

Identification of Promising Remediation Technologies for Iodine in the UP-1 Operable Unit

September 2017

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Richland, Washington 99352

Executive Summary

Iodine-129 (^{129}I) generated at the U.S. Department of Energy (DOE) Hanford Site during plutonium production was released to the subsurface, resulting in several large, though dilute, plumes in the groundwater, including the plume in the 200-UP-1 operable unit (OU). Because ^{129}I is an uncommon contaminant, relevant remediation experience and scientific literature are limited, though work is under way to better understand the fate and transport of ^{129}I in the environment and the effectiveness of potential remediation technologies. The recent *UP-1 Evaluation Plan for Iodine*¹ and report on the *Conceptual Model of Iodine Behavior in the Subsurface at the Hanford Site*² provide information on the history of contamination in the 200-UP-1 OU, relevant controlling processes (biological and geochemical), risk, the conceptual site model, and potential remedial options, which provided a foundation for this study. In this study, available information was compiled and used to categorize potential remediation technologies, culminating in a recommendation of promising technologies for further evaluation. Approaches to improve the technical information about promising technologies are also recommended in this study so that a subsequent evaluation of potential remediation alternatives can assess these technologies.

The site conceptual model and the controlling features and processes set the context for assessing remediation technologies and the data needs for the technologies. Hydraulic features of the 70-meter-deep aquifer affect iodine species transport and groundwater plume behavior, as do reactive facies with which iodine may interact (redox minerals, organic material, carbonate, microorganisms) and water chemistry conditions (pH, dissolved organic matter). In addition, the presence of co-contaminants, such as nitrate, uranium, or other compounds that participate in redox reactions, and stable ^{127}I may influence iodine transformation reactions, incorporation into solid phases, and sorption. Chemical speciation of iodine is also important because the transport properties of each iodine species are different.

The 200-UP-1 OU ^{129}I plume conceptual model, which is still evolving as data gaps are filled, encompasses waste disposal history, source flux to groundwater, contaminant distribution, and fate and transport processes. The plume size appears to be in a generally stable to decreasing size, detached from the historical source areas, but with a relatively persistent core (at ^{129}I concentrations about 10 times greater than the drinking water standard) downgradient of the source areas. That is, the plume was created in the past and a continuing contaminant source from the vadose zone is unlikely.

The broad set of potentially applicable iodine remediation methods in the *UP-1 Evaluation Plan for Iodine* formed the basis for the review of potential remediation technologies. A key component of the review was input from remediation professionals during a half-day workshop, in which the attendees assessed the completeness of the ^{129}I remediation technology list, added new technologies or variants as appropriate, and discussed specifics (development status, information needs, and potential viability) of remediation technologies within the context of the 200-UP-1 OU. Technologies on this supplemented list were reviewed and categorized as in situ groundwater treatment, ex situ treatment, or vadose zone treatment.

¹ DOE. 2015. *UP-1 Evaluation Plan for Iodine*. DOE/RL-2015-69, Draft A, U.S. Department of Energy, Richland Operations Office, Richland, WA.

² Truex, MJ, BD Lee, CD Johnson, NP Qafoku, et al. 2016. *Conceptual Model of Iodine Behavior in the Subsurface at the Hanford Site*. PNNL-24709, Rev. 1, Pacific Northwest National Laboratory, Richland, WA.

The study authors then ranked technologies by near-term priority for additional information needs. These ranked tables of technologies were used to identify the following promising remediation technologies:

Monitored Natural Attenuation (MNA)	Microbial Facilitated Volatilization
In Situ Sequestration by Calcite (iodate)	Enhanced Pump-and-Treat
In Situ Sequestration by Apatite (iodate)	Ex Situ Aqueous Adsorption
In Situ Sequestration by Iron Oxides (iodate)	Ex Situ Ion Exchange
In Situ Sequestration by Organic Carbon	Microbial Enhanced Ex Situ Ion Exchange
In Situ Sequestration by Bioaccumulation	

A detailed description is provided for each of these promising remediation technologies, including discussion of data needs that will allow evaluation of the technologies as part of a remediation alternatives assessment.

