CHAPTER 4

Technology Screening and Feasibility Studies for ISTR

4.1. Introduction. To effectively select the appropriate remedial technology, it is important to define the remediation goals. As discussed in previous sections, increases in temperature greatly affect chemical properties, and chemical, biological, and physical reactions. It is these enhancements of physical, chemical, and biological reactions that ISTR methods seek to utilize to effect remediation. Possible operations that can be performed as part of ISTR applications are:

a. Source removal/reduction/recovery (the most common application).

b. Enhance chemical reactions such as hydrous pyrolysis oxidation.

c. Enhance biological reactions.

The remediation strategy may involve one, or a combination of these options.

4.2. Identify Remedial Action Strategies. The ISTR technologies have been most commonly applied to removal of NAPL. For this reason, this is the focus that this EM will take to describe various processes. However, ISTR technologies have also been used to enhance biological processes, volatilize aqueous phase concentrations, and induce oxidation (through cyclic application of injected steam and air to cause hydrous pyolysis oxidation). The application of heat modifies chemical, physical, and biological processes and reactions, which play important roles in environmental remediation.

4.2.1. *Source Removal/Reduction/Recovery*. Typically thermal methods have been applied for source removal/reduction/recovery of NAPL. Typical industrial organic chemicals found at many hazardous waste sites (e.g., PCE, TCE, 1,1,1-TCA, benzene, ethylbenzene, toluene, and xylenes) have boiling points of less than 150ºC. The main removal mechanism where these compounds are present as NAPL involves enhanced volatilization, steam distillation (utilizing the azeotropic mixture eutectic point*), hydrous pyrolysis oxidation, and vapor-phase oxidation and pyrolysis. Source removal, reduction, and recovery also have the ability to significantly reduce the mass flux of organic chemicals from the source zone, such that when coupled with natural attenuation processes, the aqueous phase is also significantly cleaned up (Smith et al. 2000).

4.2.1.1. *Identification of Thermal Treatment Areas*. A preliminary step in the setting of remedial action objectives (RAOs) for ISTR is to identify treatment areas. The lateral and vertical extent of NAPL at a site is best defined by the use of multiple lines of evidence rather than a single measurement. Possible lines of evidence include:

* Two or more liquids when heated together will boil at a temperature (the eutectic point) below the boiling point of the individual components of that mixture. For instance, a mixture of trichloroethene in water has an eutectic point of 73.1°C, while trichloroethene in air at standard atmospheric pressure boils at 87°C.

a. Groundwater and soil chemical data.

b. Inferences from site characterization tools such as the Corps of Engineers Site Characterization and Analysis Penetrometer System (SCAPS) and the Loral Corporation Rapid Optical Screening Tool (ROST®).

c. Visual observations in groundwater or soil samples, where possible.

d. Direct measurement of NAPL in groundwater.

e. Comparison of concentrations to aqueous solubility data.

At some large or complex sites, it may be appropriate to divide the site into subareas for thermal treatment. Treatment subareas allow different parts of a site to be prioritized when the entire site cannot be treated because of implementation constraints or limited funding. The use of treatment subareas assists the phased implementation of thermal treatment. Treatment subareas may be identified and prioritized by many different factors, for example:

a. The relative amount of NAPL estimated in each subarea.

b. Relative differences in NAPL mobility, if any, between subareas.

c. The proximity of each NAPL subarea to drinking water sources/risk receptors.

d. The degree of data certainty regarding the presence of mobile NAPL in each subarea.

e. The expected future land use in each subarea.

f. The relative ease of access for implementation in each subarea.

4.2.1.2. *Setting Remedial Action Objectives*. Although remedial action objectives (RAOs) are specific to each site and regulatory program, there are several common approaches to consider in setting RAOs for ISTR. The appropriate Office of Counsel must be consulted with regard to the proper application of the laws and requirements under the various regulatory programs and patent law. There may be differences in application between the various Defense programs.

4.2.1.2.1. RAOs include general remediation goals and site-specific numerical cleanup standards that address current and potential groundwater risk pathways at a site. RAOs depend on the expected future land use of the site and the designated beneficial uses of the groundwater aquifer beneath the site. For example, when groundwater poses an actual or potential health risk and is a potential drinking water source or could affect a drinking water source, the National Contingency Plan (NCP) directs EPA to restore groundwater to Federal and state drinking water standards whenever possible, in a reasonable time [NCP, 40 CFR 300.430(a)(1)(iii)(F)].

