possible ways of resolving the problem of the polluted soils by VOC are suggested: Incineration - app. 14.800t of highly contaminated soils, and Biological decontamination ex situ: 16,800t of contaminated soils.
KEYWORDS:
determination, remediation, incineration, ex situ bioremediation

1. INTRODUCTION

NIS-RNS Oil Refinery in Novi Sad (NIS-RNS) is the only rafinery in Serbia and Montenegro which produces both energy fuels and lubricants and has the anual capacity of 2.5 mil t. The main production program included productions of: motor gasoline, diesel fuil, low sulfur fuel oil, lube oils, bitumen. NIS-RNS is a complex of process units, oils processing facilities and oil products, tankage transport and manipulative, research and laboratory space, and other facility objects.It is located in the town industrial area of Novi Sad North IV. The Area North IV is intended for building large industrial objects and covers an area of 1.735 ha. NIS-RNS covers an area of approximately 256 ha of the industrial area North IV, and is situated on the left riverbank of the Danube.

During NATO intervention in 1999, all processing units in Refinery were destroyed or damaged. After the NATO bombardment has ended the identification of the localities and areas of the soil polluted by uncotrolled splling of oil and oil derivates.

The estimated areas of poluted soils is given in the table 1.1.

Table 1.2. Estimated areas of polluted soil

Soil Tipe	Pollution Type	Estimated Area of polluted Soil (m2)
Sand	Unleaded gasoline	4.450
Sand	Leaded gasoline	8.190
Sand	Leaded gasoline	1.700
Sand	Crude oil	1.590
Sand	Crude oil	2.280
Sand	Crude oil	2.900
Sand	Crude oil	5.800
Sand, concrete	Crude oil	23.350
Sand	Kerosine+diesel Fuel+heavy fuel	7.700
Sand	Kerosine+diesel Fuel+heavy fuel	6.000
Sand	Kerosine+diesel Fuel+heavy fuel	4.200
Sand, concrete	Vacuum distillates	540
Sand, concrete	Crude oil	570
Sand, concrete	Crude oil	920
Sand, concrete	Crude oil	620
Sand, concrete	Crude oil	920
Sand, concrete	Crude oil	530
TOTAL		68.470 m2

Total area of the NIS Oil Refinery in Novi Sad is 156 ha, contamination area on the location is 85,524 m^2 (8.5 ha) and contaminated soils is around 40000 m^3(«FOCUS» Assessment Mission 2. 18 july-13 august 1999: Report Ecology). The next table showes the resault of researching on contaminated areas on 25 localities. Whith parameters such as type of contaminant onto contaminated area, lithological profile, depth and volume of contamination soil, TPH (total petroleum hydrocarbons) content in the market area in dry matter, there are three recommended remediation proces of the polluted soil on the NIS-RNS locality:

- Incineration of contaminated soils
- Ex-situ Biodegradation
- In situ biodegradation

Researching in unsaturated zone by chemical analyses of the soil samples showed that contents of TPH (total petroleum hydrocarbons) is raising from <20 to 68,000 mg/kg DM (diphenylaminochloroarsine)

After thorough research, total extents of contaminated areas is 145.600 m^2, but the most important contaminated areas are devided into tree total prioroty by the size of the area that contains contaminated soil, also one of the important parameters are the approximatly weight of contaminated soil:

- Priority I app. 22,060 m^2 (31,700t)
- Priority II app. 21.300m^2 (36.400t)
- Priority III app. 2.600m^2 (5.200t)

The feasibility studies of UNEP shows that soil contamination whith oil and oil products threatens ground and drinking water quality, and health of refinery workes. Ground remediation whith regard to oil constituents is hardly successful, if contaminated soil acts as a permanent polutant source. The proposed approach is soil remediation using thermal treatment for highly contaminated soil, and

microbiological treatment (biopiles) for less contaminated soil and refiilling of excavated soil.