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Acronyms and Abbreviations

ABEC	aqueous biphasic extraction chromatography
bgs	below ground surface
CFB	<i>Cytophaga-Flexibacter-Bacteriodes</i>
CSM	conceptual site model
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
FBBR	fluidized bed biofilm reactor
MNA	monitored natural attenuation
OSWER	Office of Solid Waste and Emergency Response
OU	operable unit
P&T	pump-and-treat
PNNL	Pacific Northwest National Laboratory
PRB	permeable reactive barrier
QA	quality assurance
ROD	Record of Decision
SAM	S-adenosyl methionine
SAMMS	self-assembled monolayers on mesoporous silica
SOM	soil organic matter
SVE	soil vapor extraction

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1.0 Introduction

Isotopes of iodine were generated during plutonium production within the nine production reactors at the U.S. Department of Energy (DOE) Hanford Site in southeastern Washington State. Reactor operations at the Hanford Site generated iodine-129 (^{129}I), an iodine isotope with a 15.7-million-year half-life, which was 1) stored in single-shell and double-shell tanks, 2) discharged to liquid disposal sites (e.g., cribs and trenches), 3) released to the atmosphere during fuel reprocessing operations, or 4) captured by off-gas absorbent devices (silver reactors) at chemical separations plants (PUREX, B-Plant, T-Plant, and REDOX). Releases of ^{129}I to the subsurface have resulted in several large, though dilute, plumes in the groundwater, including the plume in the 200-UP-1 operable unit (OU). There is also ^{129}I remaining in the vadose zone beneath disposal or leak locations. Because ^{129}I is an uncommon contaminant, relevant remediation experience and scientific literature are limited. The fate and transport of ^{129}I in the environment and potential remediation technologies are currently being studied.

This document summarizes available information about potential remediation technologies and the type of information that would be needed to determine whether these technologies could potentially be applied for the 200-UP-1 OU plume. This compilation of potential remediation technology information supports the efforts outlined in the *UP-1 Evaluation Plan for Iodine* (DOE 2015, Draft A). Background about the contamination in the 200-UP-1 OU and remedy documentation are provided below. Section 2 describes the controlling processes within the aquifer that will need to be considered to predict iodine fate and transport for natural attenuation and/or implementation of other remedies. Section 3 provides a synopsis of the current conceptual site model relevant to the 200-UP-1 OU iodine plume and evaluation of remediation approaches. A thorough review of available information was conducted to compile and categorize potential remediation technologies (Section 4), culminating in a recommendation of promising technologies for further evaluation. Section 5 describes the recommended approach to improve the technical information about promising technologies so that they can be evaluated as part of potential remediation alternatives. Section 6 describes the quality assurance (QA) program. This document provides a summary of literature information; any graphs or data presented here are “For Information Only.” A summary and conclusions from this remediation technology compilation effort are provided in Section 7.

1.1 Iodine and Co-contaminant Groundwater Contamination for the 200-UP-1 Operable Unit

For the 200-UP-1 OU, the current ^{129}I plume originated from U-Plant (216-U-1 and 216-U-2 cribs) and REDOX Plant waste sites (e.g., 216-S-1&2, 216-S-7, and 216-S-9), with the REDOX Plant waste sites being the primary sources (DOE 2014). Plume maps over a 20-year period beginning in 1993 (Figure 1) show that the 200-UP-1 ^{129}I plume (the primary ^{129}I plume in the 200 West Area) has an overall areal extent (as defined by the 1 pCi/L contour) that has oscillated, but declined. However, the plume core area, with ^{129}I concentrations greater than 10 pCi/L, has not declined. The overall plume extent is large and the plume thickness is up to tens of meters, although there is uncertainty in this estimate. Recent ^{129}I concentration results range from 1 pCi/L (i.e., at the maximum contaminant level) to 10+ pCi/L within the 200-UP-1 plume. The 90th percentile ^{129}I concentration is 3.5 pCi/L, meaning that 90% of the data for ^{129}I in the plume falls below this value (DOE 2012b). However, there are a few recently recorded groundwater concentrations that exceed 10 pCi/L (DOE 2017). Future plume behavior depends on fate and transport factors, including natural attenuation (Truex et al. 2016).



Figure 1. ^{129}I plume depictions over a 20-year period for the 200-UP-1 OU. Plume images were obtained using the Plume Status feature of the PHOENIX web-based data tool for the Hanford Site (<http://phoenix.pnnl.gov/apps/plumes/index.html>, accessed on 8/18/2015). Note that the set of wells used for plume contouring has varied over time.