4.2.1.2.2. EPA Record of Decision (ROD) guidance (USEPA 1999c) states that "different remediation objectives should be developed for the NAPL zone and for the portion of the aquifer outside of the NAPL zone." This is based on the conclusion in the guidance that, "in general, restoration of an aquifer contaminated with NAPLs to ARARs (e.g., Federal and state MCLs) or other risk-based cleanup levels in a reasonable time frame will not be attainable in the NAPL zone unless the NAPLs can be removed." The appropriate Office of Counsel should be consulted with regard to the application of this EPA guidance to the site in question.

4.2.1.2.3. In setting the remediation objectives for the NAPL zone, several different approaches are possible. The remediation objectives for the NAPL zone relevant to in situ treatment do not need to be numerical standards, but need to be measurable. Examples of non-numerical remedial goals for ISTR include the following:

a. Remove mobile NAPL.

b. Remove NAPL "to the maximum extent technically feasible."

c. Remove a specified amount of NAPL based on estimated quantities (as gallons or a percentage of the estimated total NAPL-e.g. remove 90% of the NAPL or remove 90% of the most volatile fraction of the NAPL).

d. Achieve an order of magnitude reduction of NAPL.

e. Demonstrate that "significant" NAPL recovery equals real risk reduction (e.g., by removing 90% of NAPL, the remaining 10% represents only a negligible risk).

f. Achieve a net reduction in flux of contaminant to groundwater that is lower than the assimilative capacity of the aquifer, allowing natural attenuation processes to achieve water quality goals at some point of compliance.

g. Achieve specific performance standards (e.g., heating criteria or treatment time periods).

h. Use a goal structure similar to what has been used for SVE-i.e. achieving asymptotic recovery curves indicating that a well designed, installed, operated, and optimized system has reached a point of diminishing returns.

i. Achieve indirect goals such as reducing the time or lateral extent of follow-up actions such as pump-and-treat.

j. Conduct a "cost-effective" removal of NAPL.

4.2.1.2.4. There are obvious shortcomings to several of these approaches. Remedial goals based on a specific quantity of NAPL recovery are problematic because of the uncertainty associated with estimating the initial NAPL volume. It is also difficult to quantify residual risk (or risk reduction) after ISTR to demonstrate that a specific risk-reduction goal has been achieved. Demonstrating that NAPL removal has been cost-effective raises the question of what cost per gallon of NAPL recovered is cost-effective in relation to the total groundwater remediation costs, including long-term O&M.

4.2.1.2.5. In the end, RAOs for ISTR must be determined on a site-specific basis and must fit into the overall, long-term cleanup strategy for the site. Because of the uncertainties currently associated with ISTR technology, RAOs may need to include contingencies in the event that sufficient NAPL is not recovered-e.g. contingencies to conduct follow-up actions such as pump and treat to contain NAPL sources that cannot be removed and that are considered a continuing threat to groundwater.

4.2.2. *Other Remediation Strategies.* As mentioned above, ISTR methods may be used for a variety of applications to enhance physical, chemical, and biological reactions to effect remediation. This paragraph is presented to inform the reader about the applications of ISTR where removal of NAPL has not been the goal.

4.2.2.1. *Enhance Physical Changes*. Physical changes involve changes in state (i.e., changes from solid to liquid to vapor). Thermal methods have been used to vaporize dissolved compounds in groundwater, which essentially involves boiling the groundwater. At a site in Washington State, ERH was used to reduce relatively low concentrations of chlorinated solvents in slow-moving groundwater to rapidly clean up a property for sale. Selling the site with the groundwater cleaned up would result in a higher sales price than if PCE and TCE were present in the groundwater.

