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### PRESUMPTIVE RESPONSE STRATEGY AND EX-SITU TREATMENT TECHNOLOGIES FOR CONTAMINATED GROUND WATER AT CERCLA SITES

### FINAL GUIDANCE

Office of Solid Waste and Emergency Response U.S. Environmental Protection Agency Washington, DC 20460

#### NOTICE

This document provides guidance to EPA staff. It also provides guidance to the public and to the regulated community on how EPA intends to exercise its discretion in implementing the National Contingency Plan. The guidance is designed to implement national policy on these issues. The document does not, however, substitute for EPA's statutes or regulations, nor is it a regulation itself. Thus, it cannot impose legally-binding requirements on EPA, States, or the regulated community, and may not apply to a particular situation based upon the circumstances. EPA may change this guidance in the future, as appropriate.

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#### ACRONYMS USED IN THIS GUIDANCE

ACL	Alternate Concentration Limit	NPL	National Priorities List
ARAR	Applicable or Relevant and Appropriate Requirement	OERR	Office of Emergency and Remedial Response
CERCLA	Comprehensive Environmental	ORD	Office of Research and Development
	Response, Compensation, and Liability Act of 1980, as amended by SARA	OSWER	Office of Solid Waste and Emergency Response
CERI	Center for Environmental Research Information	РСВ	Polychlorinated Biphenyl Compounds
CFR	Code of Federal Regulations	POTW	Publicly Owned Treatment Works
CSGWPP	Comprehensive State Ground Water Protection Program	RARA	Resource Conservation and Recovery Act
DNAPL	Dense Nonaqueous Phase Liquids	RD	Remedial Design
EPA	Environmental Protection Agency	RD/RA	Remedial Design/Remedial Action
ESD	Explanation of Significant Differences	RI	Remedial Investigation
FS	Feasibility Study	RI/FS	Remedial Investigation/Feasibility Study
GAC	Granular Activated Carbon	ROD	Record of Decision
LNAPL	Light Nonaqueous Phase Liquids	SACM	Superfund Accelerated Cleanup
MCL	Maximum Contaminant Level		Model
MCLG	Maximum Contaminant Level Goal	SARA	Superfund Amendments and Reauthorization Act of 1986
NAPL	Nonaqueous Phase Liquid	UV	Ultra Violet (light)
NCP	National Oil and Hazardous Substances Pollution Contingency Plan	VOC	Volatile Organic Compound

#### PREFACE

**Presumptive Remedies Initiative.** The objective of the presumptive remedies initiative is to use the Superfund program's past experience to streamline site investigations and speed up selection of cleanup actions. Presumptive remedies are expected to increase consistency in remedy selection and implementation, and reduce the cost and time required to clean up similar types of sites. The presumptive remedies approach is one tool within the Superfund Accelerated Cleanup Model (SACM) (EPA, 1992d).

**Presumptive remedies** are preferred technologies for common categories of sites, based on historical patterns of remedy selection and EPA's scientific and engineering evaluation of performance data on technology implementation. Refer to EPA Directive, *Presumptive Remedies: Policy and Procedures* (EPA, 1993d) for general information on the presumptive remedy process and issues common to all presumptive remedies. This directive should be reviewed before utilizing a presumptive remedy and for further information on EPA expectations concerning the use of presumptive remedies. **"Presumptive remedies are expected to be used at all appropriate sites,"** except under unusual site-specific circumstances (EPA, 1993d).

**Other Presumptive Remedy Guidance.** Previous fact sheets from EPA's Office of Solid Waste and Emergency Response (OSWER) have established presumptive remedies for municipal landfill sites (EPA, 1993f), for sites with volatile organic compounds in soils (EPA, 1993e) and for wood treater sites (EPA, 1995g). A presumptive response selection strategy for manufactured gas plant sites is under development. Additional fact sheets are in progress for sites contaminated with polychlorinated biphenyl compounds (PCBs), metals in soils and for grain storage sites.

**Relation of this Guidance to Other Presumptive Remedies.** The fact sheets mentioned above provide presumptive remedies (or a strategy for selecting remedies) for "source control" at specific types of sites. With respect to ground-water response, source control refers to containment or treatment of materials that may leach contaminants to ground water, or a combination of these approaches. In general, treatment is expected for materials comprising the principal threats posed by a site, while containment is preferred for low level threats (EPA, 1991c). Where contaminants have reached ground water and pose an unacceptable risk to human health or the environment, a ground-water remedy will generally be required in addition to the source control remedy and this guidance should be consulted.

Instead of establishing one or more presumptive remedies, this guidance defines a **presumptive response strategy**. EPA expects that some elements of this strategy will be appropriate for **all** sites with contaminated ground water and all elements of the strategy will be appropriate for many of these sites. In addition, this guidance identifies **presumptive technologies** for the ex-situ treatment component of a ground-water remedy, that are expected to be used for sites where extraction and treatment is part of the remedy. (The term presumptive technology is used in this guidance to denote only the ex-situ treatment component of a ground-water remedy.) Other remedy components could include methods for extracting ground water, enhancing contaminant recovery or degradation of contaminants in the subsurface, discharging treated water, preventing contaminant migration, and institutional or engineering controls to prevent exposure to contaminants.

**Applicability to RCRA Corrective Action Program.** EPA continues to seek consistency between cleanup programs, especially in the process of selecting response actions for sites regulated under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA or Superfund program) and corrective measures for facilities regulated under the Resource Conservation and Recovery Act (RCRA). In general,

even though the Agency's presumptive remedy guidances were developed for CERCLA sites, they should also be used at RCRA Corrective Action sites to focus RCRA Facility Investigations, simplify evaluation of remedial alternatives in the Corrective Measures Study, and influence remedy selection in the Statement of Basis. For more information refer to the RCRA Corrective Action Plan (EPA, 1994c), the proposed Subpart S regulations (Federal Register, 1990b), and the May 1, 1996 RCRA Corrective Action Advance Notice of Proposed Rulemaking (Federal Register, 1996).

**Use of this Guidance.** The **presumptive response strategy**, described in Section 2.1, integrates site characterization, early actions, remedy selection, performance monitoring, remedial design and remedy implementation activities into a comprehensive, overall response strategy for sites with contaminated ground water. By integrating these response activities, the presumptive strategy illustrates how the Superfund Accelerated Cleanup Model (SACM) can be applied to ground-water cleanup. Although this response strategy will not necessarily streamline the remedial investigation/feasibility study (RI/FS) phase, EPA expects that use of the presumptive strategy will result in significant time and cost savings for the overall response to contaminated ground water. By providing a mechanism for selecting achievable remediation objectives, the presumptive strategy will minimize the need for changing these objectives during remedy implementation. By optimizing the remedy for actual site conditions during implementation, the effectiveness of the selected remedy can be greatly increased, which will reduce the time and cost required to achieve remediation objectives.

The **presumptive technologies** for treating extracted ground water, identified in Section 3.1, are the technologies that should generally be retained for further consideration in the Detailed Analysis portion of the feasibility study (or in the remedial design as explained in Section 3.3.3). This guidance and its associated Administrative Record will generally constitute the Development and Screening of Alternatives portion of the feasibility study (FS) for the ex-situ treatment component of a ground-water remedy (see Section 3.3.2). In this respect, the presumptive technologies will streamline the FS for this component of a ground-water remedy in the same way that other "presumptive remedies" streamline the FS for the overall remedy for their respective site types (see EPA, 1993d).

#### **1.0 INTRODUCTION**

In implementing the Superfund and other remediation programs, cleanup of contaminated ground water has proven to be more difficult than anticipated. For many sites, the program expectation of returning ground waters to their beneficial uses (see Section 1.2.1) often requires very long time periods and may not be practicable for all or portions of the site. Thus, the ultimate cleanup goal for ground water may need to be different over different areas of the site (see Section 1.3.1). For sites where achieving the ultimate goal will require a long time period, interim remediation objectives will generally be appropriate, such as preventing further plume migration. Therefore, a critical first step in the remedy selection process is to determine the full range of remedial objectives that are appropriate for a particular site.

This guidance is intended to emphasize the importance of using site-specific remedial objectives as the focus of the remedy selection process for contaminated ground water. Those remedy components that influence attainment of remedial objectives should receive the greatest attention. For example if restoring the aquifer to beneficial use is the ultimate objective, remedy components that influence attainment of cleanup levels in the aquifer include: methods for extracting ground water, enhancing contaminant recovery, controlling subsurface contaminant sources (e.g., nonaqueous phase liquids or NAPLs, discussed in Appendix A1) or in-situ treatment of contaminants. Some or all of these remedy components should be included in remedial alternatives that are developed and evaluated in detail in the feasibility study (FS) when aquifer restoration is a remedial objective.

Although the technologies employed for treating extracted ground water and the types of discharge for the treated effluent are important aspects of a remedy, they have little influence on reducing contaminant levels or minimizing contaminant migration in the aquifer. In developing this guidance, historical patterns of remedy selection and available technical information were reviewed in order to identify presumptive technologies for ex-situ treatment of ground water. **By providing presumptive technologies, this guidance attempts to streamline selection of these technologies and shift the time and resources employed in remedy selection to other, more fundamental aspects of the ground-water remedy.** 

Although extraction and treatment has been and will continue to be used as part of the remedy for many sites with contaminated ground water, it may **not** be the most appropriate remediation method for all sites or for all portions of a given contaminant plume. Also, remedial alternatives that combine extraction and treatment with other methods, such as natural attenuation (defined in Section 2.6.5) or in-situ treatment, may have several advantages over alternatives that utilize extraction and treatment alone (see Section 2.4.2). (Remedial alternatives are evaluated against remedy selection criteria defined in the National Contingency Plan at §300.430(e)(9)(iii) (Federal Register, 1990a).) In general, the remedy selection process should consider whether extraction and treatment can achieve remedial objectives appropriate for the site and how this approach can be most effectively utilized to achieve these objectives. This guidance also describes a presumptive response strategy which facilitates selection of both short and long-term remediation objectives during remedy selection, and allows the effectiveness of the remedy to be improved during implementation.

#### 1.1 Purpose of Guidance

In summary, this guidance is intended to:

• **Describe a presumptive response strategy**, at least some elements of which are expected to be appropriate for **all** sites with contaminated ground water;

- Identify presumptive technologies for treatment of extracted ground water (exsitu treatment) that are expected to be used (see EPA,1993d) for sites where extraction and treatment is part of the remedy;
- Simplify the selection of technologies for the ex-situ treatment component of a ground-water remedy, and improve the technical basis for these selections; and
- Shift the time and resources employed in remedy selection from ex-situ treatment to other, more fundamental aspects of the ground-water remedy, as discussed above.

# **1.2** Expectations and Objectives for Ground-Water Cleanup

Careful consideration should be given to national program expectations as well as site-specific conditions when determining cleanup objectives that are appropriate for a given site.

**1.2.1 Program Expectations.** Expectations for contaminated ground water are stated in the National Oil and Hazardous Substances Pollution Contingency Plan (NCP), as follows:

"EPA expects to return usable ground waters to their **beneficial uses** wherever practicable, within a **timeframe** that is reasonable given the particular circumstances of the site. When restoration of ground water to beneficial uses is **not practicable**, EPA expects to prevent further migration of the plume, prevent exposure to the contaminated ground water, and evaluate further risk reduction." (Federal Register, 1990a; §300.430 (a)(1)(iii)(F), emphasis added.)

The Preamble to the NCP explains that the program expectations are not "binding requirements." "Rather, the expectations are intended to share collected experience to guide those developing cleanup options" (Federal Register, 1990a; at 8702).

#### 1.2.2 Objectives for Site Response Actions.

The program expectations can be used to define the following overall objectives for site response actions, which are generally applicable for **all** sites with contaminated ground water:

- Prevent exposure to contaminated ground water, above acceptable risk levels;
- Prevent or minimize further migration of the contaminant plume (plume containment);
- Prevent or minimize further migration of contaminants from source materials to ground water (source control); and
- Return ground waters to their expected beneficial uses wherever practicable (aquifer restoration).

In this guidance the term "response action" is used to indicate an action initiated under either CERCLA removal or remedial authority. "Response objective" is the general description of what a response action is intended to accomplish. Source control is included as an objective because the NCP expectation of aquifer restoration will not be possible unless further leaching of contaminants to ground water is controlled, from both surface and subsurface sources. The objectives, given above, are listed in the sequence in which they should generally be addressed at sites.

Monitoring of ground-water contamination is not a separate response objective, but is necessary to verify that one or more of the above objectives has been attained, or will likely be attained (see Section 2.1.3). Other response objectives may also be appropriate for some sites, depending on the type of action being considered and site conditions (e.g., maximizing the reuse of extracted ground water may be an appropriate objective for some sites). **Response objectives may be**  **different over different portions of the contaminant plume**, as discussed in Section 1.3.1.

#### 1.3 Lessons Learned

The most important lesson learned during implementation of Superfund and other remediation programs is that complex site conditions are more common than previously anticipated, including those related to the source and type of contaminants as well as site hydrogeology. As a result of these site complexities, restoring all or portions of the contaminant plume to drinking water or similar standards may not be possible at many sites using currently available technologies.

#### 1.3.1 Sources and Types of Contaminants.

Approximately 85 percent of sites on the CERCLA National Priorities List (NPL sites) have some degree of ground-water contamination. Contaminants have been released to ground water at a wide variety of site types and can include a variety of contaminants and contaminant mixtures. Sources of contaminants to ground water not only include facilities from which the original release occurred (e.g., landfills, disposal wells or lagoons, storage tanks and others) but also include contaminated soils or other subsurface zones where contaminants have come to be located and can continue to leach into ground water (e.g., NAPLs, see Appendix A1). Thus, the plume of contaminated ground water may encompass NAPLs in the subsurface (sources of contamination) as well as dissolved contaminants. In this case, different response objectives may be appropriate for different portions of the plume. For example, source control (e.g., containment) may be the most appropriate response objective for portions of the plume where NAPLs are present and can not practicably be removed, while aquifer restoration may be appropriate only for the remaining portions of the plume (see Section 2.5.3).

Although originating from a variety of sources, contaminants which reach ground water tend to be

those that are relatively mobile and chemically stable in the subsurface environment (e.g., less likely to sorb to soil particles or degrade above the water table). Organic and inorganic contaminants most frequently found in ground water at CERCLA sites are listed in Appendix A2. Sixteen of the 20 most common organic contaminants are volatile organic compounds (VOCs). Of the 16 VOCs, 12 are chlorinated solvents and four are chemicals found in petroleum fuels. Petroleum fuels are **light** nonaqueous phase liquids (LNAPLs, with a density lighter than water); while most chlorinated solvents are **dense** nonaqueous phase liquids (DNAPLs) in pure form (see Appendix A1).

#### **1.3.2 Factors Limiting Restoration Potential.**

At many sites, restoration of ground water to cleanup levels defined by applicable or relevant and appropriate requirements (ARARs) or riskbased levels may not be possible over all or portions of the plume using currently available technologies. Two types of **site conditions** inhibit the ability to restore ground water:

- Hydrogeologic factors, and
- Contaminant-related factors.

Recent studies by EPA and others have concluded that complex site conditions related to these factors are more common at hazardous waste sites than originally expected (EPA, 1989a, 1992b, 1992g, and 1993b; and the National Research Council, 1994). Examples of hydrogeologic or contaminant-related factors affecting the difficulty of restoring ground water are given in Figure 1. These types of site conditions should be considered in the site conceptual model, which is an interpretive summary of the site information obtained to date (not a computer model). Refer to EPA, 1993b and 1988a for additional information concerning the site conceptual model. For every site, data should be reviewed or new data should be collected to identify factors that could increase (or decrease) the difficulty of restoring ground water.

jene	ain site characteristics may lin	nit the effectiveness of subsurface real or combination of factors that may ci	d-Water Restoration Potential mediation. The examples listed below are highly itically limit restoration potential will be site specific.
	Site/Contaminant Characteristics		Remediation Difficulty Scale
	Nature of Release	Small Volume Short Duration Slug Release	Large Volume Long Duration Continual Release
221	Biotic/Aboitic Decay Potential	High	Low
) 2 -	Volatility	High	Low
	Contaminant Retardation (Sorption) Potential	Low	High
	Contaminant Phase	Aqueous, Gaseous — 🍽 Sorbe	d — DNAPLS — DNAPLS
	Volume of Contaminated Media	Small ————	Large
	Contaminant Depth	Shallow	Deep
I	Hydrogeologic Characteristics	1	
;	Stratigraphy	Simple Geology, e.g., Planar Bedding Strata	<ul> <li>Complex Geology, e.g., Interbedded and Discontinuous</li> </ul>
	Texture of Unconsolidated Deposits	Sand	Clay
	Degree of Heterogeneity	Homogeneous e.g., well-sorted sand	Heterogeneous e.g., interbedded sand and silts, clays, fractured media, karst
	Hydraulic Conductivity of Aquifer	High (>10 <sup>-2</sup> cm/sec)	→ Low (< 10 <sup>4</sup> cm/sec)
、 、	Temporal Variation of Flow Regime	Little/None	- High
	Vertical Flow	Little Component	Large Downward Flow

#### 1.3.3 Assessing Restoration Potential.

Characterizing all site conditions that could increase the difficulty of restoring ground water is often not possible. As a result, the likelihood that ARAR or risk-based cleanup levels can be achieved (restoration potential) is somewhat to highly uncertain for many sites, even after a relatively complete remedial investigation. This uncertainty can be reduced by using remedy performance in combination with site characterization data to assess the restoration potential. By implementing a ground-water remedy in more than one step or phase (as two separate actions or phasing of a single action as described in Section 2.2), performance data from an initial phase can be used to assess the restoration potential and may indicate that additional site characterization is needed. In addition to providing valuable data, the initial remedy phase can be used to attain short-term response objectives, such as preventing further plume migration. Phased implementation of response actions also allows realistic long-term remedial objectives to be determined prior to installation of the comprehensive or "final" remedy.

A detailed discussion of factors to consider for assessing restoration potential is provided in Guidance for Evaluating the Technical Impracticability of Ground-Water Restoration (EPA, 1993b; Section 4.4.4). An especially important tool for this evaluation is the site conceptual model, which should integrate data from site history, characterization and response actions. This assessment could provide justification for waiving ARARs due to technical impracticability from an engineering perspective over all or portions of a site (EPA, 1993b). It is recommended that technical assistance be enlisted from regional technical support staff or the Technical Support Project (EPA, 1994d) when evaluating technical impracticability.

**Data from remedy performance are not always necessary to justify an ARAR waiver due to technical impracticability** (see Section 2.6.3). At the completion of the remedial investigation (RI), site conditions may have been characterized to the extent needed for EPA (or the lead agency) to determine that ground-water restoration is technically impracticable from an engineering perspective (EPA, 1993b; EPA 1995b). For this case, an ARAR waiver request can be submitted to EPA (or the lead agency), and if approved, included in the Record of Decision (ROD). It will often be appropriate to include an ARAR waiver in the ROD for portions of a site where DNAPLs have been confirmed in the aquifer (see Section 2.5.3).

## 2.0 PRESUMPTIVE RESPONSE STRATEGY

#### 2.1 Definition and Basis for Strategy

Key elements of the presumptive strategy are summarized in Highlight 1. In the presumptive response strategy, site characterization and response actions are implemented in a several steps, or in a **phased approach**. In a phased response approach, site response activities are implemented in a sequence of steps, or phases, such that information gained from earlier phases is used to refine subsequent investigations, objectives or actions (EPA, 1989a, 1992b, 1993b).

#### In general for sites with contaminated ground water, <u>site characterization</u> should be coordinated with <u>response actions</u> and <u>both</u> should be implemented in a step-by-step or phased approach.