Atmogeochemical research in 17 contaminated areas showed contents of VOC(volatile organic compounds) from <0.001 to 19.300 mg/m^3 of contaminated soil.Concetracion and dispersion of the soil air contamination by VOC sampled by depth of one meter is given in map.

The Summary of the Recommended Work Process

	Type of Contamin ant	Contaminated Area(m^2)	Lithologi cal Profile	Depth of Contamination(m)	Volume of contaminated Soils(m^3)	TPH Content in the Market Area (mg/kg of dry matter)	Manual Excavation of Contaminated Soils(t)	Manual Excavation of Contaminated Soils(t)	Incineration of Contaminated Soils(t)	Ex-situ Biodegradation(t)	In-situ Biodegradation(t)	Priority
3	Ph mixture (light+ heavy product)	9,200	Send, loam, silt, clay	0.0-2.5	19.600	3.400 to 67.000	7.700	11.900	9.200	10.400		I
4	Diesel, slop	3.710	Flood sediments, mud, clay	0.0-1..5	3.00	7.900 to 28.700	2.100	900	1,400	1.600		I
5	Petrol, slop, Diesel	8,900	Send, silt, organic mud, clay	0.0-1.4	1.750	13.00 to liquid phase	700	1.050	800	950		I
7	PH mixture (heavy fuel oil, Diesel, kerosene)	2.200	Sand, clay, loam	0.0-1.4	1.750	13.000 to liquid phase	700	1.050	800	950		I
9	Ph mixture (fuel oil, Diesel, jet fuel, petrol)	1600	Sand, clay and loam	0.4-2.0	3100	4.800 to 15.000	2.300	800	1.400	1.600		I
9	Ph mixture (fuel oil, Diesel, jet fuel,petrol)	1300	sand	Bottom of crater	2100	490 to 15.00	1.900	200		1.400	700	III
11	Crude oil, slop	1.300	sand	0.5-1.3	3.100	18.100 to 38.00	300	2.800		2.200	900	III
13	Crude oil, slop, mazout	2.200	sand	0.0-0.5	1.800	6.800 to liquid phase	1.600	200	850	950		I
14	Crude oil, slop, mazout	1.200	Sand	0.0-0.5	950	Visual contamina tion –liquid phase	800	150	450	500		I
15 - 16	Ph mixture (crude oil, fuel oil, heavy fraction, lubricant oil)	1.950	Sand, loam	0.0-0.5	1500	24.600 to liquid phase	1.300	200	700	800		I

17	Atmospheric residue	8,00	Sand, loam, clay	0.5-1.4	12.800	18.000 to 45.00	1.200	11.600	3.500	7.300	2.000	II
19	Heavy fraction	4.400	Sand, flood sediments, loam, clay	0.0-2.0	10.500	9.500 to 52.000		10.500	2.900	5.900	1.70	II
Prioroty I-total		22.06			31.700		16.500	15.200	14.800	16.800	0	I
Prioroty II-total		21.30			36.400		10.300	26.100	10.000	20.600	5.80	II
Prioroty III-total		2.600			5.200		2.200	3.000	0	3.600	1.60	II
Total amount of contaminated soils		45.96			73.300		29.000	44.300	24.800	41.000	7.40	

FIGURE 1. Map of the Soil Air Contamination by VOC – Sampling Depth 1,0m

Main contaminated areas:

- Number 3, 4, 5, 6, 7, 8, 9 is contaminated by VOC detected in all measured levels.
- Number 10,11 , 23 , 25 is contaminated by VOC detected in the interval up to 1,5m below the surface.

With the level of prioraty, Incineration of contaminated soils and Ex-situ Biodegradation took the first place. By the technique of manual end mechanical excavation and disposal of 31,700t of contaminated soil is provided for remediation in two ways. The first treatment is isineration of app. 14,800t of higly contaminated soil and the second one is biological decontamination ex situ of app. 16,800t of contaminated soil. For the decontamination may be used the undamaged containers at the location of the destroyed high-capacity storage tanks.