4.2.2.1.1. Changing the physical conditions can also result in a change in the physical property of a particular compound. For instance, the viscosity of many materials is reduced using heat. This may facilitate the recovery of such materials as lube oils in the subsurface. At the Yorktown Naval Facility, steam within horizontal stainless steel wells is being used to reduce the viscosity of Navy Special Fuel Oil to facilitate recovery in a system of trenches. Engineering studies have also been performed to evaluate the feasibility of using steam, ERH, and TCH at a number of refineries to enhance the removal of lube materials currently being recovered from the subsurface using more conventional means.

4.2.2.2. *Enhance Chemical Reactions*. Hydrous pyrolysis oxidation (HPO) involves chemical oxidation in the presence of heat. Reactions between oxygen and common organic pollutants are orders of magnitude faster at or close to steam temperature than under ambient temperatures. To utilize HPO for in-situ destruction, the subsurface is heated up, typically through the use of TCH or SEE. In all TCH field projects, a large amount of water is naturally in place for the HPO reaction. Typically, the product stream contains greater than 50% water and may also contain air. In addition, steam and oxygen, or oxygen alone (typically supplied as air) are injected in a pulsed fashion, building a heated, oxygenated zone in the subsurface. When injection is stopped, pressures dissipate, resulting in condensation of steam and the contaminated groundwater returns to the heated zone for in situ treatment. The dissolved contaminants in the groundwater mix with the oxygen and condensate and, in the presence of heat, rapidly oxidize to form carbon dioxide and chloride ions (in the case of treating chlorinated compounds, such as pentachlorophenol, trichloroethene, or perchloroethene). Reaction kinetics of gas-phase oxidation and pyrolysis exhibit dramatic increases with temperature above the boiling point of water. Using HPO, it is estimated that more than 150,000 pounds of wood treating chemicals were degraded at the Visalia Pole Yard site.

4.2.2.2.1. As presented in Paragraph 2.1.1.5, chemical reactions such as hydrolysis significantly increase with temperature, especially in the cleanup of alkanes. At the time of preparation of this EM, there had been no known application of ISTR solely for the purpose of enhancing hydrolysis. However, it is believed that thermally enhanced hydrolysis of methylene chloride was a significant mechanism in the ERH remediation in Waukegan, Illinois. Further, upon review of the data from the ERH remediation in Skokie, Illinois, thermally enhanced hydrolysis may have been significant in the removal of 1,1,1-trichloroethane from the groundwater (Beyke 2006).

4.2.2.3. *Enhance Biological Reactions*. The application of heat results in increased biological activity. It is estimated that biological activity increases three-fold for each 10ºC rise in temperature. Where temperature is a limiting factor for in situ biodegradation remediation, heat may be added using ISTR methods. ERH was used in Alaska (Ft. Richardson) to provide a heat source to stimulate in situ intrinsic biodegradation of fuels during winter months (Appendix B).

4.2.2.3.1. It has been observed that biodegradation occurs during ERH, even to the boiling point of water. At a site where ERH was applied in Skokie, Illinois, (Beyke et al. 2000) cis-1,2-dichloroethene (a biodegradation daughter compound of trichloroethene) was detected throughout the treatment period. Further, concentrations of methane were also detected in the off-gas from the treatment, evidencing biological activity.

4.2.2.3.2. Steam injection coupled with simultaneous enhanced biodegradation (Basile et al. 1994) was successfully used to clean up two sites in Illinois (Adams and Smith 1998, Smith et al. 2000). At one site, it is estimated that approximately one-third of the released chlorinated solvents were destroyed by in situ biodegradation.

4.3. Measures of Success for ISTR. If residual NAPL is present, MCLs or other cleanup standards may not be achieved in groundwater at a site until some time after completion of thermal treatment. In some cases, natural degradation of the residual NAPL may be adequate to meet RAOs. At other sites, follow-up activities such as pump-and-treat or enhanced biodegradation are implemented. Depending on the size of the remediation, the benefits of ISTR may be realized in as little as 18 months, or it may require years of monitoring to assess the full benefits at a site. Therefore, different measures of "success" are needed for ISTR technologies. Success can be defined by mass removal goals, but this approach has limitations, as noted above. Narrative goals such as reducing the need for long-term pump-and-treat are also measures of success, but may not be demonstrated in the short-term.