Performance data from an initial response action are also used to assess the likelihood that ARAR or risk-based cleanup levels can be attained by later, more comprehensive actions. Although it is recognized that phased implementation may not be appropriate for all ground-water remedies, EPA expects that some elements of this strategy will be appropriate for **all** sites with contaminated ground water and that all elements will be appropriate for many of these sites. **For this reason, the response approach given in** 

### Highlight 1. Presumptive Response Strategy

- For sites with contaminated ground water, site characterization should be coordinated with response actions and both should be implemented in a phased approach (Sections 1.3.3 and 2.1).
- **Early or interim actions** should be used to reduce site risks (by preventing exposure to and further migration of contaminants) and to provide additional site data (Section 2.1.2).
- Site characterization and performance data from early or interim ground-water actions should be used to assess the likelihood of restoring ground waterto ARAR or risk-based cleanup levels (restoration potential). (Sections 1.3.3 and 2.1.2.)
- The restoration potential should be assessed prior to establishing objectives for the long-term remedy (Sections 1.3.3 and 2.1.2).
- All ground-water actions should include provisions for monitoring and evaluating their performance (Section 2.1.3).
- Ground-water response actions, especially those using extraction and treatment, should generally be implemented in more than one phase -- either as two separate actions or phasing of a single action (Sections 2.2.1 and 2.2.2).
- In addition to phasing, postconstruction refinements will generally be needed for long-term remedies, especially those using extraction and treatment (Section 2.3.1).

## Highlight 1 is a presumptive strategy for contaminated ground water.

Also, this response strategy is considered presumptive because the **basic elements were included in <u>all</u> <b>previous policy directives** concerning ground-water remediation from EPA's Office of Solid Waste and Emergency recommended use of a phased approach for site characterization and response actions, and more frequent use of early actions to reduce site risks. Better integration of site activities and more frequent use of early actions are also essential components of the Superfund Accelerated Cleanup Model (SACM), defined in EPA, 1992d.

#### 2.1.1 Benefits of Phased Approach.

Implementing investigations and actions in phases provides the following major **benefits**:

- Data from earlier response actions are used to further characterize the site and assess restoration potential;
- Attainable objectives can be set for each response phase;
- Flexibility is provided to adjust the remedy in response to unexpected site conditions;
- Remedy performance is increased, decreasing remediation timeframe and cost; and
- Likely remedy refinements are built into the selected remedy, better defining the potential scope and minimizing the need for additional decision documents.

**2.1.2 Early Actions.** "Early" refers to the timing of the start of an action with respect to other response actions at a given site. For Superfund sites, early actions could include removal actions, interim remedial actions, or early final remedial actions (EPA, 1992b and EPA, 1991b). Although initiated prior to other actions, some early groundwater actions may need to operate over a long time

period (e.g., hydraulic containment actions). In this guidance the later, more comprehensive ground-water action is called the "long-term remedy," consistent with SACM terminology (EPA, 1992e). Early actions that should be considered in response to contaminated ground water are listed in Highlight 2, categorized by response objective. **Early or interim actions should be used to reduce site risks (by preventing exposure to contaminated ground water and further migration of contaminants**) **and to provide additional site data.** 

Factors for determining which response components are suitable for early or interim actions include: the timeframe needed to attain specific objectives, the relative urgency posed by potential or actual exposure to contaminated ground water (e.g., likelihood that contaminants will reach drinking water wells), the degree to which an action will reduce site risks, usefulness of information to be gained from the action, site data needed to design the action, and compatibility with likely long-term actions (EPA, 1992e). Whether to implement early response actions and whether to use removal or remedial authority for such actions should be determined by the "Regional Decision Team" defined under SACM (EPA, 1992f) or similar decision-making body for the site.

Early or interim actions should be integrated as much as possible with site characterization and with subsequent actions in a phased approach. Once implemented, early actions will often provide additional site characterization information, which should be used to update the site conceptual model. Also, treatability studies (see Section 3.4.5) needed for selection or design of the long-term remedy should be combined with early actions whenever practical. Site characterization and performance data from early or interim ground-water actions should be used to assess the likelihood of restoring ground water to ARAR or risk-based cleanup levels (restoration potential). **The restoration** 

### Highlight 2. Early Actions That Should Be Considered

Prevent exposure to contaminated ground water:

- Plume containment
- Alternate water supply
- Well head treatment
- Use restrictions

Prevent further migration of **contaminant plume**:

- Plume containment
- Contain (and/or treat) plume "hot spots"

Prevent further migration of contaminants from sources:

- Source removal and/or treatment
  - Excavate wastes or soils and remove from site
  - Excavate soils and treat exsitu
  - Treat soils in-situ
  - Extract free-phase NAPLs (see Appendix A1)
- Source containment
  - Contain wastes or soils
  - Contain subsurface NAPLs

Provide additional site data:

- Assess restoration potential
- Combine actions with treatability studies

potential should be assessed prior to establishing objectives for the long-term remedy (see Section 1.3.3).2.1.3 Monitoring. Monitoring is needed to evaluate whether the ground-water action is achieving, or will achieve, the intended response objectives for the site (see Section 1.3.1) and other performance objectives for the action (e.g., discharge requirements). All ground-water actions should include provisions for monitoring and evaluating their performance. A monitoring plan should be developed for both early and long-term actions. In general, the monitoring plan should include:

- Response objectives and performance requirements for the ground-water action;
- Specific monitoring data to be collected;
- Data quality objectives;
- Methods for collecting, evaluating and reporting the performance monitoring data; and
- Criteria for demonstrating that response objectives and performance requirements have been attained.

Flexibility for adjusting certain aspects of monitoring during the life of the remedy should be included in the monitoring plan, such as changes in the monitoring frequency as the remedy progresses or other changes in response to remedy refinements (see Section 2.3.1). A detailed discussion of the data quality objectives process is provided in EPA, 1993j. Methods for monitoring the performance of extraction and treatment actions are discussed in EPA, 1994e.

#### 2.2 Phased Response Actions

In general, ground-water response actions, especially those using extraction and treatment, should be implemented in more than one phase. There are two options for phasing response actions - implementation of two separate actions, or implementation of a single action in more than one phase. It is recognized that phased implementation may not be appropriate for all ground-water remedies. In some cases, it may be more appropriate to install the entire remedy and then remove from service those components that later prove to be unneeded.

2.2.1 Two Separate Actions. In this approach an early or interim ground-water action is followed by a later, more comprehensive action (the longterm remedy). A flow chart of this approach is given in Figure 2. Earlier ground-water actions are used to mitigate more immediate threats, such as preventing further plume migration. Response objectives for the long-term remedy are not established until after performance of the earlier action is evaluated and used to assess the likelihood that ground-water restoration (or other appropriate objectives) can be attained. Two separate decision documents are used, in which response objectives are specified that are appropriate for each action. The earlier decision document could be an Action Memorandum or an Interim Record of Decision (Interim ROD), since the early action could be initiated under either CERCLA removal or remedial authority. This approach should be used when site characterization data are not sufficient to determine the likelihood of attaining long-term objectives (e.g., restoring ground water) over all or portions of the plume, which will be the case for many sites. In order to provide sufficient data for assessing the restoration potential, the early or interim action may need to operate for several years.

**2.2.2 Phasing of a Single Action.** In this approach the long-term remedy for ground water is implemented in more than one design and construction phase. A flow chart of this approach is given in Figure 3. Response objectives for the long-term remedy are specified in a single Record of Decision (ROD) prior to implementing the remedy. Provisions for assessing the attainability of these objectives using performance data from an initial remedy phase are also included in the ROD. Thus, phased remedy implementation and assessment of remedy performance are specified

in one ROD. A second decision document could still be required if evaluation of the first phase



#### Figure 2. Phased Ground-Water Actions: Early Action Followed by Long-Term Remedy



#### Figure 3. Phased Ground-Water Actions: Long-Term Remedy Implemented in Phases

indicates that long-term objectives or other aspects of the remedy require modification, and the modified remedy differs significantly from the selected remedy in terms of scope, performance or cost (EPA, 1991a). This approach should be used when site characterization data indicate that the likelihood of attaining long-term objectives is relatively high.

When phased remedy implementation is specified in a ROD, the Agency should ensure that the proposed plan contains sufficient information regarding the nature, scope timing and basis of future decision points and alternatives that the public is able to evaluate and comment on the proposed remedy. Example language illustrating how such an approach can be specified in the selected remedy portion of the ROD is included in Appendices B1 and B2 for hypothetical sites. These examples follow the suggested ROD language given in EPA, 1990b, although the wording has been updated to reflect this and other recent guidance (EPA, 1993b). For comparison, suggested ROD language from the EPA, 1990b is included as Appendix B4.

Phased implementation of a remedy can often be beneficial even for relatively simple ground-water actions. For example, one extraction well could be installed as the initial phase and the performance of this well would be used to determine whether any additional wells are needed **and** whether long-term objectives need to be reevaluated.

Phased implementation of an extraction and treatment remedy will require that the treatment system be designed to accommodate phased installation of the extraction system. Presumptive technologies for the treatment system and other design considerations are discussed in Section 3. Use of modular treatment components, which can be easily added or removed from the treatment system, may facilitate phased implementation or other changes in flow or contaminant concentration that may occur during the life of a remedy. Another approach is to design the treatment system for the higher flows expected from all phases of the extraction system. Some components of the remedy, such as buried portions of the piping distribution system, are difficult to install in phases and should be designed to carry the highest expected flows.

#### 2.3 Post-Construction Refinements

Even after phased implementation of a groundwater remedy, post-construction refinements will generally be needed because of the long time period over which the remedy will operate, especially for extraction and treatment remedies. The refinement portion of the long-term remedy, after phased design and construction, is shown in both Figures 2 and 3.

2.3.1 Types of Refinements. Post-construction refinements that should be considered for extraction and treatment remedies are given in Highlight 3. These refinements are intended to be relatively minor changes to the remedy (i.e., for which an Explanation of Significant Differences (ESD) or ROD Amendment would generally not be required). For example, adding a new extraction or reinjection well, or a few additional monitoring wells should be considered a minor modification to a remedy that includes a relatively large number of such wells, because the overall scope, performance and cost of the remedy are not significantly changed (EPA, 1991a). One or more such refinements should generally be implemented when the results of a remedy evaluation indicate that they are needed to increase the performance of the remedy or to decrease the remediation timeframe.

**2.3.2 Documenting Refinements.** Potential postconstruction refinements should be included in the ROD as part of the selected remedy. Listing specific remedy refinements in the ROD serves to communicate the anticipated full scope of the remedy to all concerned parties at an early date, and also minimizes the likelihood that a subsequent **ESD or ROD Amendment will be needed.** When remedy refinements are specified in a ROD, the Agency should ensure that the

### Highlight 3. Remedy Refinements for Extraction/Treatment Remedies

- Change the extraction rate in some or all wells.
- Cease extraction from some wells.
- Initiate "pulsed pumping" (see Appendix A4).
- Add or remove extraction or reinjection wells, or drains.
- Add or remove monitoring wells.
- Refine source control components of remedy.
- Refine enhanced recovery or in-situ degradation components of remedy (see Note).
- Refine ex-situ treatment components

**NOTE:** A ground-water remedy could include both extraction and treatment and insitu treatment methods.

proposed plan contains sufficient information regarding the nature, scope timing and basis of future decision points and alternatives that the public is able to evaluate and comment on the proposed remedy. Example ROD language specifying likely post-construction refinements for the extraction portion of the selected remedy is given in Appendices B1 and B2. Even if an ESD is not required, a letter or memorandum should be included in the post-ROD portion of the Administrative Record explaining the minor remedy modifications and the reasons for them. Additional information concerning documentation of remedy modifications can be found in the EPA fact sheet entitled Guide to Addressing Pre-ROD and Post-ROD Changes (EPA, 1991a).

#### 2.4 Integrating Response Actions

In general, actions in response to contaminated ground water should be planned and implemented as part of an overall strategy. Earlier actions (see Highlight 2 for examples) should be compatible with and not preclude implementation of later actions. For example, permanent facilities should not be constructed which could interfere with possible later actions (e.g., structures that would interfere with later construction of extraction wells or of a cap).

2.4.1 Integrating Source Control and Ground-Water Actions. Restoration of contaminated ground water generally will not be possible unless contaminant sources have been controlled in some manner. Source control is a critical component for active restoration remedies (e.g., extraction and treatment and in-situ methods) as well as for natural attenuation (defined in Section 2.6.5). Selection of appropriate source control actions should consider whether other contaminant sources (i.e., NAPLs) are likely to be present in addition to contaminated soils. If NAPLs are present, the vast majority of contaminant mass will likely reside in the subsurface NAPLs rather than in the surficial soils. Therefore, for this case source control actions that are intended to minimize further contamination of ground water should focus on controlling migration of contaminants from the subsurface NAPLs. Also, capping or treatment of surficial soils may be needed to prevent exposure to contaminants from direct soil contact or inhalation, but these actions alone would be ineffective in preventing further contamination of ground water at sites where NAPLs are present.

**2.4.2 Combining Ground-Water Restoration Methods.** A remedy could include more than one method for restoring ground water to its beneficial uses, such as combining extraction and treatment with natural attenuation or in-situ-treatment with extraction and treatment. Extraction and treatment is especially useful for providing hydraulic containment of those portions of the plume where contaminant sources are present (e.g., subsurface NAPLs or contaminated soils), or for containing or restoring those plume areas with relatively high concentrations of dissolved contamination ("hot spots"). However, extraction and treatment may not be the best method for restoring large areas of the plume with low contaminant levels.

Once source areas are controlled, natural attenuation may be able to restore large portions of the plume to desired cleanup levels in a timeframe that is reasonable (see Section 2.6.2) when compared with the timeframe and cost of other restoration methods. Thus, natural attenuation of some plume areas combined with extraction and treatment to contain source areas and/or plume "hot spots" may be the most appropriate restoration approach for many sites with relatively large, dilute plumes. Whether or not natural attenuation is used alone or combined with other remediation methods, the Agency should have sufficient information to demonstrate that natural processes are capable of achieving the remediation objectives for the site. EPA is currently preparing a directive that will provide more detailed discussion of EPA policy regarding the use of natural attenuation for remediation of contaminated ground water (EPA, 1996c).

By combining in-situ treatment and extraction and treatment methods it may be possible to significantly increase the effectiveness with which contaminants are removed from the aquifer. In this guidance, in-situ treatment methods for ground water are divided into two types:

- Methods that can be used to **enhance contaminant recovery** during extraction and treatment (e.g., water, steam or chemical flooding; hydraulic or pneumatic fracturing); and
- Methods for in-situ degradation of contaminants generally involve adding agents to the subsurface (i.e., via wells or treatment walls) which facilitate chemical or biological destruction, and have the

potential to be used as an alternative to extraction and treatment for long-term restoration of ground water.

Examples of both types of in-situ treatment methods are given in Appendix A3. Reinjection of treated ground water can be used as a method for enhancing contaminant recovery as well as a discharge method, if the reinjection is designed for this purpose as part of an extraction and treatment remedy. When considering enhanced recovery methods for sites with subsurface NAPLs. potential risks of increasing the mobility of NAPLs should be evaluated. Methods of in-situ degradation of contaminants most frequently used at Superfund sites include air sparging, various types of in-situ biological treatment and permeable treatment walls or gates (EPA, 1995e). Additional information concerning air sparging and permeable treatment walls is available in EPA, 1995f and EPA, 1995d, respectively. EPA encourages the consideration, testing and use of in-situ technologies for ground-water remediation when appropriate for the site.

#### 2.5 Strategy for DNAPL Sites

Dense nonaqueous phase liquids (DNAPLs) pose special cleanup difficulties because they can sink to great depths in the subsurface, continue to release dissolved contaminants to the surrounding ground water for very long time periods, and can be difficult to locate. Due to the complex nature of DNAPL contamination, a phased approach to characterization and response actions is especially important for sites where DNAPLs are confirmed or suspected. A recent EPA study concluded that subsurface DNAPLs may be present at up to 60 percent of CERCLA National Priorities List sites (EPA, 1993c). Refer to Appendix A1 for additional background information on DNAPLs.

Two types of subsurface contamination can be defined at DNAPL sites, the:

- DNAPL zone, and the
- Aqueous contaminant plume.

The **DNAPL zone** is that portion of the subsurface where immiscible liquids (free-phase or residual DNAPL) are present either above or below the water table. Also in the DNAPL zone, vapor phase DNAPL contaminants are present above the water table and dissolved phase below the water table. The **aqueous contaminant plume** is that portion of the contaminated ground water surrounding the DNAPL zone where aqueous contaminants derived from DNAPLs are dissolved in ground water (or sorbed to aquifer solids) and immiscible liquids are not present.

**2.5.1 Site Characterization.** If DNAPLs are confirmed or suspected, the remedial investigation (RI) should be designed to delineate the:

- Extent of aqueous contaminant plumes, and the
- Potential extent of DNAPL zones.

Methods and strategies for characterizing DNAPL sites as well as suggested precautions are discussed in other guidance (EPA, 1992a and 1994b) and by Cohen and Mercer, 1993. The reason for delineating these areas of the site is that response objectives and actions should generally be different for the DNAPL zone than for the aqueous contaminant plume. It is recognized that for some sites complete delineation of the DNAPL-zone may not be possible.

**2.5.2 Early Actions.** The early actions listed in Highlight 2 should be considered. Also, the following early actions are specifically recommended for DNAPL sites (EPA 1992b, 1993b):

- Prevent further spread of the aqueous plume (plume containment);
- Prevent further spread of hot spots in the aqueous plume (hot spot containment);

- Control further migration of contaminants from subsurface DNAPLs to the surrounding ground water (source control); and
- Reduce the quantity of source material (**free-phase DNAPL**) present in the DNAPL zone, to the extent practicable (source removal and/or treatment).

At DNAPL sites, hot spots in the aqueous plume often are associated with subsurface DNAPLs. Therefore, the second and third actions listed above are essentially the same.

**2.5.3 Long-Term Remedy.** The long-term remedy should attain those objectives listed above for the **DNAPL zone**, by continuing early actions or by initiating additional actions. Although contaminated ground waters generally are not considered **principal threat** wastes, DNAPLs may be viewed as a principal threat because they are sources of toxic contaminants to ground water (EPA, 1991c). For this reason EPA expects to remove or treat DNAPLs to the extent practicable in accordance with the NCP expectation to "use treatment to address the principal threats posed by a site, wherever practicable" (Federal Register, 1990a; §300.430 (a)(1)(iii)(A)). However, program experience has shown that removal of DNAPLs from the subsurface is often not practicable, and no treatment technologies are currently available which can attain ARAR or risk-based cleanup levels where subsurface DNAPLs are present. Therefore, EPA generally expects that the long-term remedy will control further migration of contaminants from subsurface DNAPLs to the surrounding ground water and reduce the quantity of DNAPL to the extent practicable.

For the **aqueous plume**, the long-term remedy should:

• Prevent further spread of the aqueous plume (plume containment);

• Restore the maximum areal extent of the aquifer to those cleanup levels appropriate for its beneficial uses (aquifer restoration).

In general, restoration of the aquifer to ARAR or risk-based cleanup levels in a reasonable timeframe will not be attainable in the DNAPL zone unless the DNAPLs are removed. For this reason, it is expected that ARAR waivers due to technical impracticability will be appropriate for many DNAPL sites, over portions of sites where non-recoverable DNAPLs are present (EPA, 1995c). Also, EPA generally prefers to utilize ARAR waivers rather than ARAR compliance boundaries for such portions of DNAPL sites (see Section 2.6.4). A waiver determination can be made after construction and operation of the remedy or at the time of remedy selection (i.e., in the ROD), whenever a sufficient technical justification can be demonstrated (EPA, 1993b; EPA 1995b). For further information refer to Section 2.6.3 of this guidance and EPA's Guidance for Evaluating the Technical Impracticability of Ground-Water Restoration (EPA, 1993b). Restoration of the aqueous plume may also be difficult due to hydrogeologic factors, such as sorption of dissolved contaminants to solids in finer grained strata. For some sites, ARAR waivers may also be appropriate for all or portions of the aqueous plume when supported by adequate justification.

#### 2.6 Areas of Flexibility in Cleanup Approach

The current response approach to contaminated ground water, as defined in the NCP and other guidance, includes several areas of flexibility in which response objectives and the timeframe in which to meet them can be adjusted to meet site specific conditions. These are briefly discussed below.