Several co-contaminants are present within the ^{129}I plumes, including chromium, nitrate, technetium-99 (^{99}Tc), uranium, and tritium. Chromium, nitrate, uranium, and technetium may be present in forms that could interact with the same reactive sediment facies as ^{129}I . These co-contaminants will be addressed by a pump-and-treat (P&T) remediation approach for the 200-ZP-1 and 200-UP-1 OUs (EPA, Ecology, and DOE 2008, 2012). The pumping operations will also affect the ^{129}I plumes because of the altered hydraulic gradients and by displacement of ^{129}I that is extracted and re-injected.

1.2 200-UP-1 Record of Decision and Evaluation Plan for Iodine

A requirement in the Record of Decision (ROD) for the 200-UP-1 OU at the Hanford Site (EPA, Ecology, and DOE 2012) is to prepare a technology evaluation plan for remediation of (^{129}I contamination in the subsurface. Currently, groundwater in the 200-UP-1 OU is contaminated with carbon tetrachloride, uranium, nitrate, chromium (total and hexavalent), ^{129}I , ^{99}Tc , and tritium. The preferred alternative in the ROD specifies 35 years active remediation using groundwater P&T, monitored natural attenuation (MNA) for portions of the contaminated groundwater, and institutional controls until cleanup levels for unrestricted use are met (DOE 2012a). Hydraulic containment of groundwater is being performed while a remediation technology evaluation for ^{129}I is conducted to support a subsequent remedial decision for the ^{129}I plume.

The first step in the remedial technology evaluation was development of a plan for the evaluation (DOE 2015, Draft A). This plan includes information about potential ^{129}I remediation technologies/approaches. The plan also includes implementation steps for the evaluation. One of the initial steps, documented herein, is to compile and review information about potential remediation technologies and identify those that hold promise and those for which some additional information is needed to determine whether they are viable for application to the 200-UP-1 plume. This remediation technology information then feeds into the process of evaluating potential remedial alternatives.

To be able to assess remedy potential, it is important to understand the relevant processes and the site conceptual model, which are discussed in the following two sections.

2.0 Controlling Processes

Iodine behavior in the subsurface is described by Truex et al. (2016). This section summarizes this information to provide context for the assessment of remediation technologies. Iodine transport and groundwater plume behavior are affected by hydraulic features that drive groundwater movement in the subsurface. Groundwater information is provided in the annual report for the Hanford groundwater monitoring program (DOE 2014). Information on subsurface flow and transport parameters has also been compiled in a number of documents (e.g., DOE 2005, 2012a; Fayer and Keller 2007; Last et al. 2006, 2009). However, iodine transport is also potentially influenced by reactive facies related to reactions (e.g., few observed oxidation/reduction transformations, Truex et al. 2016) and minimal iodide and iodate sorption (Xu et al. 2015). The general facies of importance are redox minerals, organic material, carbonate, and microorganisms. Water chemistry components, such as dissolved organic matter and pH, influence transformation reactions and transport. In addition, co-contaminants such as nitrate or other compounds that participate in redox reactions may influence iodine transformation reactions and sorption. Both ^{129}I (15.7 million year half-life) and ^{127}I (stable, non-radioactive iodine) concentrations should be considered when evaluating plume behavior and reactive facies. ^{127}I and ^{129}I are found in Hanford Site groundwater at $^{127}\text{IO}_3^-/^{129}\text{IO}_3^-$ ratios ranging from 100 to 300, indicating much higher ^{127}I concentrations in the groundwater (Zhang et al. 2013). Because ^{127}I and ^{129}I behave the same chemically, the presence of ^{127}I needs to be considered in evaluating the fate, transport, and remediation of ^{129}I .