2. METHODS

Some of Remediation Technologies will be used in process of solving this particular problem.

Incineration

Both on-site and off-site incineration use high temperatures, 870 to 1,200 °C, to volatize and combust (in the presence of oxygen) halogenated and other refractory organics in hazardous wastes. The destruction and removal efficiency (DRE) for properly operated incinerators exceeds the 99.99 percent requirement for

hazardous waste and can be operated to meet the 99.9999 percent requirement for Polychlorinated biphenyls (PCBs) and dioxins.

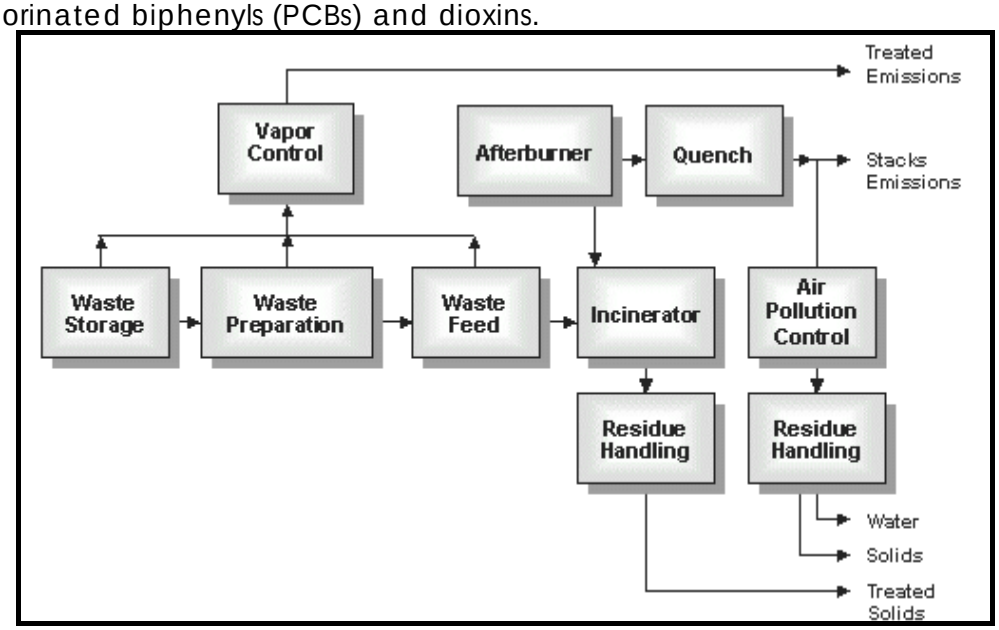

Figure 2. Incineration method

Circulating Bed Combustor (CBC)

Circulating bed combustor (CBC) uses high velocity air to entrain circulating solids and create a highly turbulent combustion zone that destroys toxic hydrocarbons. The CBC operates at lower temperatures than conventional incinerators 900 to 990°C. The CBC's high turbulence produces a uniform temperature around the combustion chamber and hot cyclone. The CBC also completely mixes the waste material during combustion. Effective mixing and low combustion temperature reduce operating costs and potential emissions of such gases as nitrogen oxide (NOx) and carbon monoxide (CO).

Fluidized Bed

The circulating fluidized bed (CFB), uses high-velocity air to circulate and suspend the waste particles in a combustion loop and operates at temperatures up to 870 °C. Another experimental unit, the infrared unit uses electrical resistance heating elements or indirect-fired radiant U-tubes to heat material passing through the chamber on a conveyor belt and operates at temperatures up to 870 °C.