**2.6.1 Beneficial Uses and ARARs.** Since EPA generally expects to return contaminated ground waters to their beneficial uses wherever practicable, the required cleanup levels for a given site should be determined from applicable or

relevant and appropriate requirements (ARARs) based on the current and expected future beneficial uses of the ground water at that site. Depending on state requirements and water quantity or quality characteristics, some ground waters are not expected to provide a future source of drinking water (e.g., EPA Class III ground waters (EPA, 1986) or similar state designations). In general, drinking water standards are relevant and appropriate cleanup levels for ground waters that are a current or future source of drinking water, but are **not** relevant and appropriate for ground waters that are not expected to be a future source of drinking water (Federal Register, 1990a; Preamble at 8732). (Drinking water standards include federal maximum contaminant levels (MCLs) and/or non-zero maximum contaminant level goals (MCLGs) established under the Safe Drinking Water Act, or more stringent state drinking water standards.) Ground waters may have other beneficial uses, such as providing base flow to surface waters or recharging other aquifers. For contaminated ground waters that discharge to surface water, water quality criteria established under the Clean Water Act, or more stringent state surface water requirements, may also be cleanup level ARARs (Federal Register, 1990a; Preamble at 8754). Thus, the beneficial uses of contaminated ground water at a particular site will generally provide the basis for determining which federal or state environmental requirements are applicable or relevant and appropriate cleanup levels. For additional information on the determination of cleanup levels, refer to EPA, 1988b, Chapter 4.

Determination of current and expected future beneficial uses should consider state ground-water classifications or similar designations. Several states have developed ground-water use or priority designations as part of a Comprehensive State Ground Water Protection Program (CSGWPP), defined in EPA, 1992h. EPA is currently developing a directive (EPA, 1996a) which will recommend that EPA remediation programs **should generally defer** to state determinations of future ground-water use -- even when this determination differs from the use that would otherwise have been determined by EPA -- when such determinations are:

- Developed as part of an CSGWPP that is endorsed by EPA, and
- Based on CSGWPP provisions that can be applied at specific sites (EPA, 1996a).

This provision of the directive, when final, is intended to supersede previous guidance contained in the Preamble to the NCP (Federal Register. 1990a; at 8733). Refer to EPA, 1996a for additional information concerning the role of CSGWPPs in the selection of ground-water remedies. When information concerning beneficial uses is not available from a CSGWPP, ground-water classifications defined in EPA, 1986 (i.e., EPA Classes I, II or III) or "more stringent" state ground-water classifications (or similar state designations) should generally be used to determine the potential future use, in accordance with the NCP Preamble (Federal Register, 1990a; at 8732-8733). Regardless of the ground-water use determination, remedies selected under **CERCLA** authority must protect human health and the environment and meet ARARs (or invoke an ARAR waiver).

Many states have antidegradation or similar regulations or requirements that may be potential ARARs. Such requirements typically focus on 1) prohibiting certain discharges, 2) maintaining ground-water quality consistent with its beneficial uses, or 3) maintaining naturally occurring (background) ground-water quality. Regulations of the third type do not involve determination of future ground-water use, and often result in cleanup levels that are more stringent than the drinking water standard for a particular chemical. Such requirements are potential ARARs if they are directive in nature and intent and established through a promulgated statute or regulation that is legally enforceable (see Federal Register, 1990a; Preamble at 8746). For further information concerning issues related to state ground-water antidegradation requirements, refer to EPA, 1990a.

2.6.2 Remediation Timeframe. "Remediation timeframes will be developed based on the specific site conditions" (Federal Register, 1990a; Preamble at 8732). Even though restoration to beneficial uses generally is the ultimate objective, a relatively long time period to attain this objective may be appropriate for some sites. For example, an extended remediation timeframe generally is appropriate where contaminated ground waters are not expected to be used in the near term, and where alternative sources are available. In contrast, a more aggressive remedy with a correspondingly shorter remediation timeframe should generally be used for contaminated ground waters that are currently used as sources of drinking water or are expected to be utilized for this purpose in the near future (Federal Register, 1990a; at 8732). A state's CSGWPP may include information helpful in determining whether an extended remediation timeframe is appropriate for a given site, such as the expected timeframe of use, or the relative priority or value of ground-water resources in different geographic areas.

A **reasonable timeframe** for restoring ground waters to beneficial uses depends on the particular circumstances of the site and the restoration method employed. The most appropriate timeframe must be determined through an analysis of alternatives (Federal Register, 1990a; Preamble at 8732). The NCP also specifies that:

> "For ground-water response actions, the lead agency shall develop a limited number of remedial alternatives that attain site-specific remediation levels within different restoration time periods utilizing one or more different technologies." (Federal Register, 1990a; §300.430(e)(4).)

Thus, a comparison of restoration alternatives from most aggressive to passive (i.e., natural attenuation) will provide information concerning the approximate range of time periods needed to attain ground-water cleanup levels. An excessively long restoration timeframe, even with the most aggressive restoration methods, may indicate that ground-water restoration is technically impracticable from an engineering perspective (see Section 2.6.3). Where restoration is feasible using both aggressive and passive methods, the longer restoration timeframe required by a passive alternative may be reasonable in comparison with the timeframe needed for more aggressive restoration alternatives. The most appropriate remedial option should be determined based on the nine remedy selection factors defined in the NCP (Federal Register, 1990a; §300.430 (e)(9)(iii)). Although restoration timeframe is an important consideration in evaluating whether restoration of ground water is technically impracticable, no single time period can be specified which would be considered excessively long for all site conditions (EPA, 1993b). For example, a restoration timeframe of 100 years may be reasonable for some sites and excessively long for others.

2.6.3 Technical Impracticability. Where restoration of ground water to its beneficial uses is not practicable from an engineering perspective, one or more ARARs may be waived by EPA (or the lead agency) under the provisions defined in CERCLA (121(d)(4)(C)). The types of data used to make such a determination are discussed in Guidance for Evaluating the Technical Impracticability of Ground-Water Restoration (EPA, 1993b). Alternative remedial strategies, to be considered when restoration ARARs are waived, are also discussed in EPA, 1993b. A finding of technical impracticability may be made in the Record of Decision (ROD) prior to remedy implementation, or in a subsequent decision document after implementation and monitoring of remedy performance.

**2.6.4 Point of Compliance.** The area over which ARAR or risk-based cleanup levels are to be attained is defined in the NCP as follows:

"For ground water, remediation levels should generally be attained throughout the contaminated plume, or at and beyond the edge of the waste management area when waste is left in place" (Federal Register, 1990a; Preamble at 8713).

Thus, the edge of the waste management area can be considered as the point of compliance, because ARAR or risk-based cleanup levels are not expected to be attained in ground water within the waste management area. In general, the term "waste left in place" is used in the NCP to refer to landfill wastes that, at the completion of the remedy, will be contained or otherwise controlled within a waste management area.

For the purposes of ARAR compliance, EPA generally does not consider DNAPLs as "waste left in place." DNAPLs are typically not located in a waste management area, as envisioned in the NCP. This is because the full extent of DNAPL contamination is often not known. DNAPLs can continue to migrate in the subsurface, and measures for controlling their migration are either unavailable or have uncertain long-term reliability. Also, as discussed in Section 2.5.3, restoration of the aquifer to ARAR or risk-based cleanup levels generally will not be attainable in a reasonable timeframe unless the DNAPLs are removed. For these reasons, EPA generally prefers to utilize ARAR waivers rather than an alternate point of compliance over portions of sites where nonrecoverable DNAPLs are present in the subsurface (EPA, 1995c).

The NCP Preamble also acknowledges that "an alternative point of compliance may also be protective of public health and the environment under site-specific circumstances" (Federal Register, 1990a; at 8753). For example, where the contamination plume is "caused by releases from several distinct sources that are in close geographical proximity...the most feasible and effective cleanup strategy may be to address the problem as a whole, rather than source by source, and to draw the point of compliance to encompass the sources of release" (Federal Register, 1990a; at 8753). The NCP Preamble goes on to say that "...where there would be little likelihood of exposure due to the remoteness of the site,

alternate points of compliance may be considered, provided contamination in the aquifer is controlled from further migration" (Federal Register, 1990a; at 8734). The Agency has not developed additional guidance on the use of alternate points of compliance at Superfund sites.

**2.6.5 Natural Attenuation.** Natural attenuation is defined in the NCP as "biodegradation, dispersion, dilution, and adsorption" of contaminants in ground water (Federal Register, 1990a; Preamble at 8734). The NCP goes on to explain that natural attenuation may be a useful remedial approach if site-specific data indicate that these processes "will effectively reduce contaminants in the ground water to concentrations protective of human health [and the environment] in a timeframe comparable to that which could be achieved through active restoration." This approach differs from the "no action" alternative because natural attenuation is expected to attain cleanup levels in a reasonable timeframe (discussed in Section 2.6.2). The NCP recommends use of natural attenuation where it is "expected to reduce the concentration of contaminants in the ground water to the remediation goals [ARAR or risk-based cleanup levels] in a reasonable timeframe."

Natural attenuation may be an appropriate remedial approach for portions of the contaminant plume when **combined with other remedial measures** needed to control sources and/or remediate "hot spots" (also see Section 2.4.2). Whether or not natural attenuation is used alone or combined with other remediation methods, the Agency should have sufficient information to demonstrate that natural processes are capable of achieving the remediation objectives for the site. One caution is that natural attenuation may not be appropriate for sites where contaminants biodegrade to intermediate compounds that are more toxic and degrade more slowly.

Additional EPA policy considerations regarding the use of natural attenuation for remediation of contaminated ground water are provided in EPA, 1996c. Although currently in draft, this EPA directive recommends that remedies utilizing natural attenuation should generally include: 1) **detailed site characterization** to show that this approach will be effective; 2) **source control measures** to prevent further release of contaminants to ground water; 3) **performance monitoring** to assure that natural attenuation is occurring as expected; and 4) **institutional controls** and other methods to ensure that contaminated ground waters are not used before protective concentrations are reached. Also, **contingency measures** may be needed in the event that natural attenuation does not progress as expected.

#### 2.6.6 Alternate Concentration Limits.

Alternate concentration limits (ACLs) are intended to provide flexibility in establishing ground-water cleanup levels under certain circumstances. In the Superfund program, EPA may establish ACLs as cleanup levels in lieu of drinking water standards (e.g., MCLs) in certain cases where contaminated ground water discharges to surface water. The circumstances under which ACLs may be established at Superfund sites are specified in CERCLA §121(d)(2)(B)(ii), and can be summarized as follows:

- The contaminated ground water must have "known or projected" points of entry to a surface water body;
- There must be no "statistically significant increases" of contaminant concentrations in the surface water body at those points of entry, or at points downstream; and
- It must be possible to reliably prevent human exposure to the contaminated ground water through the use of institutional controls.

Each of these criteria must be met and must be supported by site-specific information. Such information also must be incorporated into the appropriate portions of the Administrative Record (e.g., the RI/FS and ROD). The NCP Preamble also advises that ACLs not be used in every situation in which the above conditions are met, but only where active restoration of the ground water is "deemed not to be practicable" (Federal Register, 1990a; at 8754). This caveat in the Preamble signals that EPA is committed to the program goal of restoring contaminated ground water to its beneficial uses, except in limited cases. In the context of determining whether ACLs could or should be used for a given site, the term "practicability" refers to an overall finding of the appropriateness of ground-water restoration, based on an analysis of remedial alternatives using the Superfund remedy selection criteria, especially the "balancing" and "modifying" criteria (EPA, 1993b). (These criteria are defined in part §300.430(e)(9)(iii) of the NCP (Federal Register, 1990a.) This is distinct from a finding of "technical impracticability from an engineering perspective," which refers specifically to an ARAR waiver and is based on the narrower grounds of engineering feasibility and reliability with cost generally not a major factor, unless ARAR compliance would be inordinately costly (see Section 2.6.3 and EPA, 1993b). Where an ACL is established, such an ARAR waiver is not necessary. Conversely, where an ARAR is waived due to technical impracticability, there is no need to establish CERCLA ACLs, as defined above. When establishing an ACL, a detailed site-specific justification should be provided in the Administrative Record which documents that the above three conditions for use of ACLs are met, and that restoration to ARAR or risk-based levels is "not practicable" as discussed above.

Although alternate concentration limits are also defined in the RCRA program, users of this guidance should be aware of **several important differences in the use of ACLs by the RCRA and Superfund programs**. For "regulated units" (defined in 40 CFR 264.90) ACLs are one of the three possible approaches for establishing concentrations limits of hazardous constituents in ground water. Those options are described in 40 CFR 294.94(a). Factors considered when determining whether an ACL is appropriate for a particular facility are provided in 40 CFR 264.94(b). The use of RCRA ACLs is not strictly limited to cases where contaminated ground water discharges to surface water, or to cases where ground-water restoration is considered "not practicable" (as is the case in Superfund). However, the factors considered in the RCRA ACL decision are meant to ensure that establishment of ACLs will be protective of human health and the environment.

A specific reference to ACLs is not made in the existing framework for implementing RCRA Corrective Action at "non-regulated units" (Federal Register, 1990b and 1996). However, the Corrective Action framework recommends flexibility for the development and use of risk-based cleanup standards, based on considerations similar to those used for establishing ACLs under 40 CFR 264.94.

#### **3.0 PRESUMPTIVE TECHNOLOGIES**

### **3.1 Presumptive Technologies for Ex-Situ Treatment**

Presumptive technologies for the treatment portion of an extraction and treatment remedy (exsitu treatment) are identified in Highlight 4. Descriptions of each of the presumptive technologies are presented in Appendices D1 through D8. These technologies are presumptive for treatment of **contaminants dissolved** in ground water that has been extracted from the subsurface, and are expected to be used for this purpose at "all appropriate sites." (Refer to the Preface of this guidance and EPA, 1993d for further information concerning the Agency's expectations concerning the use of presumptive treatment technologies.)

#### Highlight 4. Presumptive Technologies For Treatment Of Extracted Ground Water

For treatment of dissolved <u>organic</u> contaminants, volatiles, semivolatiles and others (see Note):

- Air stripping
- Granular activated carbon (GAC)
- Chemical/UV oxidation (for cyanides also)
- Aerobic biological reactors

For treatment of dissolved metals:

- Chemical precipitation
- Ion exchange/adsorption
- Electrochemical methods (when only metals are present)
- Aeration of background metals

#### For treatment of **both organic and inorganic constituents**:

• A combination of the technologies listed above

**NOTE:** A given treatment train could include a combination of one or more of the presumptive technologies for treatment of **dissolved** contaminants as well as other technologies for other purposes (e.g., separation of solids) as indicated in Appendix C2.

#### 3.1.1 Design Styles within Presumptive

**Technologies.** The presumptive technologies identified in Highlight 4 refer to technology types rather than specific designs (design styles). Each presumptive technology represents a single process falls within one of these technology types (e.g., innovative air stripper designs, or innovative media for ion exchange/adsorption of metals). A listing of design styles of the presumptive technologies typically considered during Superfund remedy selection are listed in Appendix C1.

#### 3.1.2 Benefits of Presumptive Technologies.

Use of the presumptive technologies identified in this guidance will simplify and streamline the remedy selection process for the ex-situ treatment portion of a ground-water remedy by:

- Simplifying the overall selection process, since the large number and diverse assortment of these technologies have been reduced to relatively few technology types;
- Eliminating the need to perform the technology screening portion of the feasibility study (FS), beyond the analysis contained in this guidance and its associated Administrative Record. (See Section 3.3.2);
- Allowing, in some cases, further consideration and selection among the presumptive technologies to be deferred from the FS and ROD to the remedial design (RD), which prevents duplication of effort and allows selection to be based on additional data collected during the RD (see Section 3.3.3);
- Shifting the time and resources employed in remedy selection from ex-situ treatment to other, more fundamental aspects of the ground-water remedy (see Section 1.0); and
- Facilitating the use of extraction and treatment for early actions, where appropriate, since selection of the treatment component is simplified.

#### 3.1.3 Consideration of Innovative

**Technologies.** Use of presumptive technologies for treatment of extracted ground water is intended to simplify the remedy selection process,

but does not preclude the consideration of innovative technologies for this purpose in the FS or RD. Refer to the EPA fact sheet, *Presumptive Remedies: Policy and Procedures* (EPA, 1993d), for additional information. Many innovative or emerging technologies for ex-situ treatment are actually design variations of one of the presumptive technology types, as discussed above, and others may be considered on a site-specific basis. In addition, EPA encourages consideration of in-situ treatment technologies for ground-water remedies, either when combined with extraction and treatment or as an alternative to such methods (see Section 2.4.2).

#### 3.2 Basis for Presumptive Technologies

**3.2.1 Sources of Information.** Three sources of information were used to determine which technologies should be identified as presumptive for ex-situ treatment of ground water:

- Review of the technologies selected in all RODs signed from fiscal years 1982 through 1992;
- Review of capabilities and limitations of ex-situ treatment technologies from engineering and other technical literature; and
- Detailed evaluation of the technologies considered in the FS and selected in the ROD or RD for a sample of 25 sites for which at least one ex-situ treatment technology was selected.

The above information is summarized in a separate report entitled *Analysis of Remedy Selection Results for Ground-Water Treatment Technologies at CERCLA Sites* (EPA, 1996b). A total of 427 RODs selected at least one ex-situ technology for treatment of ground water, as of September 30, 1992. From these RODs, a sample of 25 sites were selected for detailed evaluation of the rationale used to select these technologies as part of the ground-water remedy.

**3.2.2 Rationale for Indentifying Presumptive Technologies.** At least one of the eight presumptive technologies, identified in Highlight 4, was selected as part of the ground-water remedy in 425 of 427 RODs, or **99.5 percent** of the time. In only five RODs were technologies other than the presumptive technologies selected as part of the treatment train. Therefore, presumptive technologies were the **only** technologies selected for ex-situ treatment of dissolved ground-water contaminants in 420 of the 427 RODs.

More importantly, all the presumptive technologies are well understood methods that have been used for many years in the treatment of drinking water and/or municipal or industrial wastewater. Engineering Bulletins or Technical Data Sheets have been developed by EPA and the Naval Energy and Environmental Support Activity, respectively, for five of the eight presumptive technologies. These publications generally include site specific performance examples, and are included as references, along with other publications, with the description of each technology in Appendix D.

In the 25 site sample, the presumptive technologies, identified in Highlight 4, were the only technologies selected in the ROD for all sites and the only technologies implemented in the RD for 24 sites. Other technologies were consistently eliminated from further consideration, usually in the technology screening step, based on technical limitations which were verified by the engineering literature. As part of this evaluation the large number and diverse assortment of technologies considered for ex-situ treatment of ground water were categorized according to the underlying treatment process. A complete listing of the technologies considered in the FS, ROD or RD for the 25 sites is given in Appendix C1, categorized by process type and with the presumptive technologies identified.

Some technologies are identified as presumptive even though they were selected in relatively few RODs. **Aeration of background metals** was identified as presumptive because this technology is often used for removal of iron and manganese, and was considered and selected for this purpose at two of the 25 sample sites. **Electrochemical methods** for metals removal were also identified as presumptive because these methods were considered at all three sample sites where metals were the only contaminants of concern, and were selected at two of these sites. **Chemical/UV oxidation** and **aerobic biological reactors** were identified as presumptive technologies for treating organic contaminants for the following technical reasons:

- A range of chemical, physical and biological treatment methods should be included in the presumptive technologies, because air stripping and granular activated carbon, alone or combined, may not provide cost effective treatment (see Section 3.4.5) for all organic contaminants.
- These methods destroy organic contaminants as part of the treatment process instead of transferring them to other media, which reduces the quantity of hazardous treatment residuals (e.g., spent carbon) that will require further treatment.
- Ongoing research and development efforts, by EPA and others, are expected to increase the cost effectiveness of these treatment methods.

### 3.3 Remedy Selection Using Presumptive Technologies

Selection of technologies for long-term treatment of extracted ground water requires an understanding of the types of technologies that will be needed, how they will be used in the treatment system and site-specific information for determining the most appropriate and costeffective technologies. **The presumptive technologies for treating** <u>dissolved</u> **contaminants in extracted ground water**, identified in Highlight 4, are the technologies that should be retained for further consideration in the Detailed Analysis portion of the feasibility study (FS). This guidance and its associated Administrative Record will generally constitute the Development and Screening of Alternatives portion of the FS for the ex-situ treatment component of a ground-water remedy, as discussed in Section 3.3.2.

Site information needed to select cost-effective treatment technologies (see Section 3..4) is often not collected until the remedial design (RD) phase. In such cases, it will generally be appropriate to specify performance requirements for the treatment system in the ROD, but defer selection of specific technologies until the RD, as discussed in Section 3.3.3.