Several observations from previous and ongoing field and laboratory studies of the iodine plume provide context for evaluating controlling features and processes of the iodine plumes, in particular for the plume in the 200-UP-1 OU. First, analyses of groundwater samples from the 200 West Area (Zhang et al. 2013) showed a mix of iodine species present with, on average, about 70% of the iodine present as IO_3^- , about 26% as organo-iodine, and a small amount (about 4%) as I^- . In addition, sequential extraction of Hanford sediment samples (Xu et al. 2015) showed a significant fraction of iodine in sediment-associated phases in addition to aqueous and adsorbed phases. Recent vadose zone sediment extractions have shown that 50% to 80% of the iodine is associated with a solid phase, and is extractable with acetate (pH 5) or acetic acid (pH 2.3), and thus may be associated with carbonates or other phases, such as iron oxides (Truex et al. 2017; Szecsody et al. 2017). These previous studies have also observed iodate reduction and association of iodate with carbonate precipitates. Collectively, this information and the additional information reported herein demonstrate that iodine behavior in the subsurface is affected by transformations and sediment interactions. As shown in Figures 2 and 3, adsorption, transformations between species, associations with organic compounds, and precipitation are all important for iodine fate and transport. The processes shown in these figures are described in more detail by Truex et al. (2016).

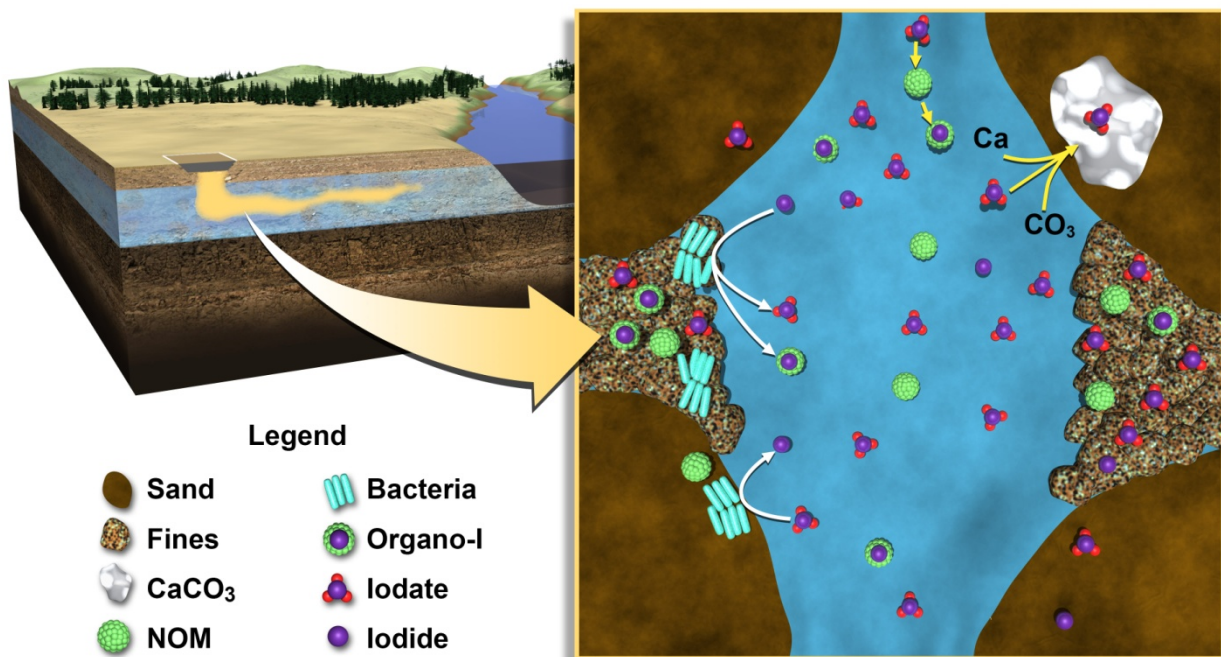


Figure 2. Conceptual overview of subsurface biogeochemical processes that affect the fate and transport of iodine. The figure does not distinguish between ^{129}I and ^{127}I because these processes are the same for both isotopes. The three primary aqueous iodine species are iodate (IO_3^-), organo-iodine, and iodide (I^-). Processes include biotic (bacteria) transformations between iodine species as shown, and potential transformations to other species, as illustrated in Figure 3. Iodate reduction may also occur abiotically (not shown) (e.g., by reactions with sediment-associated iron/manganese). Iodine species adsorb to sediment surfaces (e.g., on iron oxide deposits or phyllosilicates), with greater adsorption expected in fine-textured sediment zones (fines). Natural organic matter (NOM) may facilitate sorption and accumulation of iodine or, as a dissolved organic compound, may form mobile organo-iodine. Iodate may co-precipitate with calcium carbonate. (After Truex et al. 2016)