Infrared Combustion

The infrared combustion technology is a mobile thermal processing system that uses electrically-powered silicon carbide rods to heat organic wastes to combustion temperatures. Waste is fed into the primary chamber and exposed to infrared radiant heat (up to 1150 °C) provided by silicon carbide rods above the conveyor belt. A blower delivers air to selected locations along the belt to control the oxidation rate of the waste feed. Any remaining combustibles are incinerated in an afterburner.

Rotary Kilns

The rotary kiln is a refractory-lined, slightly-inclined, rotating cylinder that serves as a combustion chamber and operates at temperatures up to 980 °C. Incinerator off-gas requires treatment by an air pollution-control system to remove particulates and neutralize and remove acid gases (HCl, NO_x, and SO_x). Baghouses, venturi scrubbers, and wet electrostatic precipitators remove particulates; packed-bed scrubbers and spray driers remove acid gases. The duration of incineration technology ranges from short- to long-term.

Applicability:

Incineration is used to remediate soils contaminated with explosives and hazardous wastes, particularly chlorinated hydrocarbons, PCBs, and dioxins.

Limitations:

Factors that may limit the applicability and effectiveness of the process include:

- Only one off-site incinerator is permitted to burn PCBs and dioxins.
- There are specific feed size and materials handling requirements that can impact applicability or cost at specific sites.
- Heavy metals can produce a bottom ash that requires stabilization.
- Volatile heavy metals, including lead, cadmium, mercury, and arsenic, leave the combustion unit with the flue gases and require the installation of gas cleaning systems for removal.
- Metals can react with other elements in the feed stream, such as chlorine or sulfur, forming more volatile and toxic compounds than the original species. Such compounds are likely to be short-lived reaction intermediates that can be destroyed in a caustic quench.

Sodium and potassium form low melting point ashes that can attack the brick lining and form a sticky particulate that fouls gas ducts.

Data Needs:

In addition to identifying soil contaminants and their concentrations, information necessary for engineering thermal systems to specific applications includes soil moisture content and classification , the soil fusion temperature, and the soil heating value. A sieve analysis is required to accurately estimate the dust loading in the system for proper design of the air pollution control equipment.

Performance Data:

If an off-site incinerator is used, the potential risk of transporting the hazardous waste through the community must be considered. Approximately 20 commercial RCRA-permitted hazardous waste incinerators and approximately 10 transportable high temperature units are operating. The commercial units are large capacity rotary kilns with afterburners and sophisticated air pollution control systems.

EX SITU BIOREMEDIATION:

This technology uses microorganisms to degrade organic contaminants in excavated soil, sludge, and solids. The microorganisms break down contaminants by using them as a food source. The end products typically are carbon dioxide and water. Ex situ bioremediation includes slurry phase bioremediation, in which the soils

are mixed in water to form a slurry, and solid-phase bioremediation, in which the soils are placed in a cell or building and tilled with added water and nutrients. Land farming and composting are types of solid-phase bioremediation.

Biopile treatment

A full-scale technology in which excavated soils are mixed with soil amendments and placed on a treatment area that includes leachate collection systems and some form of aeration. It is used to reduce concentrations of petroleum constituents in excavated soils through the use of biodegradation. Moisture, heat, nutrients, oxygen, and pH can be controlled to enhance biodegradation. Soil piles may be covered with plastic to control runoff, evaporation, and volatilization and to promote solar heating. If there are VOCs in the soil that will volatilize into the air stream, the air leaving the soil may be treated to remove or destroy the VOCs before they are discharged to the atmosphere.

Biopile is a short-term technology. Duration of operation and maintenance may last a few weeks to several months. Treatment alternatives include static processes such as: prepared treatment beds, biotreatment cells, soil piles, and composting. Excavated soils are mixed with soil amendments and placed in aboveground

enclosures. It is an aerated static pile composting process in which compost is formed into piles and aerated with blowers or vacuum pumps.

Soil piles and cells commonly have an air distribution system buried under the soil to pass air through the soil either by vacuum or by positive pressure. The soil piles in this case can be up to 20 feet high (generally not recommended, 2-3 meters maximum). Soil piles may be covered with plastic to control runoff, evaporation, and volatilization and to promote solar heating.