#### 3.3.1 Use of Technologies in Treatment

**Systems.** Complete treatment of extracted ground water generally requires that units of more than one technology, or multiple units of a single technology (unit processes), be linked together in a treatment train. A given treatment train could include some combination of treatment technologies for the following purposes:

- 1. Separation of mineral solids and/or immiscible liquids from the extracted ground water during initial treatment (pretreatment);
- 2. Treatment of **dissolved contaminants**;
- **3.** Treatment of vapor phase contaminants from the extracted ground water or those generated during treatment;
- 4. Separation of solids generated during treatment;
- 5. Final treatment of **dissolved contaminants** prior to discharge (polishing); and

6. Treatment of solids generated during treatment.

Presumptive technologies for treatment of **dissolved contaminants** in extracted ground water (No. 2 and 5, above) are identified in Highlight 4. Examples of the types of technologies used for other purposes are given in Appendix C2, along with a listing of the general sequence of unit processes used in a treatment train. Solid residuals (such as sludges from chemical or biological processes, or spent carbon media) will generally require additional treatment or disposal, either as part of the treatment train or at a separate facility. Presumptive technologies for purposes other than for treatment of dissolved contaminants have **not** been identified in this guidance.

Use of modular treatment components, which can be easily added or removed from the treatment system, may facilitate phased implementation or other changes that may occur during the life of a remedy. Phased implementation of the extraction portion of a remedy may require that some components of the treatment system also be installed in stages. Also, modification of the treatment system over time may be needed in response to changes in the inflow rate or contaminant loadings, or to increase the effectiveness or efficiency of the treatment system.

#### 3.3.2 This Guidance Constitutes the FS

**Screening Step.** This guidance and its associated Administrative Record will generally constitute the "development and screening of alternatives" portion of the feasibility study (FS), for the ex-situ treatment component of a ground-water remedy. When using presumptive technologies, the FS should contain a brief description of this approach (see fact sheet entitled *Presumptive Remedies: Policy and Procedures* (EPA, 1993d)), and refer to this guidance and its associated Administrative Record. Such a brief description should fulfill the need for the development and screening of technologies portion of the FS for the ex-situ treatment component of the remedy.

#### 3.3.3 Deferral of Final Technology Selection to

**RD.** Although EPA prefers to collect the site information needed for technology selection prior to the ROD, it is sometimes impracticable to collect some of the necessary information until the remedial design (RD) phase. (See Section 3.4 for a summary of site information generally needed for selection of these technologies.) In reviewing remedy selection experience for a sample of sites, EPA found that at seven of 25 sites (28 percent) the type of technology selected in the ROD for treatment of extracted ground water was later changed in the RD because of additional site information obtained during the design phase (EPA, 1996b). Where EPA lacks important information at the ROD stage, it may be appropriate to defer final selection among the presumptive ex-situ treatment technologies (as well as selection of specific design styles) to the RD phase.

In this approach, EPA would identify and evaluate the technologies and provide an analysis of alternative technologies in the FS (this guidance and its associated administrative record will generally constitute that discussion). The proposed plan would identify the technologies that may be finally selected and specify the timing of and criteria for the future technology selection in sufficient detail that the public can evaluate and comment on the proposal. The ROD would also identify all ARARs and other performance specifications and information associated with discharge and treatment of the extracted ground water, including the types of discharge, effluent requirements, and specifications developed in response to community preferences. Specifying the performance criteria and other requirements in the ROD (using a type of "performance based approach") ensures that the remedy will be protective and meet ARARs. Overall, the ROD should be drafted so that the final selection of technologies at the RD phase follows directly from the application of criteria and judgments included in the ROD to facts collected during the RD phase. If the ROD is drafted in this fashion, documenting the final technology selection can generally be accomplished by including a

document in the post-ROD portion of the Administrative Record, which explains the basis of technology selection (e.g., Basis of Design Report, or memorandum to the RD file).

Advantages of deferring selection of ex-situ treatment technologies to the RD include:

- The remedy selection process is further streamlined, since final selection and the accompanying detailed analysis for these technologies is performed only in the RD not in both the FS and the RD, minimizing duplication of effort;
- Site information collected during the RD can be used to make final technology selections as well as to design the treatment train, which facilitates selection of the most cost effective technologies (see Section 3.4.5);
- The likelihood that changes in the treatment train will be made during the RD is explicitly recognized in the ROD; and
- The time and resources employed in the FS can focus on other components of the ground-water remedy that have more direct influence on attainment of **remedial objectives** for contaminated ground water (see Section 1.0).

**Cost estimates** for remedial alternatives, including the ex-situ treatment component, will need to be included in the FS regardless of whether or not technology selection is deferred to the RD. For cost estimating purposes when deferring technology selection to the RD, reasonable assumptions should be made concerning the treatment system, including assumptions concerning the presumptive technologies and likely design styles to be used. To assist in making such assumptions, advantages and limitations for the presumptive technologies are summarized in Appendix C4. Also, brief descriptions of the presumptive technologies and references for additional information are provided in Appendix D. Assumptions used for estimating treatment costs should be consistent across all remedial alternatives. All assumptions should be clearly stated as such in the FS and ROD.

Example ROD language for deferring technology selection to the RD is given in Appendix B3 for a hypothetical site. This language is only for the exsitu treatment portion of an extraction and treatment remedy and should appear in the selected remedy portion of the ROD when following this approach.

## 3.4 Information Needed for Selecting Technologies

The site information listed in Highlight 5 is generally needed to determine the treatment components of a complete treatment train for extracted ground water and to select the most appropriate technology type and design style for each component. Further detail regarding site data needed and the purpose of this information is provided in Appendix C3. Much of this information is also needed for design of the extraction component of an extraction and treatment remedy.

#### 3.4.1 When Should this Information be

Collected? The information listed in Highlight 5 is needed for design of the treatment train. Therefore, it must be collected prior to or during the design phase, for either an early action or longterm remedy. Much of this information should also be available for selecting among the presumptive technologies, since it is generally needed to determine the technologies most appropriate for site conditions. The timing of information needed during remedy selection is different when deferring technology selection to the RD than when selecting technologies in the ROD, as discussed in Section 3.3.3. However, much of this information can be collected along with similar data gathered during the remedial investigation (RI). In general, it is recommended that as much of this information as possible be obtained prior to the RD in order to minimize the

### Highlight 5. Summary of Site Information Needed For Treatment Train Design

- Total extraction flow rate
- Discharge options and requirements
  - Target effluent concentrations
    - Contaminants
    - Degradation products
    - Treatment additives
    - Natural constituents
  - Other requirements
    - Regulatory
    - Operational
  - Community concerns or preferences
- Water quality of treatment influent
  - Contaminant types and concentrations
  - Naturally occurring constituents
  - Other water quality parameters
- Treatability information

**NOTE**: Further detail is provided in Appendix C3.

need for additional site investigations during the RD and to accelerate the RD phase. much of this information can be collected along with similar data gathered during the remedial investigation (RI). In general, it is recommended that as much of this information as possible be obtained prior to the RD in order to minimize the need for additional site investigations during the RD and to accelerate the RD phase.

**3.4.2 Extraction Flow Rate**. Inflow to the treatment system is the total flow from all extraction wells or drains. Estimates of total extraction flow rate often have a **high degree of** uncertainty (i.e., one or more orders of magnitude), depending on type of data and estimation method used. Expected flow rates from extraction wells are typically estimated from hydraulic properties of the aquifer. Aquifer hydraulic properties may have considerable natural variation over the site and accurate measurement of these properties is often difficult. In order to reduce uncertainty during design of the treatment system, aquifer properties used in estimating the inflow should generally be obtained from pumping-type aquifer tests and not from "slug tests," laboratory measurements on borehole samples or values estimated from the literature.

Pumping-type aquifer tests provide a much better estimate of average aquifer properties than other methods, because a much larger volume of aquifer is tested. For the same reason, ground water extracted during pumping tests is more representative of that which will enter the treatment system, and should generally be used for treatability studies of ex-situ treatment technologies instead of samples obtained from monitoring wells. Suggested procedures for conducting pumping-type aquifer tests are given in EPA, 1993i. Methods for treatment of contaminated ground water extracted during pumping-type aquifer tests are discussed in Section 3.5.

The likely variability in the total extraction rate during the life of the remedy should also be estimated. Variability in the extraction rate could result from addition or removal of extraction wells, short-term operational changes in the system (e.g., changing the pumping rates) or seasonal fluctuations in the water table. The number of extraction wells could change as a result of implementing the remedy in phases or from post-construction refinement of the remedy (see Section 2.3.1). 3.4.3 Discharge Options and ARARs. All options for discharge of ground water after extraction and treatment should be identified and considered in the FS, especially options that include re-use or recycling of the extracted ground water. Water quality requirements for the treated effluent (i.e., effluent ARARs) may be different for each discharge option. Examples of regulatory requirements include those promulgated under the federal Safe Drinking Water Act and Clean Water Act, which would apply to discharges to a drinking water system or to surface waters, respectively; and state requirements for these types of discharge. Effluent requirements could also include those for chemicals added during treatment, contaminant degradation products, and naturally occurring constituents (e.g., arsenic), in addition to those for contaminants of concern. In general, one or more types of discharge for extraction and treatment remedies should be selected in the ROD, not deferred to the RD. ARARs for the treated effluent will determine the overall level of treatment needed, which in turn determines the type of components needed in the treatment train (see Section 3.3.1) and is a critical factor in selecting appropriate treatment technologies.

In some cases it may be appropriate to select more than one type of discharge for the selected remedy. One type of discharge may be preferred, but may not be capable of accepting the entire flow of treated effluent. For example, it may be possible to re-use or recycle a portion but not all of the discharge. It may also be desirable to reinject a portion of the treated effluent for enhanced recovery of contaminants (aquifer flushing) but prohibitively costly to reinject the entire discharge.

In addition to the types of discharge, ARARs and other specifications related to technology selection or operating performance of the treatment system should be specified in the ROD. Regulatory requirements for all waste streams from the treatment system should be specified, including those for the treated effluent; releases to the air; and those for handling, treatment and disposal of solid and liquid treatment residuals. Other specifications could include those preferred by the affected community, such as requirements to capture and treat contaminant vapors (even though not required by ARARs) or limits on operating noise. Other specifications may also be needed to maintain continued operation of the system, such as water quality conditions necessary to minimize chemical and/or biological clogging of injection wells or drains.

**3.4.4 Water Quality of Treatment Influent.** In order to design the treatment system, contaminant types and concentrations and other water quality parameters must be estimated for the total flow entering the system. Since some technologies are more effective than others in removing certain contaminant types, this is an important technology selection factor. Concentrations of naturally occurring constituents as well as background and site-related contaminants in the extracted ground water should also be measured, as discussed in Appendix C3.

**3.4.5 Treatability Studies.** Treatability studies involve testing one or more technologies in the laboratory or field to assess their performance on the actual contaminated media to be treated from a specific site. These studies may be needed during the RI/FS to provide qualitative and/or quantitative information to aid in selection of the remedy, or during the RD to aid in design or implementation of the selected remedy. Three tiers of testing may be undertaken: 1) laboratory screening, 2) bench-scale testing, or 3) pilot-scale testing. Treatability studies may begin with any tier and may skip tiers that are not needed (EPA, 1989c).

For treatment of extracted ground water, treatability studies are generally needed to accurately predict the effectiveness and total cost of a technology for a given site, including construction and operating costs; and the costs of other components that may be needed in the treatment train (see Section 3.3.1). Optimizing the cost effectiveness of the treatment train is especially important for systems designed to operate over a long time period. (In this guidance, optimizing the cost effectiveness of the treatment system is defined as meeting all treatment and other performance requirements while minimizing total costs per unit volume of water treated.) Treatability studies may also indicate that some technologies provide cost effective treatment when all of the above factors are considered, even though these technologies were infrequently selected in past RODs (e.g., chemical/UV oxidation or aerobic biological reactors). For these reasons treatability studies will be helpful in selecting among the presumptive technologies. Similarly, a presumptive treatment technology should not be eliminated from further consideration in the FS or RD simply because a treatability study is required to determine its applicability for a given site. In general, some type of treatability study should be performed prior to or during the design of any system expected to provide long-term treatment of extracted ground water, including systems using presumptive technologies.

#### 3.5 Treatment Technologies for Aquifer Tests

Although pumping-type aquifer tests are the preferred method of determining average aquifer properties (see Section 3.4.2) and this information is useful for remedy selection, such testing is often deferred to the RD phase because of the need to determine how to treat and/or dispose of the extracted ground water. To facilitate use of such tests earlier in the site response, ex-situ treatment technologies most suitable for this application are discussed below.

**3.5.1 Treatment Needs during Aquifer Tests.** In comparison to an extraction and treatment remedy, pumping-type aquifer tests (see Section 3.4.2) generate relatively small flows of contaminated ground water over a short period of time. At the time of such tests, the estimated pumping rates and contaminant loadings generally have a high degree of uncertainty. Often the total volume of ground water extracted during testing is held in storage tanks or lined ponds to prevent the discharge from affecting water levels in

observation wells and interfering with the test. Storage of the extracted ground water also allows subsequent flow to a treatment system to be controlled and optimized. For example, if storage vessels are used for both the untreated and treated water, the extracted water can be routed through the treatment system as many times as necessary to meet discharge and/or disposal requirements. Therefore, the cost effectiveness of treatment technologies (see Section 3.4.5) is less important for aquifer testing than for the long-term remedy, because of the much smaller volume of ground water to be treated and the much shorter period of operation.

#### 3.5.2 Treatment Technologies for Aquifer

**Tests.** Technologies for treating ground water extracted during aquifer tests should be able to treat a wide range of contaminant types, be available in off-the-shelf versions (short lead time for procurement), have a short on-site startup time, be relatively simple to operate, and be available in easily transportable units. Of the presumptive technologies identified above, the three most suitable for this application are:

- Granular activated carbon,
- Air stripping, and
- Ion exchange/adsorption.

Granular activated carbon can effectively remove most dissolved organic contaminants and low concentrations of some inorganic compounds. Ion exchange/adsorption can remove most metals. Air stripping may be applicable for volatile organic contaminants (VOCs) and generally is more cost effective than granular activated carbon for treating VOCs when flow rates are greater than about three gallons per minute (Long, 1993). Granular activated carbon may still be needed in conjunction with air stripping, for treating dissolved semivolatile organic contaminants, or for reaching stringent effluent requirements for VOCs. Granular activated carbon may also be needed for treatment of vapor phase contaminants separated by an air stripper. Also, treatability
studies generally are not required for the above three technologies, especially for **short-term** applications. Additional information regarding the availability and field installation of skid or trailer mounted treatment units (package plants) is available in EPA, 1995a.

Other presumptive ex-situ treatment technologies (chemical/UV oxidation, aerobic biological reactors, chemical precipitation, and electrochemical methods) generally are less suitable for aquifer testing purposes. In general, these other technologies require longer lead times for procurement and longer time on-site for startup; and have more complex operating requirements and higher capital costs.

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# **APPENDIX A**

# **Additional Background Information**

- Appendix A1: Background on DNAPL Contamination
- Appendix A2: Contaminants Most Frequently Reported in Ground Water at CERCLA NPL Sites
- Appendix A3: Examples of In-Situ Treatment Technologies
- Appendix A4: Definition and Discussion of Pulsed Pumping

# **Appendix A1: Background on DNAPL Contamination**

# **DNAPL Background**

A nonaqueous phase liquid (NAPL) is a chemical that is a liquid in its pure form, which does not readily mix with water but does slowly dissolve in water. Dense NAPLs (DNAPLs) sink while light NAPLs (LNAPLs) float in water. When present in the subsurface NAPLs slowly release vapor and dissolved phase contaminants, resulting in a zone of contaminant vapors above the water table and a plume of dissolved contaminants below the water table. The term NAPL refers to the undissolved liquid phase of a chemical or mixture of compounds and not to the vapor or dissolved phases. NAPLs may be present in the subsurface as either "free-phase" or as "residual-phase." The free-phase is that portion of NAPL that can continue to migrate and which can flow into a well. The residual-phase is that portion trapped in pore spaces by capillary forces, which can not generally flow into a well or migrate as a separate liquid. Both residual and free-phase NAPLs are sources of vapors and dissolved contaminants.

**LNAPLs** tend to pose less of a cleanup problem than DNAPLs. The most common LNAPLs are petroleum fuels, crude oils and related chemicals, which tend to be associated with facilities that refine, store or transport these liquids. Since LNAPLs tend to be shallower, are found at the water table and are associated with certain facilities, they are generally easier to locate and clean up from the subsurface than DNAPLs.

**DNAPLs** pose much more difficult cleanup problems. These contaminants include chemical compounds and mixtures with a wide range of chemical properties, including chlorinated solvents, creosote, coal tars, PCBs, and some pesticides. Some DNAPLs, such as coal tars, are viscous chemical mixtures that move very slowly in the subsurface. Other DNAPLs, such as some chlorinated solvents, can travel very rapidly in the subsurface because they are heavier and less viscous than water. A large DNAPL spill not only sinks vertically downward under gravity, but can spread laterally with increasing depth as it encounters finer grained layers. These chemicals can also contaminate more than one aquifer by penetrating fractures in the geologic layer which separates a shallower from a deeper aquifer. Thus, large releases of DNAPLs can penetrate to great depths and can be very difficult to locate and clean up.

The contamination problem at DNAPL sites has two different components, as shown in **Figures A1-1 and A1-2**, the:

- DNAPL zone, and the
- Aqueous contaminant plume.

The **DNAPL zone** is that portion of the subsurface where immiscible liquids (free-phase or residual DNAPL) are present either above or below the water table. Also in the DNAPL zone, vapor phase DNAPL contaminants are present above water table and dissolved phase below water table. The **aqueous contaminant plume** is that portion of the contaminated ground water surrounding the DNAPL zone where aqueous contaminants derived from DNAPLs are dissolved in ground water (or sorbed to aquifer solids) but immiscible liquids are **not** present. Depending on the volume of the release and subsurface geology, the DNAPL zone may extend to great depths and over large lateral distances from the entry location, as discussed above.

# Appendix A1: Background on DNAPL Contamination (continued)

Planning of site investigation and remedial activities at sites with subsurface DNAPLs should include certain precautions, to minimize the potential for further DNAPL migration resulting from such activities. Further detail on characterization of DNAPL sites is provided in EPA, 1994 and in Cohen and Mercer, 1993 (see below).

# DNAPL References

Additional information concerning DNAPL contamination can be obtained from the following references:

Cohen, R.M., and J.W. Mercer, 1993. <u>DNAPL Site Evaluation</u>, C.K. Smoley, Boca Raton, FL, 1993; and EPA/600/R-93/022, February 1993.

EPA, 1991. "Ground Water Issue: Dense Nonaqueous Phase Liquids," OSWER Publication EPA/540/4-91-002, March 1991.

EPA, 1992a. "Estimating Potential for Occurrence of DNAPL at Superfund Sites," OSWER Publication 9355.4-07FS, January 1992.

EPA, 1992b. "Dense Nonaqueous Phase Liquids -- A Workshop Summary, Dallas, Texas, April 16-18, 1991," Office of Research and Development Publication EPA/600/R-92/030, February 1992.

EPA, 1992c. "Considerations in Ground-Water Remediation at Superfund Sites and RCRA Facilities - Update," OSWER Directive 9283.1-06, May 27, 1992.

EPA, 1993b. "Guidance for Evaluating Technical Impracticability of Ground-Water Restoration," OSWER Directive 9234.2-25, EPA/540-R-93-080, September 1993.

EPA, 1994. "DNAPL Site Characterization," OSWER Publication 9355.4-16FS, EPA/540/F-94/049, September 1994.