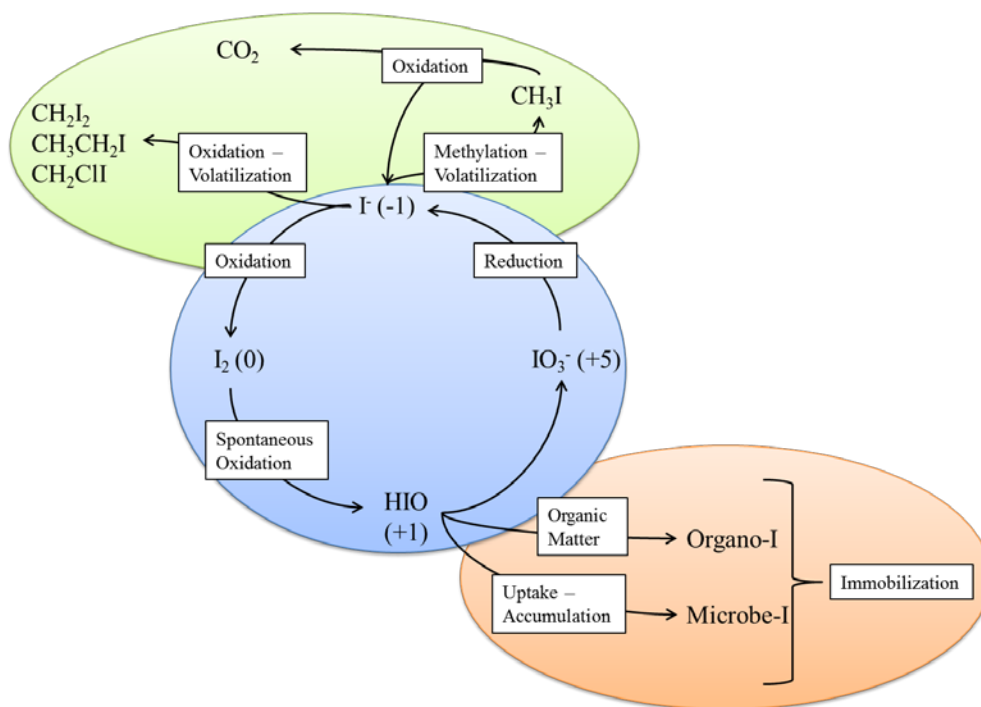


Figure 3. Biological transformations associated with iodine cycling in the environment. The blue ellipse represents predominantly aqueous-phase iodine species. The orange ellipse represents predominantly solid-phase species of iodine associated with organic compounds (organo-iodine) or accumulated in microbial biomass (Microbe-I). Some types of organo-iodine may also be mobile in the aqueous phase. The green ellipse represents predominantly gas-phase volatile organo-iodine compounds. Figure 2 provides context for some of these processes within the subsurface biogeochemical environment. (After Truex et al. 2016)

3.0 Conceptual Model

The conceptual model of the 200-UP-1 OU ^{129}I plume must consider several elements: waste disposal history, source flux to groundwater, contaminant distribution, and fate and transport processes. The information available for these elements is compiled in Truex et al. (2016). Because there are still data gaps that limit understanding and quantification of ^{129}I behavior in the subsurface, the conceptual model for the 200-UP-1 OU ^{129}I plume is still evolving.

The existing 200-UP-1 OU ^{129}I plume appears to be in a generally stable to declining condition, detached from the historical source areas, but with a relatively persistent core downgradient of the source areas where ^{129}I concentrations are about 10 times greater than the drinking water standard (Figure 1). This plume condition is consistent with recent vadose zone source investigations and groundwater data that indicate the plume was created in the past and a continuing contaminant source from the vadose zone is unlikely (Truex et al. 2016). Figure 4 shows a conceptual depiction of the 200-UP-1 OU ^{129}I plume and nominal dimensions for selected portions of the plume. This plume depiction provides a context for identifying targets for the remediation technology candidates discussed in Section 4.

