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OVERVIEW OF TECHNICAL RESOURCE DOCUMENT FOR SOLVENT CONTAMINANTS AND REMEDIAL OPTIONS AT SUPERFUND SITES

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INTRODUCTION

Solvent contamination is a persistent problem found at numerous Superfund sites. Solvents at Superfund sites are usually halogenated or nonhalogenated organic liquids whose source can be traced to many manufacturing, industrial and commercial processes and uses. Almost half of all Superfund sites listed in the record of decision (ROD) summary database contain solvents as a contaminant.

The contamination usually emanates from the improper disposal of solvents used in a wide variety of industrial and commercial applications such as manufacturing of chemicals, preparation of products and use as cleaning agents. Also the inadequate storage, mishandling and improper applications of solvents have significantly contributed to the problem. Consequently, this has resulted in affecting every medium including soil, sediment, sludge, sub-surface strata, and secondary contamination into air and water, both surface and groundwater. This persistence throughout the environment and the mobility of solvents has created a potentially serious health hazard from toxic exposures to humans. To mitigate this threat, a remedial project manager (RPM) is faced with the challenge of selecting a remedial technology which will achieve established cleanup goals.

Consequently, EPA's Office of Research and Development (ORD) developed a technical resource document (TRD) to assist RPMs and other remedial personnel in making this decision. This TRD was published November 1994, and is available through EPA's Center for Environmental Research Information (EPA/600/R-94/203). The publication discusses solvents, their properties as environmental contaminants and most importantly, the selection of treatment technologies available to reach established cleanup levels in soil at solvent contaminated Superfund sites.

The TRD classifies the appropriate remedial technologies for solvent contaminated soil into 3 main categories; separation, destruction and immobilization. "Separation" includes a group of technologies that extract or separate the contaminant from the soil matrix and form a concentrate or medium that can be more effectively treated. Therefore, this group of technologies prepare or treat solvent contaminated soil matrices for further treatment by either destruction or recovery.

The "destruction" technologies aim to permanently remove the contamination problem and includes those processes that destroy the contaminant by the use of thermal, chemical or biological means. "Immobilization" is the category that includes those methods that stop the spread or minimize the migration of solvent contamination either through the construction of physical barriers, through chemical reactions, or by a combination of both. The remediation of most Superfund solvent sites usually requires a combination of treatment technologies and contaminant control methods. Even if only a single compound type or chemical class is present, generally no single technology is capable of remediating an entire site. As a result, a treatment train is developed which may include immobilization, separation and destruction technologies to achieve site specific objectives and prerequisite cleanup levels.

The technologies discussed in this TRD are in different development stages; proven, innovative, and emerging. For example, some such as incineration and capping, have been proven

on a commercial scale. Others, such as microbial degradation and soil flushing, are less proven, or innovative, and will require site-specific treatability tests to ensure they can meet the established cleanup levels. Emerging technologies, such as horizontal barriers, are expected to be appropriate but have yet to be shown effective in site remediation. To facilitate the remedy selection process and accelerate future cleanups some of these technologies are also being designated as presumptive remedies. This approach is one tool of acceleration within the Superfund Accelerated Cleanup Model (SACM) as is described in an EPA fact sheet (EPA 540/F/93/048).

IN-SITU SEPARATION TECHNOLOGIES

The TRD describes separation technologies as those which remove contaminants from soil to form a stream for either contaminant collection or destruction. They include in-situ technologies such as soil vapor extraction (SVE), steam extraction, radio frequency (RF) heating, and soil flushing; for ex-situ treatment they include thermal desorption (TD), soil washing and solvent extraction.

SVE is an in-situ process that applies a vacuum to sub-surface soil formations through a series of wells and removes volatile solvent contaminants. The technology is being widely applied and is well documented in this TRD and referenced SVE publications. SVE is applicable to vadose zones having permeabilities of 10^{-10} cm^2 or greater and contaminants with vapor pressures greater than 0.5 Torr. Innovative technologies such as hydraulic and pneumatic fracturing have been demonstrated through EPA's SITE program and found effective for extending SVE to less permeable formations.

