SITE REMEDIATION AND GROUNDWATER DECONTAMINATION IN USA

Lawrence K. Wang

United Nations Industrial Development Organization, Vienna, Austria

Keywords: Site remediation, excavation, stabilization, solidification, vapor stripping, vacuum extraction, thermal desorption, incineration, pyrolysis, enhanced stripping, thermal extraction, subsurface volatilization-ventilation, vitrification, soil surfactant flushing, soil washing, bioremediation, bioventing, slurry bioreactor, chemical treatment, natural attenuation, groundwater decontamination, air stripping, ultraviolet radiation, oxidation, carbon adsorption, sewer discharge, liquid/liquid separation, free product recovery, trenching, containerizing, dissolved air flotation.

Contents

1. Introduction and Terminologies

2. Excavation

3. In-Situ Stabilization and Solidification of Contaminated Soils

4. In-Situ Soil Vapor Stripping or Soil Vacuum Extraction

5. Ex-Situ and In-Situ Low Temperature Thermal Desorption

6. Incineration, Thermal Destruction, Starved Air Combustion and High Temperature Pyrolysis

7. In-Situ Hot Air/Steam Enhanced Stripping and In-Situ Thermal Extraction

8. In-Situ Subsurface Volatilization and Ventilation (combined saturated zone sparging and in-situ vadose zone vapor stripping)

9. Ex-Situ Vitrification and In-Situ Vitrification

10. In-Situ Soil Surfactant Flushing and Ex-Situ Soil Washing

11. Bioremediation for Soil and/or Groundwater Decontamination

12. Slurry Bioreactor System for Soil Decontamination

13. Anaerobic-aerobic Fixed Film Biological System for Groundwater Decontamination

14. Chemical Treatment (pH adjustment, KPEG treatment)

15. Ultraviolet Radiation and Oxidation for Groundwater Decontamination

- 16. Air Stripping for Groundwater Decontamination
- 17. Granular Activated Carbon Adsorption for Groundwater Decontamination
- 18. Sewer Discharge for Groundwater Treatment

19. Liquid/Liquid Separation and Free Product Recovery for Groundwater Decontamination

20. Natural Attenuation, Natural Flushing, Trench, Containerizing

21. Dissolved Air Flotation for Groundwater Decontamination

Glossary

Bibliography

1. Introduction and Terminologies

At the end of 1993, the United Nations Industrial Development Organization (UNIDO), the World Bank, and the United Nations Environment Programme Industry and Environment Programme Activity Centre (UNEP/IEPAC) started issuing new Industrial

Pollution Prevention and Abatement Guidelines. In later years, pollution prevention, waste minimization and manufacturing process integration together have been referred to as "cleaner production" by the international community in order to build awareness of sustainable industrial development, sustainable agricultural development and environmental protection. The objectives of all these international efforts are to disseminate information on pollution prevention options, end-of-pipe treatments and cleaner production technologies. The emphasis of the international efforts has been on pollution prevention at source, treatment at the end-of-pipe and manufacturing process integration through cleaner production because there is increasing evidence of the economic and environmental benefits to be realized by preventing or reducing pollution rather than by managing hazardous wastes after they have been produced and the environment has been polluted.

Until recently, industry has not overly concerned with cleaner production, hazardous waste management and environmental protection, so there are much direct and indirect damage caused to the environment by mishandling of hazardous wastes. This chapter will discuss various in-situ, ex-situ, on-site, and off-site technologies for site remediation and groundwater decontamination assuming that the worse situation has happened, that is the environment has already been polluted by the hazardous wastes.

Site remediation and groundwater decontamination are pressing issues in all industrial and developing countries, especially European countries due to limited availability of land. As a result, much progress is being made in the development of various technologies for effectively remediating contaminated industrial, agricultural and commercial sites. These site remediation technologies developed in The Netherlands, Germany and Belgium include: vacuum extraction of volatile organic compounds from contaminated soils, in-situ washing of cadmium-polluted soil, high-temperature slagging incineration of low-level radioactive wastes, in-situ steam stripping, and a number of bioremediation and soil washing operations. The United Nations and US Environmental Protection Agency have played the leadership roles in information dissemination, technology promotion, in-depth R&D and commercialization of most of the site remediation technologies for the benefit of the entire world.