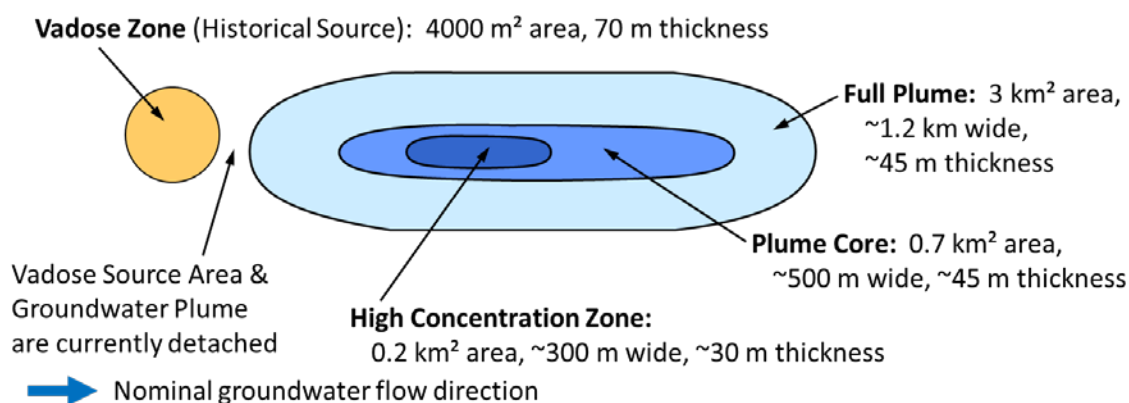


Figure 4. Conceptual depiction of the 200-UP-1 OU ^{129}I plume.

Based on samples of 200 West Area groundwater (including samples within the 200-UP-1 OU), iodine is present in the plume as a mix of iodide, iodate, and organo-iodine species. Plume behavior is impacted by differential transport of iodine species due to their different sorption characteristics. There may be transformation between iodine species occurring in the aquifer over time, as suggested by recent laboratory studies (Truex et al. 2016). Transformations occurring over time would primarily result in shifting the relative percentages of iodine species in the subsurface. These transformations would then affect the plume behavior because of differential transport of iodine species and the potential for some mechanisms to remove specific iodine species from transport. For example, co-precipitation of iodate with calcium carbonate is one potential loss mechanism. Transformations to produce more organo-iodine species would also create additional loss mechanisms through accumulation as functionally immobile organic deposits or through production of volatile organo-iodine (e.g., methyl-iodide) species (Figure 3). Microbial accumulation may also be a loss mechanism.

Data gaps associated with the conceptual model are identified in Truex et al. (2016). In summary, these data gaps fall into the following categories.

- Environmental data are needed to quantify the iodine species distribution throughout plumes and to characterize the organo-iodine species that are present.
- The mechanisms and field-relevant rates of transformation reactions need to be better understood. For instance, identifying mechanisms of observed redox transformation, quantifying microbial processes associated with transformations, and evaluating the fate of transformation products (e.g., the stability of iodate-calcite precipitates) are data gaps associated with transformation reactions.
- Improved quantitative estimates of transformation and sorption parameters for the observed iodine species are needed to support incorporation into fate and transport analyses.

4.0 Evaluation of Remediation Technologies

A broad set of potentially applicable iodine remediation methods were identified in the *UP-1 Evaluation Plan for Iodine* (DOE 2015, Draft A) based on a literature search and prior reports. That evaluation plan grouped potential remediation technologies into categories reflecting the location of the treatment, which related to the function of the treatment. The categories included ex situ treatment (for media extracted from the subsurface or secondary waste streams), surface source removal, control of contaminant flux through the vadose zone, and groundwater plume remediation. The evaluation plan provided a brief description of each technology, notes on technology maturity, and a qualitative categorization of technology cost (i.e., low, moderate, or high). The list of potential ^{129}I remediation technologies in the evaluation plan provided the starting point for reviewing, screening, and identifying promising remediation technologies for iodine in the 200-UP-1 OU that was performed in this current work.