4.3.1. When applying ISTR technologies, it is important to realize that complete removal of the source area is impractical. For a variety of compounds, reduction of source mass may be sufficient to reduce the contaminant flux to groundwater to levels that, for instance, do not represent residual NAPL, or where there is lack of rebound, which would then allow the natural assimilative capacity of the aquifer to control plume migration. This would involve evaluating natural attenuation.

4.3.2. For chlorinated solvents, this may be determined by the organic carbon demand. Each 1 mg of dissolved organic carbon oxidized via reductive dechlorination, consumes 5.65 mg of organic chlorine (Wiedemeier et al. 1996). This ratio can be used to determine organic carbon demand and the change in this organic carbon demand as the compounds degrade. Organic chlorine can be determined from the following relationship for trichloroethene.

4.3.3. For example, as two moles of TCE are reduced to ethene, six moles of chlorine (shown below as Cl_2 gas) are produced (TCE: $2C_2HCl_3 + 3H_2 \rightarrow 2C_2H_4 + 3Cl_2$).

Molecular weights: TCE 2(12.011) + 3(35.453) + 1.01 = 131.39
Chlorine 3(35.453) = 106.359
Mass Ratio of Chlorine to TCE = 106.359:131.30 = 0.81:1

Therefore, 10 mg/L of TCE would be equivalent to 8.1 mg/L of organic chlorine, which would in turn represent 1.43 (8.1÷5.65) mg/L of organic carbon demand.

4.3.4. Organic carbon demand is then compared to concentrations of organic carbon in groundwater. Where organic carbon exceeds the organic carbon demand and appropriate redox conditions are present, reductive dehalogenation is occurring and there is sufficient assimilative capacity in the aquifer. Conversely, where organic carbon demand exceeds available organic carbon in groundwater, the dehalogenation process may be inhibited.

4.3.5. Similarly, for fuels, where the oxygen demand is satisfied by the dissolved oxygen concentrations or other electron donor sources, the aquifer may assimilate continued flux to groundwater from the source area.

4.4. Feasibility Evaluation Flow Chart. Once the remediation goal is established, each ISTR technology has a range of effectiveness, depending on the desired temperature range to be achieved, the soil* type in which it will be applied, depth of contaminant, setting of contaminant (e.g., perched on a clay layer, potential for mobilization as a result of heating), and the potential for vapor recovery (i.e., the feasibility of engineering a cost-effective recovery system). Figure 4-1 presents a flow chart for evaluating site conditions to determine whether ISTR is potentially applicable for the site given its setting and infrastructure. Conditions to be evaluated include: delineation of the source area, nature of compounds to be remediated, availability of utilities, geotechnical issues, drainage in the remediation area, and drilling access issues.

4.4.1. The selection of the appropriate technology for a given site is site specific, dependent upon a variety of factors such as cost (and cash flow constraints), geology, hydrogeology, community acceptance, availability of power, depth of treatment, etc. The technologies that are the subject of this manual have been undergoing continuous improvement as more and more sites are treated. Engineering solutions have been developed to issues that have been encountered, providing the knowledge base to expand the settings where the technologies may

* ISTR technologies have seen limited testing in bedrock environments at the time of preparing this manual. As a result, the experience base does not exist to develop procedures for application in bedrock

be applicable. It is recommended that a number of vendors be contacted once it is determined that ISTR may be applicable for a given site, to evaluate the issues involved in applying the technology at said site.

4.4.2. Steam injection temperatures that can be achieved are based on the injection pressures that can be achieved. Since most environmental restoration projects are typically performed at depths of less than 30 m (100 feet), the highest temperature that can be reasonably achieved in soil using steam is approximately 170ºC (~350ºF).