# Appendix A2: Contaminants Most Frequently Reported in Ground Water at CERCLA NPL Sites <sup>1</sup>

# Organic Contaminants:

Rank	Organic Contaminants (Other Names)	Chemical <sup>2</sup> Group	Halo- <sup>2</sup> genated?	DNAPL? <sup>3</sup>	No. <sup>1</sup> Sites
1	Trichloroethylene, 1,1,2- (TCE) <sup>cs</sup>	Volatile	Yes	Yes	336
2	Tetrachloroethene (perchloroethene; PCE) <sup>cs</sup>	Volatile	Yes	Yes	170
3	Chloroform (trichloromethane) <sup>cs</sup>	Volatile	Yes	Yes	167
4	Benzene <sup>pf</sup>	Volatile	No	No	164
5	Toluene <sup>pf</sup>	Volatile	No	No	159
6	Trichloroethane, 1,1,1- (methyl chloroform; 1,1,1-TCA) <sup>es</sup>	Volatile	Yes	Yes	155
7	Polychlorinated biphenyls	PCB	Yes	Yes	139
8	Trans-Dichloroethylene, 1,2- (trans-1,2-DCE) <sup>cs</sup>	Volatile	Yes	Yes	107
9	Dichloroethane, 1,1- (1,1-DCA) <sup>cs</sup>	Volatile	Yes	Yes	105
10	Dichloroethene, 1,1- (vinylidene chloride; 1,1-DCE) <sup>es</sup>	Volatile	Yes	Yes	95
11	Vinyl chloride (chloroethylene) <sup>cs</sup>	Volatile	Yes	No	82
12	Xylene <sup>pf</sup>	Volatile	No	No	76
13	Ethylbenzene <sup>pf</sup>	Volatile	No	No	68
14	Carbon tetrachloride (tetrachloromethane) <sup>es</sup>	Volatile	Yes	Yes	68
15	Phenol	Semivol.	No	No	61
16	Methylene chloride (dichloromethane) <sup>es</sup>	Volatile	Yes	Yes	58
17	Dichloroethane, 1,2- (ethylene dichloride; 1,2-DCA) <sup>es</sup>	Volatile	Yes	Yes	57
18	Pentachlorophenol (PCP)	Semivol.	Yes	Yes	53
19	Chlorobenzene (benzene chloride) <sup>es</sup>	Volatile	Yes	Yes	48
20	Benzo(A)Pyrene	Semivol.	No	Yes	37

Appendix A2: Contaminants Most Frequently Reported in Ground Water at CERCLA NPL Sites (continued)<sup>1</sup>

# **Inorganic Contaminants:**

Rank	Inorganic Contaminants	No. <sup>1</sup> Sites
1	Lead	307
2	Chromium and compounds	215
3	Arsenic	147
4	Cadmium	127
5	Mercury <sup>4</sup>	81
6	Copper and compounds	79
7	Zinc and compounds	73
8	Nickel and compounds	44
9	Cyanides (soluble salts)	39
10	Barium	37

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NOTES:

- Number of CERCLA National Priorities List (NPL) sites for which the chemical was reported in ground water as a contaminant of concern in the Superfund Site Assessment, for either proposed or final NPL sites. This data was obtained from the Superfund NPL Assessment Program (SNAP) data base, as of August 30, 1994. At that time total of 1294 sites were listed on the NPL (64 proposed and 1230 final).
- <sup>2</sup> Classification of organic contaminants as volatile, semivolatile, PCB, or pesticide; and as halogenated or nonhalogenated is from EPA Publication, "Technology Screening Guide for Treatment of CERCLA Soils and Sludges," EPA/540/2-88/004, September 1988.
- <sup>3</sup> Classification of whether or not a chemical is a dense nonaqueous phase liquid (DNAPL) in pure form is from Cohen and Mercer, 1993 (see References).
- <sup>4</sup> In pure form mercury is also a DNAPL.
- cs These organic contaminants are <u>chlorinated solvents</u>. A total of 12 are listed.
- <sup>pf</sup> These organic contaminants are constituents of <u>petroleum fuels</u>. A total of four are listed.

# Appendix A3: Examples of In-Situ Treatment Technologies <sup>1</sup>

I. Enhanced Recovery Methods	Treatment Agents (and process type)	Agent Delivery Methods
Recirculation/flooding:		
<ul> <li>Water flooding (physical)</li> <li>Steam flooding (physical)</li> </ul>	<ul><li>Water</li><li>Heated water</li><li>Steam</li></ul>	<ul><li>Injection wells</li><li>Injection wells</li><li>Injection wells</li></ul>
- Chemical flooding <sup>2</sup> (chemical)	<ul><li>Surfactants</li><li>Solvents</li><li>Redox agents</li></ul>	<ul><li>Injection wells</li><li>Injection wells</li><li>Injection wells</li></ul>
- Nutrient flooding <sup>2</sup> (biological)	- Nitrate - Other	- Injection wells
Thermal enhanced recovery:		
- Radio frequency	- Heat	- Electrodes in wells
- Electrical resistance (AC or DC)	- Heat	- Electrodes in wells
Enhancement of secondary permeability:		
- Induced fracturing with water or or air pressure (physical)	Not applicable	Not applicable
Other methods:		
- Electromigration (electrical)	- Electric current	- Electrodes in wells

NOTES:

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<sup>1</sup> List of technologies and technology status is from EPA, 1993h (see References section of guidance).

<sup>2</sup> Chemicals or nutrients for micro-organisms, respectively, are added to reinjection water.

# Appendix A3: Examples of In-Situ Treatment Technologies (continued $)^1$

	itu Treatment Processes	Treatment Agents	Agent Delivery Methods
	al/chemical treatment:		
-	Volatilization and oxygen enhancement by <b>air sparging</b>	- Air	<ul> <li>Injection wells</li> <li>Permeable walls/gates <sup>3</sup></li> </ul>
-	Reductive dehalogenation by metal catalysts (abiotic)	<ul><li>Iron filings</li><li>Other agents</li></ul>	- Permeable walls/gates <sup>3</sup>
Biologi	cal treatment:		
-	Oxygen enhancement of aerobic organisms (also includes air sparging, above)	<ul> <li>Hydrogen peroxide</li> <li>Oxygen/surfactant (microbubbles)</li> </ul>	<ul> <li>Injection wells<sup>4</sup></li> <li>Injection wells<sup>4</sup></li> </ul>
-	Nutrient enhancement of aerobic organisms	- Nitrate - Other	- Injection wells <sup>3</sup>
-	Nutrient enhancement of anaerobic organisms to produce enzymes that degrade contaminants (cometabolism)	- Methane - Other	- Injection wells
-	Sequential anaerobic-aerobic treatment	- Methane and/or Oxygen	- Injection wells

### NOTES:

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<sup>&</sup>lt;sup>3</sup> In permeable treatment walls/gates, treatment agents are added with trench backfill materials or are injected via perforated pipes placed in the backfill. These walls are placed in the subsurface across the natural flow path of the contaminant plume. They can be combined with impermeable flow barriers in a "funnel and gate" arrangement, in which flow is directed through the treatment walls/gates.

<sup>&</sup>lt;sup>4</sup> Use of permeable treatment walls/gates to deliver treatment agents for these methods may also be feasible.

# Appendix A4: Definition and Discussion of Pulsed Pumping

# Pulsed Pumping

In pulsed pumping, some or all extraction pumps are turned off and then back on for specified periods of time (e.g., one or more monitoring periods). The on and off cycles can be continued or the extraction and treatment remedy can be returned to continuous pumping. Although not widely used in remedies to date, this method may be effective in **enhancing the recovery of contaminants from the aquifer**. Pulsed pumping can recover contaminants located in the following portions of the aquifer that are relatively unaffected during pumping:

- Upper portions of the aquifer that have been dewatered by pumping, and
- Zones with minimal ground-water flow during pumping (flow stagnation zones).

Pulsed pumping **may** also enhance contaminant recovery for aqueous phase contaminants that are sorbed to the aquifer matrix. Therefore, pulsed pumping can be initiated as a **post-construction refinement** of an extraction and treatment remedy (see Section 2.4), when an evaluation of remedy performance indicates that this technique may increase the recovery of contaminants from the aquifer.

**Pulsed pumping can also be used as a method of evaluating the effectiveness of an extraction and treatment remedy and/or the effectiveness of source control actions.** For example, if contaminant levels increase substantially when pumping is stopped, it is an indication that contaminants continue to be derived from source materials, and that additional remedial measures (e.g., source control/removal) may be necessary. These source materials could include aqueous contaminants sorbed to aquifer solids in finer-grained aquifer layers, NAPLs (refer to Appendix A1), contaminated soils, or other sources.

Pulsed pumping should generally **not be initiated** until after sufficient monitoring data has been obtained from continuous pumping to establish a statistically valid performance trend. Also, the influence of pulsed pumping on plume containment should be considered; and extraction wells used primarily for containment (i.e, at plume leading edge) should generally not be pulsed .

# **APPENDIX B**

# **ROD Language Examples For Selected Remedy**

- Appendix B1: Phased Implementation of Ground-Water Remedy
- Appendix B2: Phased Implementation of **Extraction Component** of Remedy at a DNAPL Site
- Appendix B3: **Deferring Selection** of Treatment Components to Remedial Design

Appendix B4: Suggested ROD Language from **1990 OSWER Directive** 

# **Appendix B1: Phased Implementation of Ground-Water Remedy**

## Site Conditions:

At **hypothetical Site 1** (an LNAPL site) surficial soils and the underlying ground water in Aquifer C are contaminated with volatile organic compounds (VOCs). At this site, Aquifer C is currently used as a source of drinking water, with several wells located on-site and in the estimated path of the contaminant plume.

**Early actions** were used for exposure prevention and source control. Under Superfund **removal authority**, an alternate water supply was provided to several residences, and leaking drums and heavily contaminated soils were excavated and taken off-site for disposal. A soil vapor extraction system was installed as an **interim remedial action**. No further source control actions are planned. DNAPLs are not likely to be present in the subsurface because most of the contaminants are LNAPLs rather than DNAPLs in pure form. The selected ground-water remedy relies on extraction and treatment for preventing further migration of the contaminant plume and for restoration of Aquifer C. **The selected remedy will be implemented in two construction phases.** 

## **ROD Language for Extraction Component of Remedy :**

The following, or similar language, should appear in the **Selected Remedy** section of the ROD:

The **ultimate goal** for the ground-water portion of this remedial action is to restore Aquifer C to its beneficial uses. At this site, Aquifer C is currently used as a source of drinking water. Based on information obtained during the remedial investigation and on a careful analysis of all remedial alternatives, EPA and the State of \_\_\_\_\_ believe that the selected remedy will achieve this goal.

The extraction portion of the ground-water remedy will be implemented in two phases. In phase one, a sufficient number of extraction wells will be installed with the objective of minimizing further migration of the contaminant plume. It is currently estimated that two to four extraction wells will be required for phase one.<sup>1</sup> After construction of phase one is completed, the extraction system will be carefully monitored on a regular basis and its performance evaluated. Operation and monitoring of phase one for a period of up to one year may be needed to provide sufficient information to complete the design of phase two.

In phase two, additional extraction wells will be installed with the objective of restoring Aquifer C for use as a source of drinking water, in addition to maintaining the remedial objectives for phase one. Restoration is defined as attainment of required cleanup levels in the aquifer, over the entire contaminant plume. Cleanup levels for each ground-water contaminant of concern are specified in Table \_\_\_\_\_ of the ROD. Current estimates indicate that an additional two to four extraction wells may be required to attain these cleanup levels within a timeframe of approximately 20 years.<sup>1</sup> However, monitoring and evaluation of the performance of phase one will be used to determine the actual number and placement of wells for phase two.

# Appendix B1: Phased Implementation of Ground-Water Remedy (continued)

The selected remedy will include ground-water extraction for an estimated period of 20 years, during which the system's performance will be carefully monitored, in accordance with the monitoring plan defined in Section \_\_\_\_\_ of the ROD, and adjusted as warranted by the performance data collected during operation. **Refinement** of the extraction system may be required, if EPA determines that such measures will be necessary in order to restore Aquifer C in a reasonable timeframe, or to significantly reduce the timeframe or long-term cost of attaining this objective. **Refinement of the extraction system may include any or all of the following:** 

- 1) Adjusting the rate of extraction from some or all wells;
- 2) Discontinuing pumping at individual wells where cleanup goals have been attained;
- 3) Pulsed pumping of some or all extraction wells to eliminate flow stagnation areas, allow sorbed contaminants to partition into ground water, or otherwise facilitate recovery of contaminants from the aquifer; and
- 4) Installing up to two additional ground-water extraction wells to facilitate or accelerate cleanup of the contaminant plume.<sup>1</sup>

It is possible that performance evaluations of the ground-water extraction system - after completion of phase one, during implementation or operation of phase two, or after subsequent refinement measures - will indicate that restoration of Aquifer C is technically impracticable from an engineering perspective. If such a determination is made by EPA, the ultimate remediation goal and/or the selected remedy may be reevaluated.<sup>2</sup>

# NOTES:

- **1.** Although not required in a ROD, the **estimated number of wells** is included in this example for the following reasons, to:
  - Provide a **basis for estimating the cost** of the selected remedy, including upper and lower costs for phase one, phase two and the potential refinement measures;
  - Provide some **specificity regarding how the extraction component of the remedy will be used in the overall remediation strategy**, because changes in the extraction system directly influence the time period required to attain the remedial objectives for this site; and to
  - Provide some **bounds for the scope, performance and cost of the selected remedy**, which will assist in determining whether future, post-ROD remedy modifications require an Explanation of Significant Differences (see Section 2.4 of this guidance).
- 2. Reevaluation of the ultimate remediation goal and/or the selected remedy would generally require an ESD or ROD amendment.

# Appendix B2: Phased Implementation of Extraction Component of Remedy at a DNAPL Site

## **Site Conditions:**

At **hypothetical Site 2** (a DNAPL site), ground water in Aquifer A is contaminated with volatile and semivolatile organic contaminants (no metals as contaminants of concern). DNAPLs have also been observed in this aquifer. At this site, Aquifer A is not currently used as source of drinking water, but several wells are located off-site in the estimated path of the contaminant plume.

The selected remedy includes extraction and treatment for hydraulic containment of the likely **DNAPL-zone** (see Appendix A1 of this guidance) and for restoration of the aquifer outside the DNAPL-zone. Reinjection of a portion of the treated ground water will be used to enhance recovery of contaminants from the aquifer. It has been determined that aquifer restoration within the DNAPL-zone is technically impracticable from an engineering perspective, as explained in the <u>Statutory Determinations</u> section of the ROD. The remedy will be implemented in two construction phases.

## **ROD Language for Extraction Component of Remedy :**

The following, or similar language, should appear in the **Selected Remedy** section of the ROD:

The **ultimate goal** for the ground-water portion of this remedial action is to restore the maximum areal extent of Aquifer A to its beneficial uses. At this site Aquifer A is potentially useable as a source of drinking water and is currently used off-site for this purpose. Based on information obtained during the remedial investigation and on a careful analysis of all remedial alternatives, EPA believes that the selected remedy will achieve this goal.

The extraction portion of the ground-water remedy will be implemented in two phases. In phase one, a sufficient number of extraction wells will be installed to achieve two remedial objectives for Aquifer A: 1) minimizing further migration of contaminants from suspected subsurface DNAPL areas to the surrounding ground water; and 2) minimizing further migration of the leading edge of the contaminant plume. It is currently estimated that three to five extraction wells will be required for phase one.<sup>1</sup> After construction of phase one is completed, the extraction system will be carefully monitored on a regular basis and its performance evaluated. This evaluation may provide further information concerning the extent of the DNAPL-zone. Operation and monitoring of phase one for a period of up to two years may be needed to provide sufficient information to complete the design of phase two.

In phase two, additional extraction wells will be installed with the objective of restoring the maximum areal extent of Aquifer A for use as a source of drinking water, in addition to maintaining phase one objectives. Reinjection wells and related pumping equipment for flushing a portion of the treated ground water through the aquifer (water flooding) will also be installed in order to enhance the recovery of contaminants. Restoration is defined as attainment of required cleanup levels in the aquifer, over the portion of the contaminant plume outside the DNAPL-zone. Cleanup levels for each ground-water contaminant of concern are specified in Table \_\_\_\_; although cleanup level ARARs within the DNAPL-zone have been waived by EPA due technical impracticability from an engineering perspective, as discussed in Section \_\_\_\_\_ of the ROD. Current estimates indicate that these cleanup levels can be attained in the portion of Aquifer A outside the DNAPL-zone within a timeframe of approximately 25 years.

# Appendix B2: Phased Implementation of Extraction Component of Remedy at a DNAPL Site (continued)

Current estimates also indicate that an additional two to six extraction wells and two to four reinjection wells may be required for phase two.<sup>1</sup> However, monitoring and evaluation of the performance of phase one will be used to determine the actual number and placement of wells for phase two.

The selected remedy will include ground-water extraction for an estimated period of 25 years, during which the system's performance will be carefully monitored, in accordance with the monitoring plan defined in Section \_\_\_\_\_ of the ROD, and adjusted as warranted by the performance data collected during operation. **Refinement** of the extraction system may be required, if EPA determines that such measures will be necessary in order to restore the maximum areal extent of Aquifer A in a reasonable timeframe, or to significantly reduce the timeframe or long-term cost of attaining this objective. **Refinement of the extraction system may include any or all of the following:** 

- 1) Adjusting the rate of extraction from some or all wells;
- 2) Discontinuing pumping at individual wells where cleanup goals have been attained;
- 3) Pulsed pumping of some or all extraction wells to eliminate flow stagnation areas, allow sorbed contaminants to partition into ground water, or otherwise facilitate recovery of contaminants from the aquifer;
- 4) Installing up to two additional ground-water extraction wells to facilitate or accelerate cleanup of the contaminant plume; and<sup>1</sup>
- 5) Installing up to two additional reinjection wells.<sup>1</sup>

It is possible that performance evaluations of the ground-water extraction system - after completion of phase one, during implementation or operation of phase two, or after subsequent refinement measures - will indicate that restoration of portions or all of Aquifer A is technically impracticable from an engineering perspective. If such a determination is made by EPA, the ultimate remediation goal and/or the selected remedy may be reevaluated.<sup>2</sup>

# NOTES:

\_\_\_\_\_

- **1.** The reasons for including the **estimated number of wells** in this example are discussed in the Notes section of the previous example, Appendix B2.
- 2. Reevaluation of the ultimate remediation goal and/or the selected remedy would generally require an ESD or ROD amendment.

# Appendix B3: Deferring Selection of Treatment Components to Remedial Design

# Site Conditions:

**Hypothetical Site 2** is the same site used in the previous example, Appendix B2. Most of the treated ground water will be discharged to the nearby Muddy River, although a portion (20 to 30 percent) will be reinjected to Aquifer A to enhance contaminant recovery. Contaminant-specific and other water quality requirements for discharge to the Muddy River were specified by the state and are listed in Table \_\_\_\_\_\_ of the ROD. Other specifications for the treatment system are also listed in the ROD, which include filtering of suspended mineral solids to minimize clogging of reinjection wells; and treatment of vapor phase organic contaminants from air stripping or other processes, as requested by the local community.

## **<u>ROD Language for Treatment Component of Remedy</u>** :

The ex-situ treatment component of the ground-water remedy will utilize presumptive technologies identified in Directive 9283.1-12 from EPA's Office of Solid Waste and Emergency Response (OSWER), included as Attachment \_\_\_\_\_ of the ROD. Since contaminants of concern include volatile and semivolatile organic compounds, one or more of the presumptive technologies - air stripping, granular activated carbon (GAC), chemical/UV oxidation and aerobic biological reactors - will be used for treating aqueous contaminants in the extracted ground water. Other technologies will also be needed in the treatment system for removal of suspended mineral solids and treatment of vapor phase contaminants. The actual technologies and sequence of technologies used for the treatment system will be determined during remedial design. Final selection of these technologies will be based on additional site information to be collected during the remedial design. (See Section 3.4 and Appendix C3 of OSWER Directive 9283.1-12 for a discussion of site information needed for selection and design of the ex-situ treatment system.) Based on this additional information and sound engineering practice the treatment system shall be designed to:

- Attain the chemical-specific discharge requirements and other performance criteria specified in Table \_\_ and Section \_\_ of the ROD; and
- Treat, or be easily modified to treat, the expected flow increase from phase one to phase two of the extraction system.

Other design factors shall include:

- Maximizing long-term effectiveness,
- Maximizing long-term reliability (i.e., minimize the likelihood of process upsets), and
- Minimizing long-term operating costs.

Additional information concerning presumptive technologies for the ex-situ treatment component of the remedy is provided in OSWER Directive 9283.1-12. Descriptions of each of the presumptive technologies are presented in Appendices D1 through D8, and advantages and limitations of each of these technologies are listed in Appendix C4 of this directive.