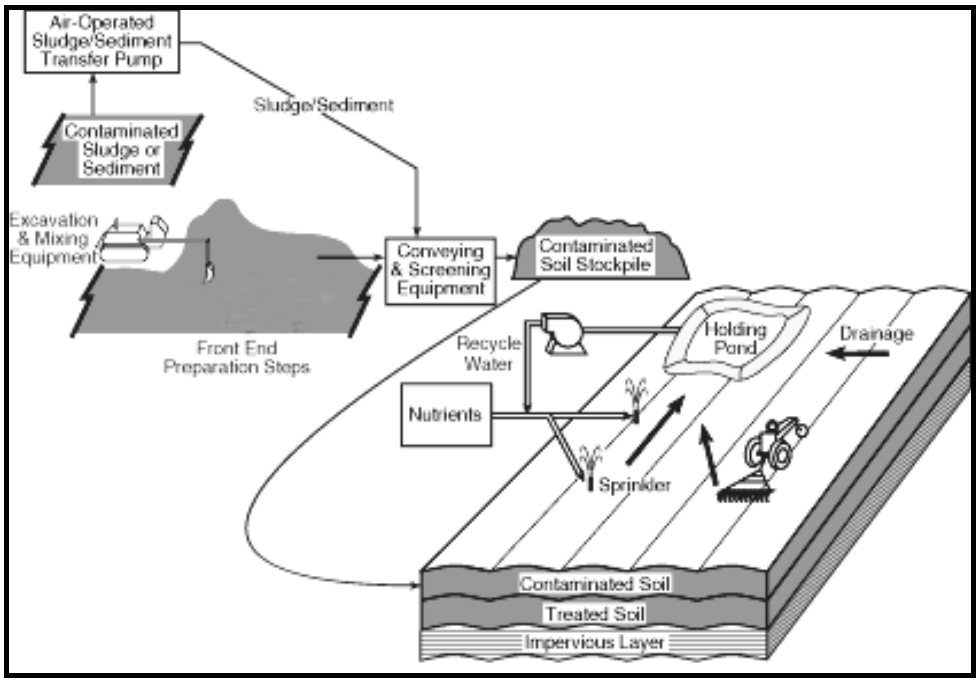

Figure 3. Typical Biopile for Solid Phase Bioremediation

Applicability:

Biopile treatment has been applied to treatment of nonhalogenated VOCs and fuel hydrocarbons. Halogenated VOCs, SVOCs, and pesticides also can be treated, but the process effectiveness will vary and may be applicable only to some compounds within these contaminant groups.

Limitations

Factors that may limit the applicability and effectiveness of the process include:

- Excavation of contaminated soils is required.
- Treatability testing should be conducted to determine the biodegradability of contaminants and appropriate oxygenation and nutrient loading rates.
- Solid phase processes have questionable effectiveness for halogenated compounds and may not be very effective in degrading transformation products of explosives.
- Similar batch sizes require more time to complete cleanup than slurry phase processes.
- Static treatment processes may result in less uniform treatment than processes that involve periodic mixing.

TERRAFERM Biosystem Erde

Regeneration of soil will be performed by **TERRAFERM Biosystem Erde**.The weight of oil contaminated soil that will be treat is 16,000 t and TPH concentracion target level is 1,000 mg/kg soil.The TPH concentracion is determinated by FT-IR instrument.Terraferm bio system earth is effected a biological rent procedure for the reorganization of organically loaded soils, the dismantling of the pollutants in a so-called intensive gang.

3. CONCLUSION

Soil remediation using incineration method for highly contaminated soil and ex situ biological decontamination (microbiological tretment by biopiles) are the necessary and most acceptable methods for bioremediation of the polluted soil on the NIS-RNS locality.

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