The hazardous substances at contaminated sites cannot be properly managed without knowing the correct terminologies. According to the 1978 Resource Conservation and Recovery Act (RCRA) of the USA, a waste is considered hazardous when it poses a threat to human health or the environment. The US Comprehensive Environmental Response, Compensation and Liability Act (CERCLA, otherwise known as Superfund) was established in 1980. Under the 1984 reauthorization of the RCRA, the USEPA land disposal restrictions (LDRs, also known as 'land bans') of 1985-90 were imposed. Using the toxicity characteristic leaching procedure (TCLP), a concentration of any listed constituent in the leachate at or above these levels designates the wastes as hazardous. The waste remains hazardous until treated to reduce its leachability below the toxicity characteristic (TC) levels. The heavy metal levels apply not only to the definition of a hazardous waste, but to the LDR maximum leaching levels for disposal of "characteristic waste" at an RCRA treatment, storage and disposal facility (TSDF), otherwise known as a secure landfill.

At an industrial, commercial or agricultural site that has been contaminated by hazardous wastes, both the environmental samples (such as contaminated soil, air or groundwater), and hazardous wastes (such as PCB-containing transformers, waste oil, waste gasoline, old chemicals, spent activated carbons, precipitated heavy metals, etc.) must be handled with care in accordance with government rules and regulations and standard engineering practices.

Characterization of hazardous wastes and environmental samples is a critical step in determining how a hazardous waste or sample should be handled. The first step in waste and sample characterization is to determine the phase of the wastes or samples. Nonaqueous-phase liquids (NAPLs) are organic liquids that are relatively insoluble in water. There are two classifications of nonaqueous-phase liquids (NAPLs):

- 1. Light nonaqueous-phase liquids (LNAPLs), such as jet fuel, kerosene, gasoline and nonchlorinated industrial solvents (benzene, toluene, etc), which have densities smaller than that of water and will tend to float vertically through aquifers
- 2. Dense nonaqueous-phase liquids (DNAPLs), such as chlorinated industrial solvents (methylene chloride, trichloroethylene, trichloroethane, dichlorobenzene, trans-1,2-dichloroethylene, etc.), which have densities greater than that of water, and will tend to sink vertically through aquifers.

The next step is to determine whether or not the hazardous wastes or samples can be handled separately, together in bulk, or in packaged form. Only qualified environmental engineers can wisely decide how the hazardous wastes or samples should be properly handled. Mixing small quantity of hazardous substances with other non-hazardous substances, water or soil may generate a larger quantity of hazardous wastes, creating more environmental troubles or even danger. There are two kinds of hazardous wastes to be handled:

- 1. Designated hazardous waste: a designated hazardous waste is one that is specifically listed by the national government (such as the US environmental Protection Agency) as hazardous (such as hydrogen cyanide).
- 2. Characteristic hazardous waste: one that exhibits any one of the characteristics of ignitability, corrosiveness, reactivity or extractive procedure (EP) toxicity.

Furthermore, an ignitable waste is defined as any liquid with a flash point of less than 60 O Celsius, any nonliquid that can cause a fire under certain conditions, or any waste classified by the national government (such as the US Department of Transportation) as a compressed ignitable gas or oxydizer. A corrosive waste is defined as any aqueous material that has a pH less than or equal to 2, a pH greater than or equal to 12.5, or any material that corrodes SAE 1020 steel at a rate greater than 0.25 inches per year. (1 inch = 2.54 cm). A reactive waste is defined as one that is unstable, changes form violently, is explosive, reacts violently with water, forms an explosive mixture with water, or generates toxic gases in dangerous concentrations. An extractive procedure toxicity (EP Toxicity) waste is one whose extract contains concentrations of certain constituents in excess of those stipulated by the national government's drinking water standards (such as the USEPA Safe Drinking Water Act in the USA).

The third step is to determine whether or not the hazardous wastes or samples should be treated or handled in-situ or ex-situ, which are defined as follows:

- In-situ treatment: the hazardous wastes or environmental samples are not removed from the storage or disposal area to be processed. In general, treatment is accomplished by mixing a reagent into the waste storage zone by some mechanical means such as auger, backhoe, rotary tilling device, etc. Site remediation by "in-situ solidification" is a typical example.
- Ex-situ treatment: the hazardous wastes or environmental samples are removed from the storage or disposal area to be processed elsewhere through a mechanical system. Soil remediation by excavation and incineration is a typical example. Another example is application of the "pump-and-treat" technology for groundwater decontamination.

Another step is to decide whether or not the ex-situ treatment should be carried out on site or off site, defined as follows:

- On site treatment: the hazardous wastes or environmental samples are not removed from the contaminated site to be processed. Any kind of in-situ treatment is on site treatment. Application of the pump-and-treat technology for groundwater decontamination at the contaminated site is an ex-situ treatment as well as an on site treatment. On-site treatment systems consist mainly of mobile or transportable equipment, installation, labor, and support services.
- Off site treatment: the hazardous wastes or environmental samples are removed from the contaminated site to be processed. If the contaminated soil must be excavated from the site and transported to another location for incineration, it is an ex-situ treatment as well as an off site treatment. Off-site treatment systems involve mainly fixed operations using non-mobile or non-transportable equipment.