# Appendix B3: Deferring Selection of Treatment Components to Remedial Design (continued)

For the purpose of estimating the approximate cost of the treatment component of the selected remedy, the following treatment sequence is assumed for aqueous contaminants: flow equalization tanks, a gravity oil-water separator, an air stripper, followed by GAC units. GAC will also be used to treat vapor phase contaminants from the air stripper. The GAC units will be thermally reactivated at an off-site facility. Separated DNAPL compounds will be recycled if possible, but since the actual composition of the recovered liquids is unknown, costs for incineration at an off-site facility were used for the cost estimate.

# Appendix B4: Suggested ROD Language from 1990 OSWER Directive

Recommended language for the Selected Remedy section of the ROD was given in OSWER Directive 9283.1-03, entitled "Suggested ROD Language for Various Ground-Water Remediation Options," dated October 10, 1990. For the RODs in which the final remedy without a contingency is selected, this Directive recommended that "the following type of language should appear in the <u>Selected Remedy</u> section of the ROD:"

The goal of this remedial action is to restore ground water to its beneficial use, which is, at this site, (specify whether this is a potential or actual drinking water source, or is used for nondomestic purposes). Based on information obtained during the remedial investigation and on a careful analysis of all remedial alternatives, EPA < (optional) and the State/Commonwealth of \_\_\_\_\_\_ > believe that the selected remedy will achieve this goal. It may become apparent, during implementation or operation of the ground-water extraction system and its modifications, that contaminant levels have ceased to decline and are remaining constant at levels higher than the remediation goal over some portion of the contaminated plume. In such a case, the system performance standards and/or the remedy may be reevaluated.

The selected remedy will include ground-water extraction for an estimated period of \_\_\_\_\_ years, during which the system's performance will be carefully monitored on a regular basis and adjusted as warranted by the performance data collected during operation. Modifications may include any or all of the following:

- *a) at individual wells where cleanup goals have been attained, pumping may be discontinued;*
- *b) alternating pumping at wells to eliminate stagnation points;*
- *c) pulse pumping to allow aquifer equilibration and to allow adsorbed contaminants to partition into ground water; and*
- *d) installation of additional extraction wells to facilitate or accelerate cleanup of the contaminant plume.*

To ensure that cleanup goals continue to be maintained, the aquifer will be monitored at those wells where pumping has ceased on an occurrence of every \_\_\_\_\_ years following discontinuation of ground-water extraction.

# **APPENDIX C**

# **Ex-Situ Treatment Technologies for Ground Water**

- Appendix C1: Ex-Situ Technologies Considered in Sample of 25 Sites
- Appendix C2: Other Components Needed for Treatment Trains
- Appendix C3: **Information Needed** for Selection of Technologies and Design of Treatment Train
- Appendix C4: Advantages and Limitations of Presumptive Treatment Technologies

## Appendix C1: Ex-Situ Technologies Considered in Sample of 25 Sites

Technologies that were **considered** for treatment of extracted ground in the sample of 25 sites reviewed in detail (EPA, 1996b) are listed below. These technologies were either considered in the feasibility study (FS), or considered and/or selected in the record of decision (ROD) or remedial design. The technologies are listed according to overall process type, and by design style within each type. Those technologies identified as **presumptive technologies** are also indicated. For further information on how presumptive technologies were identified, refer to Section 3.2 of this guidance and EPA, 1996b.

For Treatment of **Organic** Contaminants:

#### **Presumptive Technologies:**

#### Air stripping:

- Packed tower
  - Ambient temperature
  - Higher temperature
- Aeration methods
  - Ambient temperature
  - Higher temperature
- Cascade falls

### Granular activated carbon (GAC)

#### **Chemical/UV oxidation:**

- Chemical oxidation alone
  - Ozone
  - Hydrogen peroxide
  - Chlorine compounds
  - Potassium permanganate
- Chemical with UV oxidation
  - Ozone
  - Hydrogen peroxide
- UV oxidation alone (photolysis)
- Alkaline chlorination (**for cyanide**)
- Unspecified oxidation methods

#### Aerobic biological reactors:

- Attached growth
  - Trickling filter
    - Rotating biological contactors
    - Fixed bed
- Suspended growth
  - Activated sludge
  - Sequencing batch reactors
  - Aeration ponds/lagoons
  - Unspecified suspended growth
- Unspecified aerobic reactors

#### Chemical precipitation:

For Treatment of **Metals**:

- Hydroxide precipitants
  - Sodium hydroxide
  - Lime
  - With prior chemical reduction

\_\_\_\_\_

- Sulfide precipitants
  - Sulfur dioxide
  - Sodium sulfide
  - Sodium bisulfide/bisulfites
  - With prior chemical reduction
  - Unspecified sulfide precipitant
- Other precipitation methods
  - Ferrous sulfate
  - Potassium permanganate
  - Activated consumable element
  - Unspecified chemical precipitation

# Ion exchange/adsorption:

- Fixed bed
  - - Impregnated/synthetic resin
  - Activated alumina
- Electrodialysis
- Unspecified ion exchange

## **Electrochemical methods:**

- Electrochemical reduction
- Magnetically activated

#### Aeration of Background Metals:

- Aeration basin
- Cascade aeration
- Other aeration methods

# Appendix C1: Ex-Situ Technologies Considered in Sample of 25 Sites (continued)

For Treatment of **Organic** Contaminants:

\_\_\_\_\_

# **Other Technologies Considered:**

#### **Chemical treatment:**

- Hydrolysis
- Catalytic dehydrochlorination
- Catalytic dechlorination
- Chlorinolysis

#### **Thermal Destruction:**

- Incineration
- Calcination
- Wet air oxidation
- Supercritical water oxidation
- Microwave discharge/plasma

## High temperature separation:

- Steam stripping
- Distillation

## Membrane filtration:

- Reverse osmosis
- Ultrafiltration

## Anaerobic biological treatment:

- Anaerobic biological reactor
- Enzymatic degradation

## Liquid-liquid extraction:

- Solvent extraction
- Liquid carbon dioxide extraction

#### **Evaporation:**

• Evaporation basin

## Land treatment:

- Surface spreading
- Spray irrigation

# For Treatment of Metals:

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Granular activated carbon (for metals)

**Reverse Osmosis** 

**Biological treatment of metals** 

# Appendix C2: Other Components Needed for Treatment Trains<sup>1</sup>

	Solid or Liquid Separation Technologies	Effluent Polishing Technologies <sup>2</sup>	V	apor Phase Treatment Technologies <sup>3</sup>
•	Oil/grease separation <sup>4</sup>	• Activated carbon	•	Activated carbon
•	Filtration <sup>5</sup>	• Ion exchange	•	Resin adsorption
•	Coagulation <sup>5</sup>	• Neutralization	•	Catalytic oxidation
	(or flocculation)		•	Thermal incineration
٠	Clarification <sup>5</sup> (or sedimentation)		•	Acid gas scrubbing
			•	Condensation

#### **General Sequence of Unit Processes Used in Aqueous Treatment Trains**

Sequence	Unit Treatment Process	Treatment Stage
Begin	Equalize inflow	Pretreatment
-	Separate solid particles	Pretreatment
	Separate oil/grease (NAPLs)	Pretreatment
	Remove metals	Treatment
	Remove volatile organics	Treatment
	Remove other organics	Treatment
	Polish organics <sup>2</sup>	Post-treatment
	Polish metals	Post-treatment
End	Adjust pH, if required	Post-treatment

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#### NOTES:

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- In addition to the presumptive technologies listed in the guidance, other treatment components are needed either prior to (pretreatment) or subsequent to (post-treatment) the presumptive technologies. <u>This listing is not intended to be presumptive</u>. Not listed are technologies that may be required for treatment residuals, such as spent carbon.
- <sup>2</sup> Effluent polishing technologies are those used for the final stage of treatment prior to discharge, and can include pH adjustment (neutralization) as well as additional removal of aqueous constituents.
- 3 Vapor phase contaminants released during water treatment may need to be contained and treated. This includes organic contaminants volatilized during air stripping, from biological treatment, or other gases released from chemical oxidation, reduction or biologic processes (e.g., hydrochloric acid, hydrogen sulfide, methane, etc.).
- 4 Methods for separation of oil and/or grease from water include, but are not limited to, gravity separation and dissolved air floatation. These methods can be used to remove NAPLs from the extracted ground water.
- <sup>5</sup> These technologies can be used to remove solid particles at the beginning of the treatment train or for removal of other solids resulting from chemical precipitation, chemical/UV oxidation or biological treatment.

#### Information Needed

1. Total extraction flow rate:

- Total extracted flow
- Flow variability
- Uncertainty of estimate

Purpose of Information

**Inflow** to the treatment system is the total flow from all extraction wells. Since this flow must also be discharged, large flows may determine the availability of some discharge options. Flow rate and concentration determines the mass loading (mass per unit water volume) of each contaminant entering the treatment system. The mass loading determines the dimensions and capacities of treatment vessels, and whether continuous flow or batch design are used for each treatment unit. Flow is also a factor for selecting among the presumptive treatment technologies because some are less cost effective for high or low flows.

Variable inflow rates may require use of flow equalization tanks, batch instead of continuous flow operation or use of modular treatment units that can be added or subtracted from the treatment train. Some technologies can handle variable flow more easily than others. Variable extraction rates may result from short-term operational changes, seasonal changes or phased well installation.

Uncertainty in the flow estimate can result from natural variability of aquifer properties over the site, and from the method used to measure these properties. Since flow is a critical design parameter, additional characterization may be needed to reduce the level of uncertainty. Estimates of the total extraction rate should be based on pumping type aquifer tests, since this method provides a much better estimate of average aquifer properties than other methods.

## Information Needed

#### 2. Discharge options and effluent requirements:

- Options available
- Target effluent concentrations, each option
  - Contaminants
  - Contaminant degradation products
  - Treatment additives
  - Natural constituents
  - Water quality parameters
- Other requirements, each option
  - Regulatory
  - Operational
- Community concerns or preferences

Purpose of Information

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Options for discharge of treated ground water could include: discharge to surface waters; discharge to a drinking water system; reuse or recycling for other purposes (e.g., industrial processes); infiltration or reinjection to shallow subsurface or reinjection to the same aquifer; or discharge to POTW. Target effluent concentration levels for both contaminants and naturally occurring constituents may be markedly different for each discharge option.

Effluent requirements could include those for chemicals added during treatment, contaminant degradation products, naturally occurring constituents (e.g., arsenic), and water quality parameters (e.g., suspended solids) in addition to maximum concentration levels for chemicals of concern. These requirements will determine the overall level of treatment needed, which in turn determines the type of components needed in the treatment train and is a critical factor in selecting appropriate treatment technologies.

Each discharge option may have different water quality requirements for the treated effluent, from both a **regulatory** and **operational** standpoint. For example, reinjection to the subsurface must meet substantive federal and/or state requirements for underground injection (regulatory) as well as minimize chemical and biological clogging of injection wells or infiltration lines (operational). Use of the best available technology (BAT) could also be a regulatory requirement. The **affected community** may also have concerns or preferences regarding the type of discharge.

**Target effluent concentrations** determine the overall removal efficiency the treatment train must attain for each constituent. For example, if the target effluent level is 10 mg/L and the inflow concentration is 1000 mg/L, then the treatment train must attain an overall removal efficiency of 99.0 percent (1000 - 0.99(1000) = 10). The treatment train may need to include more than one type of technology, or multiple units of a single technology, in order to attain the required overall removal efficiency.

#### Information Needed

#### 3. Water quality of treatment influent:

- Contaminant types and concentrations:
  - Inorganic chemicals
  - Organic chemicals
  - Concentration changes over time
  - Nonaqueous phase liquids (NAPLs)
- Naturally occurring constituents:
  - Major cations (metals) and anions
  - Organic chemicals
  - Radionuclides

Purpose of Information

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**Contaminant types and concentrations** must be estimated for the total flow entering the treatment system. Since some technologies are more effective in removing certain contaminant types, this is an important technology selection factor. Inflow concentrations are needed to determine the removal efficiency of the treatment train, as discussed above.

The design should consider the potential for inflow concentrations to change over time. Contaminant concentrations usually decrease as remediation progresses. Also, short term increases may occur if a "hot spot" of more highly contaminated ground water is captured by the extraction system. Samples obtained from **pumping type aquifer tests provide better estimates of average contaminant concentrations**, because such samples are obtained from a relatively large aquifer volume.

If present, subsurface **NAPLs** (refer to Appendix A1) may become entrained in the extracted ground water. These immiscible liquids should be removed in a pretreatment step (process used prior to other treatment methods). Also, a specialized extraction system may be needed to remove free-phase NAPLs from the subsurface.

Naturally occurring or non-site related constituents may need to be removed to prevent interference with treatment processes and may be a factor in technology selection. Metals such as iron, manganese, and calcium can leave mineral deposits (scaling) on air stripper packing and on activated carbon or other treatment media. If not accounted for, these metals can also cause premature exhaustion of ion exchange capacity and increased consumption of reagents in chemical oxidation or precipitation processes. Iron also promotes biological fouling in air strippers. Heavy metals (e.g., lead, mercury) and cyanides can be toxic to microorganisms in biological reactors. Metals can also form deposits on well screens of extraction or reinjection wells (encrustation) or promote biological fouling (clogging) on well screens.

Information Needed

#### 3. Water quality of influent (continued):

- Other water quality parameters:
  - Indicator parameters
  - Design parameters

Purpose of Information

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Dissolved **organic constituents** (e.g., from decay of organic materials or from landfill leachate) can interfere with adsorption of targeted compounds and can cause premature exhaustion of activated carbon. Metal-organic complexes can interfere with chemical oxidation or precipitation processes.

If present, naturally occurring **radionuclides** can accumulate in treatment media or residuals (e.g., activated carbon or chemical sludges) resulting in potential exposure hazards for personnel and additional transportation and disposal considerations.

Other water quality parameters are used as effluent quality standards, indicator parameters, or design parameters for treatment processes. **Indicator parameters** are used to indicate the presence of other constituents. For example, total dissolved carbon (TDC) is a measure of the relative level of dissolved organic constituents. Gross alpha and gross beta particle activity are relatively simple measurements that indicate the relative abundance of **naturally occurring radionuclides**. Other indicator parameters include: total dissolved solids (TDS), chemical oxygen demand (COD), biological oxygen demand (BOD) and total suspended solids (TSS). Temperature and pH are **design parameters** for most treatment processes.

Also, high levels of total suspended solids (TSS) in extracted ground water may indicate that extraction wells are not properly designed or developed. Most treatment technologies require that suspended solids in excess of certain level be removed during pretreatment, where acceptable levels may differ for each technology.

# Information Needed

#### 4. Treatability information:

- From technical literature
- Treatability studies
  - Laboratory screening
  - Bench-scale testing
  - Pilot-scale testing
- Modeling predictions
- Projections of effluent quality

Purpose of Information

Treatability information is needed to select technology types and design styles from among the presumptive technologies; and for selection and design of other components of the treatment train. The particular mix of contaminants and naturally occurring constituents can vary considerably for different sites. Treatability information is available in the **technical literature** for some technologies, including air stripping and granular activated carbon (GAC).

**Treatability studies** include 1) laboratory screening, 2) bench-scale testing, or 3) pilot-scale testing. These studies may begin with any tier and skip tiers that are not needed (see Section 3.4 of guidance). **Computer models** for predicting treatment performance are available for some technologies.

In general, treatability studies should be performed prior or during the design of any system expected to provide **long-term treatment** of extracted ground water, including systems using presumptive technologies. Treatability studies are needed to accurately predict the effectiveness and cost of a technology for a given site, including construction and operating costs; and the costs of other components of the treatment train. Optimizing the cost effectiveness of the treatment train (i.e., minimizing the total cost per unit volume of water treated) is especially important for systems designed to operate over a long time period.

Treatability studies **may reveal unexpected site conditions**, such as the presence of naturally occurring compounds that interfere with the planned treatment process or that metal contaminants can be effectively removed by removing mineral solids. Such studies are also needed to determine pretreatment requirements, and requirements for treating aqueous, vapor and solid waste streams resulting from a particular treatment process. Treatability studies are needed to determine optimum chemical reagents and reagent quantities for pH adjustment; oxidation, reduction or precipitation of contaminants; and parameters for design of biological and other reactors.

Treatability studies should be performed on samples obtained from **pumping type aquifer tests** instead of from monitoring wells, because such samples are more representative of contaminated ground water that will enter the treatment system. Samples obtained for treatability studies should be obtained after several hours of pumping.

# Appendix C4: Advantages and Limitations of Presumptive Treatment Technologies

Technology	Advantages	Limitations
Treatment T	Technologies for the Removal of Organic Con	taminants
Air Stripping	<ul> <li>Successfully used in hundreds of groundwater applications</li> <li>Low operating cost relative to other technologies (e.g., energy usage is relatively low).</li> <li>Operationally simple system requiring a minimum of operator assistance.</li> <li>Treatability studies often not required for selection or design, but are recommended.</li> <li>Trained contractors available to implement the technology.</li> </ul>	<ul> <li>Contaminants transferred to air, and treatment of air emissions may be required.</li> <li>Pretreatment for metals removal and pH control may be needed to reduce fouling and corrosion.</li> <li>Post-treatment (polishing) may be required.</li> <li>Large surges in influent concentrations can reduce removal efficiency because the efficiency for an individual compound is fixed regardless of influent concentrations.</li> <li>Air stripping is not as effective for compounds with low Henry's law constants or high solubilities.<sup>b,c</sup></li> <li>Cold weather can reduce efficiency.</li> </ul>
Granular Activated Carbon	<ul> <li>Successfully used for contaminated ground water at many Superfund and underground storage tank sites.</li> <li>Operationally simple system requiring a minimum of operator assistance.</li> <li>Regularly used as a <u>polishing</u> step following other treatment technologies.</li> <li>Treatability studies generally not required, but are recommended (information is available from carbon vendors).</li> <li>Trained contractors available to implement the technology.</li> <li>Generally a cost-effective alternative as single- step treatment for flows less than about 3 gpm.<sup>d</sup></li> </ul>	<ul> <li>Activated carbon is generally too costly for use as a single-step treatment if ground-water chemistry requires high carbon usage rates.</li> <li>Contaminants are not destroyed but are transferred to another media (i.e., spent carbon must be regenerated or disposed of properly).</li> <li>Pretreatment for suspended solids removal is often required.</li> <li>Pretreatment for metals removal and pH control may be needed to reduce fouling and corrosion.</li> <li>Organic compounds that have low molecular weight and high polarity are not recommended for activated carbon (e.g., acetone).</li> <li>Naturally occurring organic compounds may exhaust carbon bed rapidly and may interfere with the adsorption of targeted chemicals.</li> </ul>

# Appendix C4: Advantages and Limitations of Presumptive Treatment Technologies (continued)

Technology	Advantages	Limitations
Chemical/ UV Oxidation	<ul> <li>Where oxidation is complete, organic contaminants are <u>destroyed</u> and not transferred to other media; minimal residuals generated.</li> <li>Effective on a wide variety of volatile and semivolatile organics, including chlorinated organics, as well as cyanide and some metals.</li> <li>Operating costs can be competitive with air stripping and activated carbon.</li> </ul>	<ul> <li>Incomplete oxidation will leave original contaminants and possibly toxic oxidation products; activated carbon polishing may be required.</li> <li>Capital costs may preclude small-scale applications, especially for ozone systems.</li> <li>Metals may precipitate during oxidation, requiring filtration post-treatment and residuals disposal.</li> <li>UV light sources are subject to fouling and scaling from solids, iron compounds, carbonates, etc. Pretreatment may be required to remove these substances.</li> <li>Process must be closely monitored to ensure contaminant destruction and to prevent safety hazards.</li> <li>Peroxide and other chemical oxidants must be properly stored and handled.</li> <li>Site-specific treatability studies are necessary (process may require large quantities of oxidizer to destroy target compound(s) if reactive nontarget compounds are present).</li> </ul>
Aerobic Biological Reactors	<ul> <li>Organic contaminants <u>degraded</u>, often with minimal cross-media environmental impacts.</li> <li>Proven effective for many organic compounds.</li> <li>Some systems (e.g., trickling filters and rotating biological contactors) have minimal energy requirements and generally low capital and operating costs.</li> <li>Can be designed to require a minimum of operator attention.</li> <li>Relatively simple, readily available equipment.</li> <li>Trained contractors available to implement the technology.</li> </ul>	<ul> <li>A residual organic sludge is generated that must be disposed of properly.</li> <li>Some compounds are difficult or impossible to degrade (recalcitrant) or slow to degrade.</li> <li>Difficulties acclimating microorganisms to contaminants are possible; requires longer startup time than other technologies to achieve effective steady-state performance</li> <li>Volatile organics may require air emission controls or pretreatment to remove them.</li> <li>Variations in flow or concentration may require significant operator attention to prevent microorganisms from being killed.</li> <li>Cold weather can cause operational difficulties.</li> <li>Treatability studies are needed for selection and design.</li> <li>Pretreatment may be needed to remove contaminants toxic to the microorganisms, such as heavy metals.</li> <li>Low organic loading and the potential for supplementary nutrients and food sources must be considered.</li> </ul>