SVE is usually combined with carbon adsorption or thermal destruction to treat the vapor and liquid waste streams. Other combinations include condensation, biological degradation, and ultraviolet oxidation. Contaminated groundwater can be treated and discharged. Highly contaminated soil tailings must be collected for treatment by another technology, such as incineration. Typical costs for SVE range from $10 - $150 per ton.

Steam extraction or steam injection physically separates volatile and semivolatile organics from soil, sediment, and sludge. The process uses a combination of thermal and mechanical energies generated by steam, hot air, infrared elements, and electrical systems to volatilize contaminants from soil into the vapor phase. Steam extraction is an emerging technology that appears promising, particularly if used in conjunction with SVE. Due to the heating of soil, steam extraction can remove more of the less volatile compounds than SVE. Limited field experience has demonstrated 90% removal of volatile and semivolatile compounds, with better recovery in higher permeability zones and lower recoveries of high aqueous-phase solubility compounds in lower permeability regions. The technology can be used in combination with carbon adsorption to treat both condensed water and vapor streams. Estimates place costs for a stationary system at $50-$300 per cubic yard.

Radio frequency heating is an innovative treatment technology for rapid and uniform in-situ heating of large volumes of soil. The process uses electromagnetic wave energy to heat the soil evenly to the point where volatile and semivolatile contaminants are vaporized in the soil matrix, and vented electrodes recover the formed gases. The concentrated extracted gas and particulate streams can be incinerated or subjected to other treatment methods such as carbon adsorption. The technology is applicable to material that typically volatilize in the temperature range of 80° to 300°C such as aliphatic and aromatic fractions of jet fuels and gasoline, chlorobenzene, trichloroethylene, dichloroethane, and tetrachloroethylene, and is predominantly for sandy soils. Costs vary between $50 - $90 per ton.

Soil flushing is another innovative technology that extracts contaminants from soil with water or other suitable aqueous solutions. Soil flushing introduces extraction fluids into soil using an in-situ injection or infiltration process. This method may apply to all types of soil contaminants, including halogenated aliphatics, aromatics, polar organic compounds and metals. It is used in series with other treatments that destroy contaminants or remove them from the recirculating extraction fluid and groundwater, such as carbon adsorption, metal precipitation and air stripping. Costs range from $50 - $120 per cubic yard.

EX-SITU SEPARATION TECHNOLOGIES

Thermal desorption is also a separation technology but is used for excavated soil. It uses indirect or direct heat exchange to volatilize contaminants and water from soil into a carrier gas stream for further treatment. The carrier gas stream may be either air or an inert gas. Depending on the process selected, this technology heats contaminated media to temperatures between 200° and 1,000° F. Off-gases may be burned in an afterburner, catalytically oxidized, condensed for disposal, or captured by carbon adsorption beds. Thermal desorption can successfully treat most of the contaminants found at solvent sites. It cannot effectively separate metals (arsenic, cadmium, lead, zinc, chromium) or PAHs with boiling points above 1,000° F. Mercury, a volatile metal, can be treated with some thermal desorption units. Bench, pilot, and full scale studies have demonstrated that thermal desorption achieves treatment efficiencies of 99 percent or greater for VOCs and semivolatile organic compounds (SVOCs). Some higher temperature units can treat PCBs, pesticides, and dioxins/furans. Costs range from $80 - $350 per ton.

Soil washing, also for excavated soil, is a water-based process for mechanically scrubbing excavated soil to remove contaminants by dissolving or suspending them in the wash solution, or by concentrating them into a smaller volume of soil through particle size separation techniques. Soil washing systems that incorporate both techniques yield the greatest success for soils contaminated with heavy-metal and organic contaminants. The soil-washing process uses various additives (surfactant, acids, chelating agents) to increase separation efficiencies. After successful testing, the washed soil can be returned to the site or reclaimed. The aqueous phase and the clay/silt/sludge fraction contain high concentrations of contaminants. These two streams become waste feed for other on-or off-site treatment by incineration, thermal desorption, or bioremediation. Soil washing is only now becoming more popular in the United States, but has been more widely used in Europe. Costs are from $50 - $205 per ton.