Mobile operations are generally taken to mean that the process equipment is on wheels and that the entire site remediation operation can be rapidly moved, set up and made ready for operation at a new contaminated site within a few days. Transportable operations mean that the process equipment may be broken down into a number of segments that must be transported separately and are assembled at the operational site, often within a few weeks or months.

Once an industrial, agricultural, or commercial site is seriously contaminated by the hazardous waste, the U.S. government will list the site as a hazardous waste contaminated site, or a Superfund site. Delisting is an amendment to the lists of hazardous wastes or hazardous waste sites that is granted by the national government when it is shown that a specific waste stream or waste site no longer has the hazardous characteristics for which it was originally listed.

Restoration of any industrial, agricultural, commercial or even residential sites that have been seriously contaminated by hazardous wastes is termed "site remediation." A contaminated site may involve contaminated soil and/or groundwater. Purification of any groundwater by either in-situ or ex-situ means is called groundwater decontamination. Site remediation is a broader term that includes groundwater decontamination.

Where water penetrates, some of the hazardous wastes dissolve, as there is no such thing as a completely insoluble material. Accordingly, when a hazardous waste, treated or not, is exposed to water, its rate of dissolution can be measured. This dissolution process is termed "leaching." The water is "leachant," and the contaminated water that has passed through the waste is the "leachate." The capacity of hazardous waste material to leach is called its "leachability."

A test can be conducted either in-situ, ex-situ, on-site or off-site using an actual waste sample or a simulated synthetic waste sample to determine whether or not a particular process method or equipment can be used to treat the waste sample. Such a test is called a treatability test or treatability study.

Since most site remediation projects involve the use of on-site treatment systems, it is necessary to define the required on-site service as follows in normal chronological sequence: (1) obtaining samples of the hazardous waste, (2) preliminary laboratory treatability test, (3) preliminary price quote, (4) meeting with customer, field sampling, and preliminary meetings with the regulatory agency, (5) final laboratory treatability tests, (6) firm quotation to customer, (7) regulatory approval, (8) mobilization, (9) setup at job site or the contaminated site , (10) site remediation, treatment of the wastes and environmental samples, (11) close-down and cleanup at job site and return to home base, (12) final laboratory leaching and physical tests on the solid and/or groundwater produced by the job to satisfy contract requirements and to protect warranty, (13) completion of a final project report , (14) possible follow-up sampling and laboratory testing of waste samples at various times if required by contract or desired by contractor for information or warranty protection.

When groundwater is contaminated by hazardous wastes, the groundwater can either be treated in place using in-situ technologies or be pumped from subsurface to the ground surface for ex-situ treatment. The latter ex-situ groundwater decontamination technology is also called the pump-and-treat technology. Information about analytical methods for determination of the concentrations of pollutants in solid and hazardous wastes can be obtained from governmental agencies.

The best demonstrated available technologies (BDAT) for site remediation that are specially recommended by USEPA and many industrial nations are: incineration, soil washing, chemical treatment, low temperature thermal desorption, and solidification. According to the frequency of applications or popularity, the most popular soil decontamination technologies are the following, in decreasing order:

- 1. excavation,
- 2. in-situ subsurface volatilization and ventilation/aeration,
- 3. bioremediation,
- 4. thermal destruction or incineration,
- 5. soil vapor stripping or soil vacuum extraction,
- 6. soil washing or soil scrubbing,

- 7. stabilization and solidification,
- 8. natural attenuation, and
- 9. chemical treatment (pH adjustment).

The most popular groundwater decontamination technologies are the following, in decreasing order:

- 1. air stripping,
- 2. carbon adsorption,
- 3. bioremediation,
- 4. sewer discharge,
- 5. liquid/liquid (oil/water) separation
- 6. in-situ flushing,
- 7. trenching, and
- 8. containerizing

2. Excavation

Contaminated soil may be excavated by mechanical means for treatment and/or disposal or treated in-situ. Excavation can be completed in a few days or several months depending on volume of material and site-specific complexities. Excavation is the most commonly used unit operation for removing contaminated soil. However, its applicability so far is limited to small volumes of contaminated soil and shallow excavations.