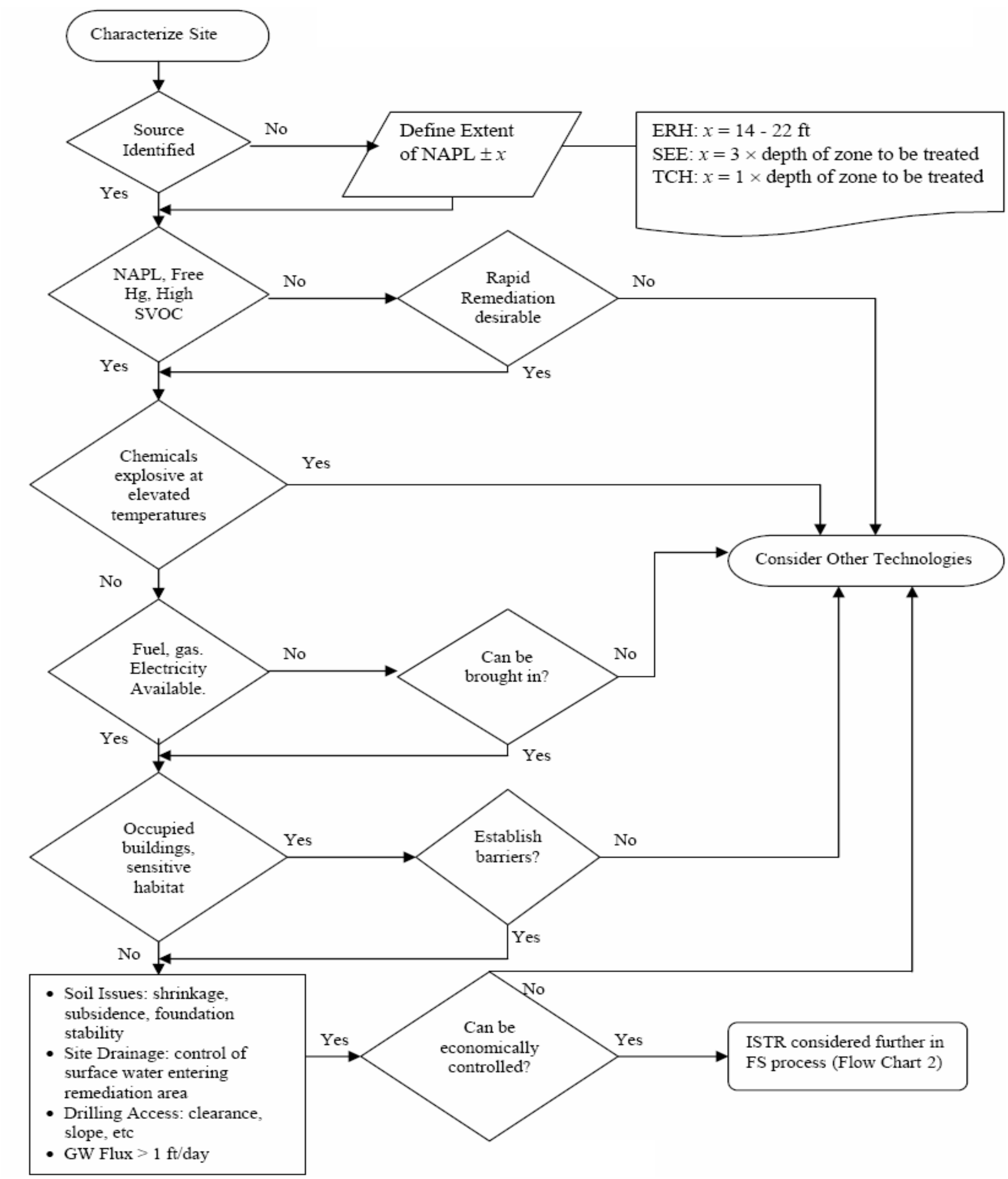

Figure 4-1. Evaluation of Site Characteristics.

4.4.3. ERH and thermal conductance methods heat the subsurface relatively evenly. Steam injection, on the other hand, is susceptible to the steam following zones of higher hydraulic conductivity. Unfortunately, contaminants in soil can migrate by diffusion into very tight layers from which they require very long times for removal again by diffusion. In highly anisotropic conditions (e.g., braided stream deposits, fractured bedrock) injected steam is susceptible to following paths of least resistance and may not heat the desired zone. Depending upon the degree to which anisotropy is present, zones where steam is not conveyed will be heated by conduction and convection.