To facilitate identification of promising remediation technologies, a three-step approach was taken. The first step involved obtaining input from remediation experts with broad expertise ranging from microbiology to geochemistry to waste processing to applied in situ remediation, and beyond. An afternoon workshop was convened with about 20 scientists and engineers participating. After describing the conceptual site model for the 200-UP-1 OU (Section 3) and the controlling geochemistry and microbiology processes (Section 2), the attendees went through the existing list of remediation technologies (from the evaluation plan [DOE 2015]) to provide comments. The intention was to 1) assess the completeness of the technology list for ^{129}I remediation, adding variants of list technologies or entirely new technologies not currently listed, and 2) discuss technology development status, information needs, and potential as a viable remediation technology within the context of the 200-UP-1 OU. The workshop was informative and achieved its aim of finding additional technologies (or technology variants) and shedding light on remediation technology potential for ^{129}I remediation. Some attendees were tasked with providing additional information and references regarding specific technologies.

The second step in the process of identifying promising remediation technologies involved reorganizing the remediation technology list, adding additional information, and prioritizing technologies with respect to research needs and potential usefulness. The potential remediation technologies were reorganized into three categories: in situ groundwater remediation, ex situ groundwater remediation, and vadose zone remediation. The technologies on these three lists were tabulated with a brief description, information about the technology development status, and input on the type of information that the technology would need to allow an initial evaluation of effectiveness, and a priority ranking. The development status was defined using the codes shown in Table 1, which ranged from a conceptual remediation technology to a remediation technology that has been demonstrated for ^{129}I . Multiple development status codes were allowed per technology. The notes on information needs to evaluate the technology were derived from discussion during the workshop and follow-up information provided by the participants. The final piece in this second step was for the authors of this study to go through each technology and determine a consensus ranking for the near-term priority of the technology (or long-term priority, in the case of vadose zone technologies). That is, the development status, potential effectiveness, and type of information requirements were considered to give a remediation technology a ranking of high (H), medium (M), low (L), or unranked (—) priority for near-term research needs. Unranked technologies were those that 1) are well established and do not need additional research or 2) have a low likelihood of applicability in the 200-UP-1 OU setting and for which no additional research is warranted.

The subsections below discuss the three groups of remediation technologies derived from this second step, and Section 4.4 discusses the final step of identifying promising technologies.

Table 1. Codes used to describe the development status of ^{129}I remediation technologies.

Code	Description of Technology Status
1	Demonstrated for iodine (one or more species) in the field
2	Demonstrated for another contaminant in the field
3	Demonstrated in the laboratory for iodine (one or more species)
4	Demonstrated for another contaminant in the laboratory
5	Literature (journal articles or technical report) is available showing a basis for the technology
6	Conceptual remediation technology supported by literature/paper study/modelling

4.1 In Situ Groundwater Remediation

In situ groundwater remediation technologies apply actions in the groundwater aquifer in the subsurface. Because iodine is not subject to destruction, these technologies primarily work by reduction of aqueous mobility (which in turn reduces the groundwater concentration), conversion to another phase, or capture/removal (or a combination of these). While the evaluation plan (DOE 2015) identified certain types of remediation, the outcome of the workshop was a range of potential remediation technology variants (Table 2). Specifically, there are eight sequestration technologies, six technologies for capture/removal (some including phase transition), and two technologies for changing the redox state of the iodine to facilitate sequestration or capture. Several of these technologies have been demonstrated in the field for iodine or other contaminants, others have been demonstrated in the laboratory, and some are conceptual or reported in the literature. Six of these technologies were ranked as high priority for near-term study and two as medium priority. Five technologies were considered questionable for the 200-UP-1 OU setting (e.g., the aquifer may be too deep for the technology to be practical) and were recommended to be considered for the “screened-out” list.

4.2 Ex Situ Groundwater Remediation

Ex situ technologies are not directly applicable to the 200-UP-1 groundwater, but may be required as part of another treatment technology (such as P&T or soil vapor extraction) or to treat secondary waste, including generating final waste forms. Many of the ex situ (aboveground) remediation technologies in Table 3 are well understood processes for other contaminants, with only a couple having been used specifically for iodine (in the nuclear power industry). A few of the technologies have been demonstrated at the laboratory scale, but not in the field. Three technologies were ranked high priority because of their applicability to aboveground treatment for P&T remediation. Some of the other technologies target secondary waste streams, so their priority should be re-evaluated as treatment train options are developed.

4.3 Vadose Zone Remediation

The vadose zone remediation technologies target a reduction in contaminant mass flux to the groundwater, which would cut off the source generating the groundwater plume for the 200-UP-1 OU.