3. In-Situ Stabilization and Solidification of Contaminated Soils

The process terms of chemical fixation, immobilization, stabilization and solidification have been used interchangeably. The following are the common terminologies:

- 1. stabilization: this refers to techniques that reduce the hazard potential of a waste by converting the contaminants into their least soluble, mobile, or toxic form. The physical nature and handling characteristics of the waste are not necessarily changed by stabilization.
- 2. solidification: this refers to techniques that encapsulate the waste in a monolithic solid of high structural integrity. The encapsulation may be of fine waste particles (micro-encapsulation) or of a large block or container of wastes (macro-encapsulation). Solidification does not necessarily involve a chemical interaction between the wastes and the solidifying reagents, so it may mechanically bind the waste into the monolith. Contaminant migration is restricted by vastly decreasing the surface area exposed to leaching and/or by isolating the wastes within an impervious capsule.

Solidification and stabilization are nevertheless used interchangeably in the field. In actual site remediation operations, the process immobilizes contaminants in soils and sludges by binding them in a concrete-like, leach-resistant matrix. Contaminated hazardous waste materials are collected, screened to remove oversized material and introduced to a batch mixer. The hazardous waste material is then mixed with water,

with a chemical reagent, with some selected additives, and with fly ash, kiln dust or cement. After it is thoroughly mixed, the treated waste is discharged from the mixer. Treated waste is a solidified mass with significant unconfined compressive strength (UCS), high stability and a rigid texture similar to that of concrete. This process treats soils and sludges contaminated with toxic organic compounds, hazardous metals, inorganic compounds, and oil and grease. Batch mixers of various capacities can treat different volumes of hazardous waste.

4. In-Situ Soil Vapor Stripping or Soil Vacuum Extraction

Soil vapor stripping (SVS), soil vapor extraction (SVE), soil venting (SV), vacuum extraction (VE) and soil vacuum extraction (SVE) are the terms used interchangeably to describe a process that removes volatile organic compounds (VOC) from the vadose, or unsaturated, soil zone by vacuum stripping. These compounds can often be removed from the vadose zone before they contaminate groundwater. The extraction process uses readily available equipment, including extraction and monitoring wells, manifold piping, a vapor and liquid separator, a vacuum pump, and an emission control device such as an activated carbon adsorption filter. After the contaminated area is completely defined, extraction wells are installed and connected by piping to the vacuum extraction and treatment system.

First, a vacuum pump draws the subsurface contaminants from the extraction wells to the liquid/gas separator. The vapor-phase contaminants are then treated with an activated carbon adsorption filter or a catalytic oxidizer before the gases are discharged to the atmosphere. Subsurface vacuum and soil vapor concentrations are monitored with vadose zone monitoring wells.

The technology is effective in most hydro-geological settings and can reduce soil contaminant levels from saturated conditions to a non-detectable level. The process even works in less permeable soils (clays) with sufficient porosity. Dual vacuum extraction of groundwater and vapor quickly restores groundwater quality to drinking water standards. In addition, the technology is less expensive than other remediation methods such as incineration.

Typical contaminant recovery rates range from 20 to 2500 pounds (1 pound = 454 grams) per day depending on the degree of site contamination and the VOCs to be removed. The vacuum extraction or soil vapor stripping technology effectively treats soils containing virtually any VOCs and has successfully removed over 40 types of chemicals from soils and groundwater, including toxic organic solvents and gasoline-and diesel-range hydrocarbons. Nevertheless, the range of applicability of vacuum extraction or soil vapor stripping process is bound by the following constraints:

- 1. The hazardous substances to be removed must be volatile or at least semi-volatile (a vapor pressure of 0.5 torr or greater);
- 2. The hazardous substances to be removed must have relatively low water solubility, or the soil moisture content must be quite low;
- 3. The hazardous substances to be removed must be in the vadose zone (above the groundwater table) or in the case of LNAPLs, must be floating on it;

4. The soil must be sufficiently permeable to permit the vapor extraction wells to draw air through all of the contaminated domains at a reasonable rate;

The SVS or VE process cannot remove heavy metals, most pesticides, water-soluble solvents (acetone, alcohols, etc.) or PCBs because their vapor pressures in moist soils are too low. The technology, however, is relatively cheap and rapid, has a comparatively low environmental impact, and results in the elimination of hazardous substances or their concentration into a small volume of highly concentrated, easily handled wastes that may be disposed of by incineration or recycled for reuse.