4.4.4. Depth of treatment is a critical issue. The spacing of heater wells, electrodes, and injection wells is based on what is known as an aspect ratio. For thermal conduction, the (heater) well spacing should not exceed the thickness of the heated zone (Stegemeier and Vinegar 2001). Well spacing, not the thickness of the heated zone, determines the time required to heat the formation. As such, this is defined as a 1:1 aspect ratio (distance between heater wells: thickness of zone to be treated).[*] For ERH, the spacing of the electrodes is based on soil type, applied voltage, and electrical resistance of the soil/groundwater system to be treated. Typical spacing between electrodes is 2.6 to 6.1 m (8.5 to 20 feet). Therefore, at depths of greater than 2.6 to 6.1 m, the ERH aspect ratio is less than 1:1, indicating that significant drilling is required to treat a large, deep area. For steam injection in the vadose zone, the aspect ratios that have been used range from 3:1 to 5:1. In the saturated zone, steam sparging aspect ratios have ranged from 1:1 to 3:1.

4.5. Evaluation of Short-Term Impacts of ISTR. The short-term impacts of a remedial action are evaluated in terms of the potential effects on human health and the environment during implementation of the action as well as site issues. The assessment of short-term impacts is primarily based on four key factors:

a. Potential short-term risks to and protection of the community during implementation of a remedial action.

b. Potential impacts to and protection of workers during a remedial action, and the effectiveness and reliability of protective measures.

c. Potential environmental impacts of the remedial action, and the effectiveness and reliability of mitigation measures during implementation.

d. Impacts to soils and foundations.

4.5.1. As with other remediation technologies, ISTR presents the potential for exposure of nearby communities to site contaminants via fugitive emissions of vapors, incomplete hydraulic control and capture of contaminated groundwater and vapors, and on- and off-site management of process wastes generated by the action. Short-term risks also include dust generated during construction and noise from equipment operation and drilling. During implementation, access

* It should be noted that most applications of TCH have involved heater well spacings of 6 to 8 ft (1.8 to 2.4 m). Depending on the desired goal, the heater well spacing can also exceed the thickness of the zone targeted for treatment. If the objective of TCH is to accomplish in situ steam distillation, rather than to achieve superheated temperatures, aspect ratios of somewhat greater than 1:1 can be utilized.

restrictions and engineering controls can be used to protect the public from construction and O&M-related activities at the site. During active thermal heating and cool-down, engineering controls would be necessary to control potential exposure routes to the surrounding community. The controls may include groundwater and vapor extraction; on-site physical and chemical treatment of vapor, water and air waste streams; and off-site treatment and disposal of process wastes at permitted disposal facilities.

4.5.2. Extensive performance monitoring requirements, including well-field measurement of temperature, pressure, and steam distribution, rates and effectiveness of contaminant removal, and treatment plant discharges to the air and groundwater, are important elements of the remedy. Specific monitoring activities to ensure protection of the surrounding community could include monitoring of fugitive and stack emissions (treatment units and boilers), dust and opacity, noise and groundwater.

4.5.3. Short-term impacts on workers associated with ISTR include potential exposures to construction-related risks (ranging from the risks of working around mobile equipment to trips, slips and falls), potential worker exposure to NAPL and dissolved-phase contaminants, unique physical hazards (high temperatures and high-voltage electricity) during installation and O&M of the remedy, and fugitive air emissions. These risks and the protective measures to address them are discussed in Paragraph 10.2.

4.5.4. Potential ISTR short-term impacts on the environmental receptors identified at a site are primarily fugitive emissions from treatment operations and the direct thermal effects of actively heating soil. Other potential environmental impacts are associated with construction activities, such as noise, traffic and dust. Mitigation measures include engineering controls similar to those used for community protection. Sites located near surface water bodies present special concerns in terms of potential impacts and mitigation measures. Different statutory requirements exist for conducting ecological assessments at a site. If endangered species have been identified at a Federal Superfund site, consultation with Federal and state Natural Resource Trustees is required prior to implementation of a remedy.

4.5.5. TCH and ERH have the ability to reduce soil moisture content. This could have the potential for soil shrinkage in expansive clays, potentially impacting foundations. Data evaluations to date have shown that under ERH applications, moisture content is reduced by approximately 50% in the vicinity of the water table in clay soils. Moisture content above the water table remains relatively consistent owing to the continued steaming from below during treatment. The thickness of the zone experiencing reductions in moisture content is believed to be a factor of the duration of heating and the hydraulic conductivity of the soils.