Technology	Advantages	Limitations
Treatment Technologies f	for the Removal of Inorganic Contamin	aants
Chemical Precipitation	<ul> <li>Most commonly used method for removing soluble heavy metal ions from contaminated water.</li> <li>Pretreatment for solids and iron generally not required.</li> <li><u>Hydroxide Precipitation</u></li> <li>Reliable method, chemicals relatively easy to handle, and not costly.</li> <li><u>Carbonate Precipitation</u></li> <li>Reliable method, calcium carbonate easy to handle, and not costly.</li> <li>Effectively removes a variety of soluble metals.</li> <li><u>Sulfide Precipitation</u></li> <li>Reliable method.</li> <li>High removal efficiency over a broader pH range.</li> <li>Relatively insensitive to most chelating agents.</li> <li>Can remove chromates and dichromates without reducing hexavalent chromium to trivalent form if ferrous ions are present or added.</li> </ul>	<ul> <li>A residual sludge is generated that must be treated and/or disposed of properly; metals are not usually easy to recover from sludge.</li> <li>Up to four times stoichiometric chemical additions may be required, especially for sulfide precipitation (see below).</li> <li>Hydroxide Precipitation</li> <li>Organics or complexing ions may form chelates/complexes instead of insoluble metal hydroxides.</li> <li>Optimum pH is different for each metal hydroxide, one pH may not effectively treat all soluble metal ions; successive treatments may be required.</li> <li>pH must be controlled within a narrow range.</li> <li>Naturally occurring sulfate in ground water may react with lime to form gypsum, which increases sludge, can clog filters, and can coat pipelines (caustic soda addition can reduce this problem but increases costs and dissolved solids [sodium salts] that must be removed from treated ground water).</li> <li>Carbonate Precipitation</li> <li>Calcium carbonate is not effective for ground water with high alkaline content.</li> <li>Pretreatment to remove organic, chelating, or oil and grease contaminants may be required.</li> <li>Sulfide Precipitation (Soluble Sulfide)</li> <li>Excess sulfide ions that are not precipitated remain in solution. They may be removed by using aeration to convert them from ionic to oxide form (sulfate).</li> <li>pH control between 8 and 9.5 is required to avoid release of hydrogen sulfide gas.</li> <li>Cost is high compared to hydroxide and carbonate precipitation</li> <li>Sulfide Precipitation (Insoluble Sulfides)</li> <li>Ferrous sulfide is used in amounts greater than that required by stoichiometric considerations.</li> <li>Produces more sludge than soluble sulfide or hydroxide processes.</li> </ul>

# Appendix C4: Advantages and Limitations of Presumptive Treatment Technologies (continued)

Technology	Advantages	Limitations
Treatment Technologies f	for the Removal of Inorganic Contami	nants (continued):
Ion Exchange/ Adsorption	<ul> <li>High removal efficiencies for heavy metals.</li> <li>Suitable for use as a <u>polishing</u> step after other technologies.</li> <li>Technology is reasonably well understood.</li> <li>On-site backflushing of exchange media allows immediate reuse.</li> </ul>	<ul> <li>Resins are usually costly and may not be cost-effective for large treatment loadings.</li> <li>Generates large volume of backflush solution (approximately 2.5 to 5% of the original ground-water flow rate) that is concentrated in the metals removed and requires treatment or disposal.</li> <li>Requires bench-scale testing to determine operational requirements and suitability of prospective resins.</li> <li>Beds can be fouled by particulate matter, oxidizing agents, oils, greases, biological growths, and intra-bed precipitates; therefore, pretreatment may be needed.</li> <li>Resins may be irreversibly harmed by aromatics and certain other organic compounds; and by iron, manganese, and copper if enough dissolved oxygen is present. Pretreatment may be needed.</li> <li>Spent resins require treatment before disposal.</li> </ul>
Electro- chemical Methods	<ul> <li>High removal efficiencies for certain heavy metals.</li> <li>Can treat both metals and cyanide simultaneously.</li> <li>Technology is reasonably well understood.</li> <li>Requires little floor space due to short residence time for hexavalent chromium reduction.</li> <li>Requires minimal operator attention.</li> <li>Low operating costs compared to chemical reduction or precipitation.</li> <li>Requires no chemical addition.</li> </ul>	<ul> <li>Particulate matter, oxidizing agents, oils, greases, biological growths may reduce process efficiency; therefore, pretreatment may be needed.</li> <li>Hexavalent chromium reduction generates a heavy metal precipitate that must be removed from solution in a subsequent clarification or settling process.</li> <li>A heavy metal sludge residual may be generated that may require treatment (dewatering and/or fixation) and that will require disposal.</li> <li>A spent acid rinse solution may be generated that requires treatment or disposal.</li> <li>Electrodes must be replaced occasionally.</li> </ul>

# Appendix C4: Advantages and Limitations of Presumptive Treatment Technologies (continued)

#### NOTES:

<sup>a</sup> U.S. Environmental Protection Agency. 1991. Engineering Bulletin: Air Stripping of Aqueous Solutions. EPA/540/2-91/022. 8 pp.

<sup>b</sup> B. Lamarre. 1993. Selecting an air stripper (what to consider!) *The National Environmental Journal*: 26-29.

<sup>c</sup> G. M. Long. 1993. Clean up hydrocarbon contamination effectively. *Chemical Engineering Progress*: 58-66.

# **APPENDIX D**

# **Descriptions of Presumptive Treatment Technologies**

Appendix D1: Air Stripping Appendix D2: Granular Activated Carbon Appendix D3: Chemical/UV Oxidation Aerobic Biological Reactors Appendix D4: Appendix D5: **Chemical Precipitation** Appendix D6: Ion Exchange/Adsorption Electrochemical Methods Appendix D7: Appendix D8: Aeration of Background Metals

# **Appendix D1: Air Stripping**

Air stripping uses volatilization to transfer contaminants from ground water to air. In general, water is contacted with an air stream to volatilize dissolved contaminants into the air stream. Stripping of a specific chemical depends on the equilibrium vapor pressure of that chemical as expressed by its Henry's law constant.

# Applicability

Air stripping is *applicable* to most of the volatile organic compounds (VOCs) as well as volatile inorganics such as ammonia and hydrogen sulfide. VOCs with high solubility in water (e.g., acetone) are more difficult to air strip. Air stripping is *potentially applicable* to certain halogenated semi-volatile organic compounds (SVOCs). It is *not applicable* to nonhalogenated SVOCs; heavy organics such as PCBs, dioxins/furans and pesticides; or inorganic metal compounds (U.S. EPA, 1991).

Air stripping is most effective for contaminants with a dimensionless (molar volume) Henry's law constant greater than 0.01 (or  $2.4 \times 10^{-4}$  atm-m<sup>3</sup>/gmol at  $25^{\circ}$  C). (Henry's law constants are available in U.S. EPA [1990]). Removal efficiencies greater than 99 percent are difficult to achieve for certain compounds. In general, other treatment technologies will be required for such chemicals when ground-water concentrations are high (e.g., above 10,000 ppm or 1 percent).

# **Contaminant Fate**

Contaminants are not destroyed by air stripping but are physically separated from contaminated ground water and transferred to air. Depending on the level of contaminants in the air discharge, the contaminated air stream may need further treatment. Additional polishing treatment of the aqueous effluent also may be necessary, depending on discharge requirements.

## Design

Air strippers are designed for a specific target chemical (either the predominant contaminant or the most difficult-to-strip contaminant) with a desired target removal efficiency. The air stripping process is well understood and the technology is well developed. Air stripping has an extensive track record in a variety of applications.

The most frequently used configuration is a packed tower equipped with an air blower. The ground water is fed into the top of the stripper and the air is introduced at the bottom, creating a countercurrent gas-liquid contact. Random plastic packing is frequently used to improve gas-liquid contact. Structured packing and steel packing may also be used. Packed-tower air stripper design involves specification of stripper column diameter and packing height for a specified ground-water flow rate and air-to-water ratio. Shallow-tray aeration devices provide an alternative gas-liquid contacting system that provides a more compact, lower profile system that is less subject to fouling.

## Alternative Techniques/Enhanced Methods

- For high flow rates (over 1,000 gpm), cooling towers (large structures with cascading water primarily used to cool water using countercurrent ambient air flow) may provide a cost-effective alternative to conventional packed towers.
- Shallow tray air strippers or diffused tank aeration units are less susceptible to fouling problems than packed towers and may be preferable where the water to be treated contains high concentrations of certain inorganics (e.g., iron).

# Alternative Techniques/Enhanced Methods (continued)

- Because the efficiency of air stripping increases at higher temperatures, increasing the influent ground-water temperature (typically about 55° F) using a heat exchanger can increase the stripper's removal efficiency, especially for less volatile contaminants.
- Steam stripping methods, which use steam rather than air as the stripping medium, can be used to remove highly soluble contaminants and SVOCs not usually amenable to air stripping. However, operation costs for steam stripping can be two to three times greater than air stripping, depending on the cost of steam. In this guidance, these methods are not considered a type of air stripping and are not identified as a presumptive technology for ex-situ treatment of ground water.

### Pre/Post-treatment

- Pretreatment to remove iron and other metals and to control hardness may be necessary to reduce fouling and mineral deposition in packed tower air strippers.
- Granular activated carbon is sometimes used to polish the treated water from an air stripper to further reduce organic contaminant levels and meet discharge requirements.
- Contaminants in the air discharge may be reduced by activated carbon adsorption, catalytic oxidation, or incineration to meet air emission requirements.

## Selected References

Lamarre, B. 1993. Selecting an air stripper (what to consider!). The National Environmental Journal: 26-29.

Nyer, E.K. 1985. Groundwater Treatment Technologies. Van Nostrand Reinhold, New York, NY. 187 pp.

Nyer, E.K. 1993. Practical Techniques for Groundwater and Soil Remediation. CRC Press, Inc., Boca Raton, FL. 214 pp.

Okoniewski, B.A. 1992. Remove VOCs from wastewater by air stripping. Chemical Engineering Progress: 89-93.

U.S. EPA Environmental Protection Agency. 1990. Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF) - Air Emission Models. EPA/450/3-87-026. Office of Air Quality Planning and Standards, Research Triangle Park, NC. Appendix D.

U.S. Environmental Protection Agency. 1991. Engineering Bulletin: Air Stripping of Aqueous Solutions. EPA/540/2-91/022. Office of Research and Development, Cincinnati, OH. 9 pp.
## **Appendix D2: Granular Activated Carbon**

Activated carbon removes contaminants from ground water by adsorption. The adsorption process takes place in three steps: (1) contaminant migration to the external sorbent surface; (2) diffusion into the sorbent pore structure; and (3) adsorption onto the sorbent surface. The principal form of activated carbon used for ground-water treatment is granular activated carbon (GAC). GAC is an excellent sorbent due to its large surface area, which generally ranges from 500 to 2,000 m<sup>2</sup>/g.

## Applicability

GAC is *applicable* to a wide variety of contaminants including: halogenated volatile and semivolatile organics, nonhalogenated volatile and semivolatile organics, PCBs, pesticides, dioxins/furans, most organic corrosives, metals, radioactive materials, inorganic cyanides, and certain oxidizers. GAC is *potentially applicable* to certain organic cyanides, and it is *not applicable* to asbestos, inorganic corrosives, and reducers (U.S. EPA, 1991). GAC is sometimes used alone for ground-water treatment. However, GAC is typically used for polishing aqueous effluents or controlling air emissions from other treatment technologies.

The adsorption capacity of activated carbon varies for specific organic compounds and for different types of GAC (based on the origin of coal and the percent binder used in the manufacture of the GAC). Contaminant-specific adsorption isotherms for a given type of GAC are generally available from the carbon manufacturer.

## **Contaminant Fate**

Contaminants are not destroyed by carbon adsorption, but are physically separated from contaminated water and transferred to carbon. After exhaustion, the spent carbon may be reactivated, regenerated, incinerated, or disposed of. Thermal reactivation and incineration destroy most or all adsorbed organic contaminants. Steam or hot gas regeneration is not appropriate for spent GAC from treatment of contaminated ground water but can be used for spent GAC from air emission control devices. GAC used for metals sorption may require disposal. If disposed of, spent GAC may have to be managed as a hazardous waste.

### Design

Activated carbon is a well-developed, widely used technology with many successful ground-water treatment applications, especially for secondary polishing of effluents from other treatment technologies. Contaminated ground water is contacted with a fixed GAC bed in a vessel. Flow direction is generally vertically downward, although an upward flow configuration is also possible. Fixed-bed configurations are also used for air emission control.

Adsorber design involves determining total carbon requirements and the number and dimensions of vessels needed to house the carbon. The amount of carbon required for a given application depends on the loading of adsorbable constituents in ground water (or contaminated air stream), the carbon's adsorption capacity for these constituents, and the carbon reactivation (or regeneration) frequency. Depending on the ground-water suspended solids content, it may be necessary to periodically backwash down flow carbon beds to relieve pressure drop associated with solids accumulation.

### Alternative Techniques/Enhanced Methods

 Staged bed (multiple beds operated in series) and pulsed bed (carbon beds operated with nearly continuous "pulsed" addition of fresh carbon and withdrawal of spent carbon) designs can be used if higher removal efficiencies are required.

### Alternative Techniques/Enhanced Methods (continued)

- Because the adsorption capacity of GAC is much higher for gas phase treatment than for liquid phase treatment, it is often more economical to use an air stripper followed by gas phase GAC to treat the air stripper exhaust than to use GAC alone for ground-water treatment.
- GAC is not identified as a presumptive technology for removal of metals dissolved extracted ground water. Spent carbon used for metals removal can be difficult to regenerate and may require treatment and/or disposal as a hazardous waste. Although GAC can remove low concentrations of certain metals, it has not been widely used for this purpose (U.S. EPA, 1991).

### Pre/Post-treatment

- Pretreatment may be required to remove natural organic matter, such as fulvic and humic acids, that may interfere with the adsorption of the target contaminants or rapidly exhaust the GAC.
- Naturally occurring radionuclides, if present in ground water, can accumulate in the GAC during treatment, which could result in potential exposure hazards for operating personnel and the spent carbon may require treatment and/or disposal as hazardous waste.
- Thermal reactivation, using heat alone or steam, is typically used as a post-treatment method for the spent carbon. The carbon is reactivated in a high-temperature reactor under reducing conditions. Most organic contaminants are thermally degraded during the reactivation process.

#### Selected References

Long, G.M. 1993. Clean up hydrocarbon contamination effectively. *Chemical Engineering Progress*, 89(5):58-67.

Stover, E.L. 1988. Treatment of herbicides in ground water. Ground Water Monitoring Review: 54-59.

Stenzel, M.H. 1993. Remove organics by activated carbon adsorption. *Chemical Engineering Progress*: 36-43.

U.S. Environmental Protection Agency. 1991. *Engineering Bulletin: Granular Activated Carbon Treatment*. EPA/540/2-91/024. Office of Emergency and Remedial Response, Washington, D.C. 8 pp.

# Appendix D3: Chemical/UV Oxidation

Chemical oxidation uses chemical oxidizing agents to destroy toxic organic chemicals and cyanide compounds (CN) in ground water. Commonly used oxidizing agents include: ozone, hydrogen peroxide, hypochlorites, chlorine, and chlorine dioxide. Ozone and hydrogen peroxide are generally preferred for removing organics and CN from ground water because chlorine-based oxidants can produce toxic byproducts (e.g., HCI, chlorinated organics). Ultraviolet light (UV) is often used in conjunction with ozone and/or hydrogen peroxide to promote faster and more complete destruction of organic compounds (reaction rates may be increased by factors of 100 to 1,000).

## Applicability

Chemical oxidation is *applicable* to both volatile and semivolatile organic compounds and cyanide compounds. Chemical oxidation is *potentially applicable* to PCBs, dioxins/furans, and metals (oxidation can be used to precipitate metals under certain conditions). Chemical oxidation is *not applicable* to asbestos and radioactive materials (U.S. EPA, 1991).

Chemical oxidation generally is effective for concentrations less than 500 µgL, but has been used for certain compounds at concentrations ranging up to several thousand mg/L. UV can enhance the oxidation of compounds that are resistant to chemical oxidation alone (e.g., PCBs). Iron or copper catalysts may be required for efficient destruction of certain organic compounds (e.g., phenols).

### **Contaminant Fate**

Complete oxidation decomposes hydrocarbons into carbon dioxide and water, although chlorinated organic compounds also yield chloride ions. CN is oxidized to ammonia and bicarbonate by hydrogen peroxide in an alkaline environment. If oxidation is incomplete, toxic constituents may remain, or intermediate degradation products can be formed that may be toxic. These toxic substances may be removed using GAC as a secondary or polishing treatment step.

#### Design

Chemical oxidation is a proven and effective technology that is carried out in either batch or continuous reactors. Oxidants are generally added to contaminated ground water in a mixing tank prior to introduction into the reaction vessel (reactor). The use of ozone as the oxidizing agent requires an onsite ozone generator and an ozone decomposition unit or other ozone emission control device. The use of hydrogen peroxide as the oxidizing agent requires storage tanks and special handling protocols to ensure operator safety. The use of chlorine as the oxidizing agent may produce HCI gas. If HCI is produced, an acid gas removal system may be necessary.

UV lamps, if used, are typically enclosed in quartz tubes submerged inside the reaction vessel. The tubes are subject to fouling or scaling from compounds such as iron oxide or calcium carbonate and from biological flocs from microorganisms in ground water. If fouling occurs, oxidation rates are drastically reduced.

Site-specific treatability studies are generally recommended for chemical oxidation systems. Extensive pretreatment may be required to condition ground water for effective oxidation. If UV lamps are used, the studies must evaluate the potential for fouling or scaling of the quartz tubes at the ground-water composition, oxidant concentration, and UV intensity conditions anticipated for long-term system operation. If fouling or scaling is likely, pretreatment and/or physical methods for keeping the tubes clean (e.g., wipers) may be required. If metals are to be removed by oxidation, solids should be removed by clarification or filtration prior to UV oxidation. Provisions for removing precipitated metal sludges also may be necessary.

## Alternative Techniques/Enhanced Methods

- UV radiation can be used in combination with a chemical oxidizing agent to increase the effectiveness of oxidation, especially for difficult-to-oxidize compounds.
- Metal catalysts, such as iron or copper, can be used in combination with a chemical oxidizing agent to increase the effectiveness of oxidation for certain types of compounds.
- Hydrodynamic cavitation is an innovative technology recently demonstrated under EPA's SITE program that uses forced cavitation of gas to enhance destruction of organics during UV oxidation processes.

### Pre/Post-treatment

- Pretreatment may be necessary to remove solids, microorganisms, calcium carbonate, iron oxides, and/or other metals that can interfere with the oxidation process or UV transmission. A pretreatment sequence of precipitation, flocculation, clarification, and/or filtration steps may be necessary.
- Post-treatment of the aqueous effluent with GAC may be necessary if destruction is not complete
  or if toxic byproducts are formed during oxidation.
- If toxic metals precipitate during the oxidation process, treatment and/or proper disposal of the resulting sludge may be required.

### Selected References

U.S. Environmental Protection Agency. 1990. *CERCLA Site Discharges to POTWs Treatability Manual.* EPA/540/2-90/008. Office of Emergency and Remedial Response. PB91-921269/CCE. NTIS. Springfield, VA. pp. 11-7 to 11-17.

U.S. Environmental Protection Agency. 1991. *Engineering Bulletin: Chemical Oxidation Treatment.* EPA/540/2-91/025. Office of Emergency and Remedial Response, Washington, D.C. 8 pp.