The SVS or VE process was first demonstrated at a Superfund site in Puerto Rico. Terra Vac has since applied the technology at fifteen additional Superfund sites and at more than 400 other waste sites throughout USA, Europe and Japan. The process was also demonstrated under USEPA supervision at the Groveland Wells Superfund site in Groveland, Massachusetts, in 1987-1988, in which soils contaminated by trichloroethene (TCE) were successfully remediated. In Groveland, average reductions were 92% for sandy soils and 90% for clays, and field evaluations have yielded the following conclusions:

- 1. VOCs can be reduced to non-detectable levels; however, some residual VOC concentrations usually remained in the treated soils.
- 2. Volatility of the contaminants and site soils is a major consideration when applying this technology.
- 3. Pilot demonstrations are necessary at sites with complex geology or contaminant distributions.
- 4. Treatment costs are typically \$40 per ton of soil, but can range from \$10 to \$150 per ton of soil depending on requirements for gas effluent or wastewater treatment. (1989 costs)
- 5. Contaminants should have a Henry's constant of 0.001 or higher.



Bibliography

Cassidy, D.P. (2001). *Biological Surfactant Production in a Biological Slurry Reactor Treating Diesel Fuel Contaminated Soil*. pp.87-94. Water Environment Research. Volume 73, No. 1. February. [A scientific article introducing a new process for soil decontamination]

USEPA (1986). *Reclamation and Redevelopment of Contaminated Land: US Case Studies.* Report No. EPA/600/2-86/066. August. US Environmental Protection Agency, Washington DC, USA. [A government publication summarizing the case studies for land reclamation and redevelopment]

Wang, L.K, Kurylko L., and Hrycyk O. (1996). *Site Remediation Technology*. 14 pp. US Patent, September 1996. US Patent and Trademark Office, Washington, DC, USA. [A new technology for site remediation]

Wang, L.K. (1990). *Decontamination of Groundwater and Hazardous Industrial Effluents by High-Rate Air Flotation Processes*. Great Lakes `90 Conference Proceedings, Hazardous Materials Control Research Institute, Silver Spring, Maryland, USA. Sept. 1990. [A scientific paper introducing a new technology for groundwater decontamination]

Wang, L.K. (1995). Groundwater Decontamination Using Sequencing Batch Processes. Water Treatment, pp. 121-134, Volume 10, No. 1995, 1995. [A new technology for groundwater decontamination]

Wang, L.K., Kurylko L. and Hrycyk O.. (1995). *Biological Process for Groundwater and Wastewater Treatment*. 8 pp. US Patent, September 1995. US Patent and Trademark Office, Washington, DC, USA. [A new biotechnology for groundwater decontamination]

Wang, L.K. and Kurylko L. (1995). *Liquid Treatment System with Air Emission Control*. 14 pp. US Patent, March 1995. US Patent and Trademark Office, Washington, DC, USA. [A new technology for groundwater decontamination without causing air pollution problems]

Wang, L.K. and Pereira N.C. (1986). *Handbook of Environmental Engineering: Biological Treatment Processes*. 498 pp. Volume 3, Humana Press, Clifton, NJ, USA. [A handbook introducing the technologies for biological treatment processes in detail]

Wang, L.K., Krouzek J.V. and Kounitson U. (1995). *Case Studies of Cleaner Production and Site Remediation*. 136 pp. United Nations Industrial Development Organization (UNIDO), Vienna, Austria. Training Manual No. DTT-5-4-95. [A UNIDO training manual introducing many international experiences and successful case histories related to cleaner production and site remediation, toward sustainable industrial and agricultural development]

Wang, L.K., Kurylko L. and Wang M.H.S. (1994). *Sequencing Batch Liquid Treatment*. 19 pp. US Patent. October 1994. US Patent and Trademark Office, Washington, DC, USA. [A new technology for groundwater decontamination]

Wang, L.K., Kurylko L., and Hrycyk O. (1992). *Removal of Volatile Compounds and Surfactants from Liquid.* 6 pp. US Patent, June, 1992. US Patent and Trademark Office, Washington, DC, USA. [A new technology for groundwater decontamination]

Wang, L.K., Kurylko L., and Wang M.H.S. (1994). *Combined Coarse and Fine Bubble Separation System*. 23 pp. US Patent, January 1994. US Patent and Trademark Office, Washington, DC, USA. [A new technology for groundwater decontamination]

Weber, R.E., Wang L.K. and Pavlovich J.J.. (1992). *Separation of Liquids with Different Boiling Points with Nebulizing Chamber*. 8 pp. US Patent, October, 1992. US Patent and Trademark Office, Washington, DC, USA. [A new technology for oil-water separation, or any liquid-liquid separation]

Wilson, D. J. and Clarke A.N. (eds). (1994). *Hazardous Waste Site Soil Remediation*. 567 pp. Marcel Dekker, NYC, NY, USA. [A informative textbook, with emphasis on soil remediation]