Solvent extraction is similar to soil washing but uses organic solvents to remove contaminants from soil instead of water solutions. Solvent extraction is more appropriate for organic contaminants than inorganics and metals; it reduces contaminant volume by concentrating them in the extract phase. The three broad categories of the solvent extraction process are conventional solvent extraction, critical solution temperature fluid, and supercritical fluid extraction. Solvent extraction is not generally used for extracting inorganics/metals, but would be specified for a solvent contaminated site if there were other, more difficult to remediate compounds, such as PCBs, which could not be treated by SVE or bioremediation. Costs are high, ranging from $100-$500 per ton.

DESTRUCTION TECHNOLOGIES

The destruction technologies described in this TRD are for remediation of contaminated soil, sludge, and sediment at solvent sites and can be divided into three categories: thermal, chemical, and biological. Destruction technologies either destroy or detoxify hazardous wastes by altering the chemical structure of the constituents or breaking down the chemical structure into its basic components. They include incineration, pyrolysis, biodegradation and chemical dehalogenation.

Incineration treats organic contaminants in solids, liquids, and gases by subjecting them to temperatures greater than 1,000° F in the presence of oxygen. This causes the volatilization and combustion of the organic contaminants and converts them to carbon dioxide, water, hydrogen chloride, nitrogen oxides, and sulfur oxides. Three common types of incineration systems can treat contaminated solids; the rotary kiln, the infrared incinerator, and the circulating fluidized bed (CFB) units. The rotary kiln and the infrared units contain a primary chamber that usually operates in the temperature range of 1,000° F - 1,800° F. The rotary kiln is a refractory-lined, slightly-inclined, rotating cylinder that serves as a combustion chamber. The infrared unit uses electric resistance heating elements or indirect-fired radiant U-tubes to heat material passing through the chamber on a conveyor belt. The CFB uses air to circulate and suspend waste in a combustion loop and operates from 1,500° F - 1,800° F. Pyrolysis differs from incineration in that it uses heat in the absence of oxygen to volatilize and decompose organics including PAHs, PCBs, and dioxins. Clean solids are discharged and the gases are condensed or incinerated. It operates between 1,000° F - 2,200° F. Pyrolysis is best for a mixture of organic wastes which have PCBs or dioxin as a component because it is energy intensive and expensive and may not be appropriate for solvents only. Costs for incineration and pyrolysis are similar ranging from $200-$1,500 per ton excluding added costs for waste stream treatment.

Chemical dehalogenation is a remedy applicable to contaminated soil, sludge and sediment at solvent sites. The dehalogenation process is effective potentially in detoxifying chlorinated organic contaminants such as dioxins, PCBs and chlorobenzenes. This converts the more toxic compounds into less toxic, sometimes more water-soluble products and leaves compounds that are more readily separated from the soil and treated. In the dehalogenation of chlorinated aromatic compounds, a nucleophilic substitution reaction replaces a chlorine atom with an ether or hydroxyl group. Dehalogenation of chlorinated aliphatic compounds occurs through an elimination reaction and the formation of a double or triple carbon-carbon bond.

Bioremediation uses microorganisms to biochemically degrade or transform organic contaminants. It attempts to foster and optimize the natural bioremediation and biotransformation processes which occur in soils. Complete degradation of organic contaminants to carbon dioxide, water, and inorganic products may be achievable in some cases. In terms of degree of contaminant removal and final residual levels, the extent of treatment achievable in bioremediation depends upon various factors including the types of contaminants present, and processes used, and site-specific environmental conditions. In general, bioremediation does not achieve contaminant destruction efficiencies comparable to incineration. Performance comparisons with other contaminant removal or destruction processes should be made on a case-by-case basis. Even when lower contaminant removal or destruction is achieved, as long as remedial action goals are met, bioremediation may be a favored alternative based upon factors such as cost, implementability, and public acceptability.