U.S. Environmental Protection Agency. 1993. *Superfund Innovative Technology Evaluation Program. Technology Profiles. Sixth Edition.* EPA/540/R-93/526. Office of Research and Development, Washington, DC.

U.S. Navy. 1993. *UV/Oxidation Treatment of Organics in Ground Water*. NEESA Document Number 20.2-051.7. Navy Energy and Environment Support Activity, Port Hueneme, CA. 11 pp.

## **Appendix D4: Aerobic Biological Reactors**

Biological reactors use microorganisms to degrade organic contaminants in ground water in ex situ reactors. There are two basic types of ex situ biological treatment processes: aerobic reactors and anaerobic reactors. Aerobic reactors use oxygen to promote biodegradation and are widely used. Anaerobic reactors degrade organics in the absence of oxygen. This guidance focuses on aerobic biological treatment because anaerobic treatment processes are not widely used for ground-water treatment.

# Applicability

Aerobic biological reactors are *applicable* to a wide variety of halogenated and nonhalogenated volatile and semivolatile organics. Aerobic biological reactors are *potentially applicable* to heavy organics, such as PCBs and certain pesticides, and organic and inorganic cyanides, but are generally not as effective for such recalcitrant compounds. Aerobic processes are *not applicable* to metals, asbestos, radioactive materials, or corrosive or reactive chemicals (U.S. EPA, 1992).

#### Contaminant Fate

Organic compounds are decomposed to carbon dioxide and water (aerobic processes) or to methane and carbon dioxide (anaerobic processes). Volatile organics are also removed by volatilization as a competing mechanism. Microbial growth produces an excess organic sludge (biomass) that must be disposed of properly. This sludge may concentrate metals and recalcitrant organic compounds that are resistant to degradation. Biodegradation may produce decomposition byproducts that are emitted to the air or dissolved in the effluent, and these decomposition byproducts may require additional treatment.

### Design

**Ex situ** biological treatment of ground water is conducted in bioreactors. The primary factors influencing bioreactor design are the microbial organic utilization rates and the peak organic loading rate (i.e., flow rate times organic concentration). Treatability tests are necessary to determine these and other design parameters. Under most circumstances, bioreactors require a significant startup time to acclimate the microorganisms to the specific contaminants being treated before the bioreactor will operate at optimal degradation rates. There are two general types of bioreactor design:

- In suspended growth reactors, microbes are kept suspended in water using mechanical aerators or diffused air systems. These aeration systems also keep the solution well mixed, improving contact between microbes and dissolved contaminants and supplying oxygen to the system. Activated sludge systems are the most common suspended growth bioreactors. Other examples include aerated ponds or lagoons, stabilization ponds (using both algae and bacteria), and sequencing batch reactors.
- In attached growth reactors, biomass is attached to a solid substrate, such as sand, rock, plastic, activated carbon, or resin. Reactor design is dependent upon the surface area of substrate media available for biomass growth. Examples include trickling filter, rotating biological contactor, fluidized bed, fixed bed, and roughing filter designs.

## Alternative Techniques/Enhanced Methods

 Direct addition of powdered activated carbon (PAC) into suspended growth bioreactors can both improve removal efficiency and reduce the likelihood of process upsets by buffering the concentrations of toxic compounds at levels amenable to biodegradation.

# Appendix D4: Aerobic Biological Reactors (continued)

## Alternative Techniques/Enhanced Methods (continued)

- Microbial augmentation (the addition of specially cultured microorganisms) may be used to increase the system's removal efficiency for certain difficult-to-degrade contaminants.
- Anaerobic reactors (digesters) may be preferred for the treatment of certain ground-wate r contaminants (e.g., certain chlorinated organics) that are difficult to degrade aerobically .
   However, anaerobic reactors have not been identified as a presumptive technology for the following reasons: 1) anaerobic processes have not been widely used for ground-water treatment; 2) reaction rates are slower than for aerobic processes, which result in longe r startup times (for acclimation) and longer treatment times; and 3) such reactors have a greater sensitivity to process upsets, especially where flow and contaminant concentrations vary over time. These factors generally result in higher operation and maintenanc e requirements and costs, and lower performance efficiencies than for aerobic processes i n ground-water applications.

### Pre/Post-treatment

- Chemical precipitation (for metals) or other pretreatment (e.g., PAC addition for organics) may be required to reduce (or buffer) concentrations of compounds that are toxic t o microorganisms.
- Carbon adsorption post-treatment may be used to reduce contaminant concentrations in the treated water to meet discharge requirements.
- Because certain aerated bioreactor designs (e.g., mechanically aerated activated sludg e systems, aerated p onds and lagoons) present difficulties for direct capture and control of air emissions, an air stripper (with emission controls) may be a cost-effective treatment prior to biodegradation if volatile contaminant emissions need to be controlled. For other bioreactor designs, such as diffu sed-aeration activated sludge and trickling filter systems, air emissions are more easily captured and can be treated using carbon adsorption, catalytic oxidation, or incineration.

### Selected References

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Flatman, P.E., D.E. Jerger, and L.S. Bottomley. 1989. Remediation of contaminated groundwater using biological techniques. *Ground Water Monitoring Review*: 105-119.

U.S. Environmental Protection Agency. 1979. Selected Biodegradation Techniques for Treatment and/or Ultimate Disposal of Organic Materials. EPA-600/2-79-006. Office of Research and Development, Cincinnati, OH.

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U.S. Environmental Protection Agency. 1992. *Engineering Bulletin: Rotating Biological Contactors*. EPA/540/S-92/007. Office of Research and Development, Cincinnati, OH. 8 pp.

# **Appendix D5: Chemical Precipitation**

Chemical precipitation chemically converts dissolved metal and/or other inorganic ions in ground water into an insoluble form, or precipitate. Metal ions generally precipitate out as hydroxides, sulfides, or carbonates and are removed as solids through clarification and filtration. In this guidance, chemical precipitation is defined to include chemical precipitation of metals by oxidizing or reducing agents, as well as any pH adjustment (neutralization) and solids removal steps required.

## Applicability

Chemical precipitation is *applicable* to dissolved metal and other inorganic ions (such as arsenate and phosphate). Chemical precipitation is *not applicable* to volatile or semivolatile organic compounds (U.S. Navy, 1993).

### **Contaminant Fate**

Dissolved metals are converted to insoluble forms, which are subsequently removed by flocculation, clarification, and/or filtration. The solid residue (chemical sludge) containing the metal contaminant then must be treated and/or disposed of properly.

## Design

The process generally takes place at ambient temperatures. Batch reactors are generally favored for lower flowrates (e.g., up to about 50,000 gpd), and usually use two tanks operating in parallel. Each tank can act as a flow equalizer, reactor, and settler, thus eliminating separate equipment for these steps. Continuous systems have a chemical feeder, flash mixer, flocculator, settling unit, filtration system (if used), and control system for feed regulation. Site-specific treatability tests are required to determine the optimum type and dosage of precipitation chemicals, necessary pretreatment steps, and post-treatment requirements for aqueous effluent and sludge residuals.

There are three types of precipitation chemicals:

- Metal hydroxides are formed by the addition of alkaline reagents (lime or sodium hydroxide). Precipitation is then initiated by adjusting pH to the optimum level for the particular metal ion. Maintaining pH levels within a relatively narrow optimum range is usually necessary to achieve adequate metal precipitation. Pretreatment with oxidizing or reducing chemicals (e.g., hydrogen peroxide, ferrous sulfate) may be necessary to precipitate some metals (e.g., iron, manganese, chromium) in their least soluble form. Natural organic matter can inhibit the formation of insoluble metal hydroxides by forming metal-organic complexes. Metal hydroxide precipitation is typically effective for arsenic, cadmium, chromium (+3), nickel, zinc, manganese, copper (+2), tin (+3), and iron (+3).
- Metal sulfides are formed by the addition of either soluble sulfides (e.g., hydrogen sulfide, sodium sulfide, or sodium bisulfide) insoluble sulfides (e.g., ferrous sulfide). Sodium sulfide and sodium bisulfide are most commonly used. Sulfur dioxide and sulfur metabisulfite have also been demonstrated for chromium reduction prior to precipitation. Metal sulfides have lower solubilities than metal hydroxides, and effective metal removal efficiencies can be achieved over a broader pH range. The method is mainly used to remove mercury and lead and may be used to remove arsenic, cadmium, chromium (+3,or +6), silver and others. Sulfide precipitation also can be used to treat filtered ground water after hydroxide precipitation.

## Alternative Techniques/Enhanced Methods

- **Metal carbonates** are formed by the addition of calcium carbonate or by adding carbon dioxide to metal hydroxides. Solubilities of metal carbonates are intermediate between the solubilities of metal hydroxides and metal sulfides. Insoluble metal carbonates are easily filtered from treated ground water. The method is particularly good for precipitating lead, cadmium, and antimony.
- Sodium xanthate has shown promise as a precipitation agent similar to sodium sulfide.

### Pre/Post-treatment

- Pretreatment to adjust pH is normally required to obtain the lowest precipitate solubility.
- Pretreatment may be necessary to oxidize iron or manganese compounds or reduce hexavalent chromium compounds into forms that can be readily precipitated.
- Depending on discharge requirements, the aqueous effluent may need pH adjustment and/or further polishing. Activated alumina or ion exchange media are regenerable treatment options for effluent polishing for metals. Activated carbon also may be used but spent carbon may require treatment and disposal as a hazardous waste.
- The sludge may require stabilization treatment by addition of lime/fly ash or portland cement to
  reduce permeability and the leachability of metals prior to disposal. In some cases, metals may
  be recovered from the residue for reuse, but this is generally not economical.

#### Selected References

Monopoli, A.V. 1993. Removing dissolved inorganics from industrial wastewater. *The National Environmental Journal:* 52-56.

U.S. Environmental Protection Agency. 1987. *Handbook on Treatment of Hazardous Waste Leachate.* EPA/600/8-87/006. Office of Research and Development, Cincinnati, OH. pp. 44-45.

U.S. Environmental Protection Agency. 1990. *CERCLA Site Discharges to POTWs Treatability Manual.* EPA/540/2-90/008. Office of Emergency and Remedial Response. PB91-921269/CCE. NTIS, Springfield, VA. pp. 11-23 to 11-36.

U.S. Navy. 1993. *Precipitation of Metals from Ground Water*. NEESA Document Number 20.2-051.6. Navy Energy and Environment Support Activity. Port Hueneme, CA. 11 pp.

## Appendix D6: Ion Exchange/Adsorption

Ion exchange removes metal contaminants from water by passing contaminated ground water through a granular solid or other porous material, usually an impregnated resin, that exchanges sorbed ions (e.g., H<sup>+</sup>, OH<sup>-</sup>, Na<sup>+</sup>, Li<sup>+</sup>, CO<sub>3</sub><sup>--</sup>) for contaminants dissolved in ground water. The ion exchange media are selected to have sorptive affinity for the ionic forms (cation or anion) of the contaminants being removed. The ion exchange media can therefore be either cationic, anionic, or a mixture of the two. Because ion exchange is a reversible process, resins can be regenerated by backwashing with a regeneration solution (e.g., brine; strong or weak acids or bases). Conventional ion exchange resins are generally too costly for large-scale ground-water treatment and are predominantly used for polishing of aqueous effluents after other treatment processes.

## Applicability

lon exchange is *applicable* to ionic contaminants such as dissolved metals or nitrates. Ion exchange is *not applicable* to non-ionic contaminants such as most organic compounds.

## **Contaminant Fate**

Contaminants are removed from ground water through sorption onto the exchange media. When most of the exchange sites of the media become filled, the exchange media are regenerated by backflushing with a suitable regeneration solution. The concentrated backflush solution must then be disposed of or stripped of its contaminants. Exchange resins can generally be regenerated many times and have a relatively long useful life.

## Design

Various resin types are available to tailor systems to discrete ionic mixes. For example, acid exchangers replace cations in water with hydrogen ions and base exchangers replace anions with hydroxide ions. Weak acid and base exchangers are selective for more easily removed ions while strong acid and base exchangers are less selective, removing most ions in the ground water. Generally, ease of cation and anion removal follows an affinity sequence specific to the ions in question. Synthetic resins are available with unique selectivity sequences. The wide variety of resins and other ion exchange media (e.g., activated alumina, biological materials) that are available make the selection of an appropriate exchange media a critical design step. Information on the applicability of specific resins may be obtained from resin manufacturers. In addition, ion exchange resins generally have an optimum pH range for effective metals removal. pH control may be required to achieve maximum removal efficiency from ground water.

A typical ion exchange installation has two fixed beds of resin. While one is in operation, the other is regenerated. Batch, fixed column, and continuous column bed designs can be used. Downflow column designs are generally preferred. Continuous column systems eliminate the need for backwashing but are not commonly used because of the complexity of the resin removal mechanics.

Flow rates up to 7,000 gpm have been reported for ion exchange systems. However, conventional ion exchange is generally cost-effective for ground-water treatment only at low flow rates or low contaminant concentrations. It is therefore primarily used as a polishing step following chemical precipitation or other treatment.

# Appendix D6: Ion Exchange/Adsorption (continued)

## Alternative Techniques/Enhanced Methods

- Activated alumina is an anionic exchange medium comprised of granulated, dehydrated aluminum hydroxide. Activated alumina is effective for removing fluoride, selenium, chromium (+6), and arsenic ions, which are exchanged for hydroxide ions. Adjustment of pH may be necessary to achieve optimal removal efficiency. The alumina is regenerated with a sodium hydroxide solution.
- Biological materials (e.g., algae, crop residues) have recently shown great promise as an innovative ion exchange media for metals. Biological media are significantly less costly than conventional resins (cents per pound vs. dollars per pound), and may become more commonly used for metals removal from ground water.
- Electrodialysis uses alternately placed cation and anion permeable membranes (made of ion exchange resin) and an electrical potential to separate or concentrate ionic species.
- Activated carbon adsorption can also be used to remove inorganics at low concentrations.
   However, activated carbon is not identified as a presumptive technology for removal of metals dissolved extracted ground water. Spent carbon used for metals removal can be difficult to regenerate and may require treatment and/or disposal as a hazardous waste.

### Pre/Post-treatment

- Pretreatment may be required to remove suspended solids at concentrations greater than about 25 mg/L or oil at concentrations greater than about 20 mg/L. Large organic molecules also can clog resin pores and may need to be removed.
- pH adjustment may be necessary to achieve optimal metals removal.
- The backwash regeneration solution must be treated to remove contaminants.
- Post-treatment of spent ion exchange media may be required to recover concentrated contaminants or management as a hazardous waste may be required.

### Selected References

Clifford, D., Subramonian, S., and Sorg, T.J., 1986. "Removing Dissolved Inorganic Contaminants from Water," *Environmental Science and Technology*, Vol. 20, No. 11.

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U.S. Environmental Protection Agency. 1990. *CERCLA Site Discharges to POTWs Treatability Manual.* EPA/540/2-90/008. Office of Emergency and Remedial Response. PB91-921269/CCE. NTIS. Springfield, VA. pp. 11-102 to 11-112.

# **Appendix D7: Electrochemical Methods**

Electrochemical processes use direct electrical current applied between two immersed electrodes to drive chemical oxidation-reduction reactions in an aqueous solution. Historically, electrochemical processes have been used to purify crude metals or to recover precious metals from aqueous solutions. Positively charged metal ions are attracted to the negatively charged electrode (the cathode), where they are reduced. The reduced metals typically form a metallic deposit on the cathode. Negatively charged ions are attracted to the positively charged electrode (the anode), where they are oxidized.

For contaminated ground water treatment, electrochemical cells have been used for the reduction (and subsequent precipitation) of hexavalent chromium to trivalent chromium. In this process, consumable iron electrodes are used to produce ferrous ions ( $Fe^{2+}$ ) at the anode and hydroxide ions ( $OH^-$ ) at the cathode. An oxidation-reduction reaction then occurs between the ferrous, chromium, and hydroxide ions to produce ferric hydroxide  $Fe(OH)_3$  and chromic hydroxide  $Cr(OH)_3$ , which subsequently precipitate from solution.

# Applicability

Electrochemical processes are *applicable* to dissolved metals. It is most commonly used in ground water treatment for the reduction and precipitation of hexavalent chromium. The process also may be applicable to removing other heavy metals including arsenic, cadmium, molybdenum, aluminum, zinc, and copper ions. Electrochemical processes have also been used for the oxidation of cyanide wastes (at concentrations up to 10 percent). Electrochemical processes are *not applicable* to organic compounds or asbestos.

# **Contaminant Fate**

Dissolved metals either deposit on the cathode or precipitate from solution. Precipitates form an inorganic sludge that must be treated and/or disposed of, typically in a landfill. Spent acid solution, which is used to periodically remove deposits formed on the electrodes, will also require proper treatment and disposal. Cyanide ions are hydrolyzed at the anode to produce ammonia, urea, and carbon dioxide.

# Design

Electrochemical reactors generally operate at ambient temperatures and neutral pHs. Both batch reactors and continuous flow reactors are commercially available. A typical electrochemical cell for hexavalent chromium reduction consists of a tank, consumable iron electrodes, and a direct current electrical supply system. An acid solution is used to periodically clean the iron electrodes, which need to be replaced when they are significantly consumed. Reactor residence times required for treatment depend on the contaminants present as well as the degree of mixing and current density. Reduction of hexavalent chromium generally requires short residence times (approximately 10 seconds), whereas treatment of cyanide compounds requires longer process times.

# Pre/Post-treatment

- Pretreatment may be necessary to remove suspended solids.
- Settling or clarification post-treatment may be necessary to remove the precipitated trivalent chromic and ferric hydroxides formed during hexavalent chromium electrochemical reduction.

## Pre/Post-treatment (continued)

 The sludge may require stabilization prior to disposal by addition of lime/fly ash or portland cement to reduce permeability and metal leachability. In some cases, metals may be recovered from the plated electrode or precipitated residue, but this is generally not economical for typical groundwater applications.

### Selected References

Englund, H.M. and L. F. Mafrica. 1987. *Treatment Technologies for Hazardous Waste*. APCA Reprint Series RS-13. Air Pollution Control Association, Pittsburgh, PA. pp. 43-44.

U.S. Environmental Protection Agency. 1990. A Compendium of Technologies Used in the Treatment of Hazardous Wastes. EPA/625/8-87/014. Office of Research and Development. PB91-90-274093. NTIS. Springfield, VA. p. 23.

# **Appendix D8: Aeration of Background Metals**

Aeration (contact with air) removes some metals from water by promoting chemical oxidation and the formation of insoluble hydroxides that precipitate from the water. Aeration for metals removal differs from air stripping in that precipitation rather than volatilization is the desired effect of the technology. *Applicability* 

Aeration techniques are useful for the removal of limited number of dissolved cations and soluble metal compounds. This method is well suited for the removal of background metals such as iron and manganese which is necessary as part of a selected remedy such as pretreatment to air stripping. Methods of aeration for metals include aeration tanks, aeration basins, or cascade aeration. Aeration methods are usually not sufficient as an independent technology for iron and manganese, but are utilized as a step in the treatment process. Often, the air-water contact in tank and cascade aeration is not enough to obtain high removal efficiencies. Spray basins are limited by area, wind, and ice particle formation (Nyer, 1985).

## **Contaminant Fate**

Dissolved metals are oxidized to insoluble hydroxides which precipitate from solution, and can then can be subsequently removed by flocculation, sedimentation, and/or filtration.

## Design

The three types of aeration systems:

- Aeration tanks bubble compressed air through a tank of water.
- Cascade aeration occurs when air is made by turbulent flow and agitation.
- Spray or aeration basins use an earthen or concrete basin with a piping grid and spray nozzles that spray the water into the air in very fine droplets.

Related methods include aeration used to remove volatile organic contaminants from water are considered to be a type of air stripping, as discussed in Section 2.1.1. The use of aeration to promote aerobic biological treatment processes is considered to be an element of biological treatment as discussed in Section 2.1.4.

# Pre/Post Treatment

- Aeration is often a pretreatment for other remediation technologies, such as air stripping, to remove certain metals.
- Aeration can be followed by other treatments such as flocculation, sedimentation, and/or filtration to remove oxidized metals.

# Selected References

Betz. 1962. Betz Handbook of Industrial Water Conditioning. Trevose, PA. pp.19-22

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