Three principal bioremediation processes generally apply to soils at solvent sites: solid-phase, slurry-phase, and in-situ bioremediation. The solid-phase method places contaminated soil in a thin layer in a lined treatment bed. It is relatively simple and inexpensive and may be effective for a wide range of contaminants, but is land intensive due to the thin soil layer required for aerobic microbial activity.

Slurry-phase bioremediation involves excavated soil or sludge that is mixed with water in a tank or lagoon to create a slurry, which is then mechanically agitated. The procedure adds appropriate nutrients and controls the level of oxygen, pH, and temperature. Potential advantages of slurry-phase treatment as compared to solid-phase bioremediation includes the possibility for more effective treatment due to the high degree of mixing, and the effective contact between contaminated soils and nutrients.

In-situ bioremediation promotes and accelerates natural processes in undisturbed soil. Under appropriate conditions, this technology can destroy organic contaminants in place without the high costs of excavation and materials handling. It can involve recirculation of extracted groundwater that is supplemented above ground with nutrients and oxygen. Vacuum or injection methods can supply oxygen to the subsurface soil. Bioventing combines in-situ bioremediation with SVE to destroy semivolatile and some nonvolatile compounds that cannot be treated by SVE alone. It is an emerging technology that takes advantage of aerobic biodegradation of organics by using forced air to carry an adequate supply of oxygen to subsurface soils. Recent studies also have attempted to bioremediate chlorinated solvents by cometabolism using low-molecular weight alkanes such as methane.

Costs for bioremediation range from $80-$150 per cubic yard for slurry and solid phase treatments, and $8-$15 per pound of contaminant for in-situ treatment.

IMMOBILIZATION TECHNOLOGIES

Technologies described in this group by the TRD include containment and solidification/stabilization (S/S) processes designed to minimize contaminant migration. Containment is a common component in the overall remediation of a solvent site and involves capping systems and vertical/horizontal barriers. It also requires that long-term monitoring be performed.

Capping can range from a native soil cover or plastic sheets to a RCRA subtitle C composite cover. Common vertical barriers include slurry walls in excavated trenches, group curtains formed by injecting grout into soil borings, cement-bentonite filled borings or holes formed by withdrawing beams driven into the ground, and sheet-pile walls formed of driven steel. Horizontal barriers underlie a sector of contaminated soil without removing any material. S/S technologies either physically reduce the mobility of a contaminant (solidification) or chemically alters or binds the contaminant (stabilization). Stabilization can be performed without solidification, while solidification usually includes stabilization. Solidification also includes the use of binders for waste bulking to facilitate the handling of liquid wastes.

Costs for the containment technologies are affected by many variables and are outlined in the TRD. Costs for some common S/S systems range from $75-$400 per ton for landfilling on site.

WATER TREATMENT TECHNOLOGIES

Although the focus of this TRD is soil remediation, groundwater treatment is also generally addressed. Groundwater treatment can be performed by both in-situ and ex-situ technologies. The effectiveness of an ex-situ technology is dependent upon removing contaminants along with the groundwater. This process usually is referred to as pump and treat. If it proves too difficult, other technologies such as steam extraction or surfactant flushing can be used to improve contaminant removal with the groundwater. Groundwater technologies are discussed in more detail in this TRD and referenced publications. The following summarizes the water treatment technologies applicable to solvent sites:

Separation/Concentration Technologies		Destruction Technologies
Adsorption	Membrane separation	Chemical oxidation
Filtration	Precipitation	Biological treatment
Ion exchange	Oil/water separation	
Air stripping	Air sparging	
Reverse osmosis		