Because data shows that the groundwater iodine plume is detached from the vadose zone source (Section 3), all of the vadose zone remediation technologies in Table 4 are of low priority in the near term. If, in the future, the vadose zone is determined to be a source of concern, then the long-term priority designation given in Table 4 will guide information needs.

Table 2. In situ groundwater remediation technologies.

Technology	Brief Description	Status ^(a)	Initial Evaluation Information Needs	Near-Term Priority
Monitored Natural Attenuation (MNA)	Natural processes reduce the mass or concentration of the contaminant plume.	2, 3, 4, 5	Quantify natural transformation, sorption, and sequestration processes specific to UP-1 conditions. Evaluate iodine species distribution across the plume.	H
In Situ Sequestration by Calcite (iodate)	Volumetric or PRB treatment with calcite-forming solution to induce iodate precipitation.	3	Quantify solubility of Ca-iodate precipitates in relation to Ca-carbonate precipitates. Evaluate mechanism to force carbonate precipitation in situ.	H
In Situ Sequestration by Apatite (iodate)	Volumetric or PRB treatment to incorporate iodate into apatite mineral(s).	2, 3, 4, 5	Quantify 1) conditions and rates for iodate incorporation into apatite and 2) the solubility of iodate-substituted apatite.	H
In Situ Sequestration by Bioaccumulation	Uptake and sequestration of iodine compounds by microbes.	5, 6	Assess literature and perform laboratory studies to identify and evaluate the performance and sequestration longevity of candidate microbes.	H
Microbial Facilitated Volatilization	Microbial iodine methylation + SVE capture of methyl iodide.	5, 6	Assess literature and ongoing laboratory results to identify and evaluate the method for iodine and co-contaminants.	H
Enhanced Pump-and-Treat	P&T with injection of compounds to increase iodine mobility, including a pH 9.3 carbonate solution to exchange iodate from solid phase carbonates and an aqueous reductant, sodium dithionite, to reduce iodate to iodide (which exhibits less sorption).	2, 6	Assess literature to identify candidate enhancement chemicals and geochemistry related to iodine mobility enhancement and the impact on other aquifer constituents. Quantify iodine mobility enhancement and impact on other constituents for promising chemicals. Conduct a modeling study to evaluate various enhanced P&T configurations.	H (design study)
In Situ Sequestration by Iron Oxides (iodate)	Volumetric treatment to adsorb or co-precipitate iodate with iron oxide compounds.	3, 4, 5, 6	Assess literature and evaluate geochemistry related to potential sequestration processes. Quantify 1) conditions and rates for iodate incorporation into iron oxide precipitates and 2) the solubility of precipitates incorporating iodate.	M

Technology	Brief Description	Status ^(a)	Initial Evaluation Information Needs	Near-Term Priority
In Situ Sequestration by Organic Carbon	Volumetric or PRB treatment to accumulate iodate or iodide into stable, low-solubility organic matter.	5, 6	Assess literature and evaluate biogeochemistry related to potential sequestration processes. Quantify 1) conditions and rates of iodate and/or iodide incorporation into soil organic matter and 2) the solubility of organic material incorporating iodine.	M
In Situ Sequestration by Alkaline Treatment	Use alkaline treatment followed by buffering to dissolve aluminosilicate to promote “armoring” compounds that coat/incorporate iodine and decrease long-term iodine mobility.	4	Assess literature and evaluate geochemistry related to potential sequestration processes. Quantify 1) conditions and rates related to incorporation/coating of iodine compounds during alkaline buffering/ cycling and 2) the resulting mobility reduction.	L
In Situ Sequestration by Metals (iodide)	Volumetric or PRB treatment to create Ag-, Hg-, or Cu-iodide compounds.	1, 3	Evaluate regulatory acceptability of introducing toxic metals into the subsurface.	L
In Situ Sequestration by Iron Sulfide	Volumetric treatment to precipitate iodine with iron sulfide compounds.	5, 6	Assess literature and evaluate geochemistry related to iodine redox transformations and potential sequestration processes. Quantify 1) conditions and rates for iodate incorporation into iron sulfide precipitates and 2) the solubility of precipitates incorporating iodate.	L
Zero Valent Iron	Nano- or micro-sized zero valent iron particles to promote hydrogen generation and redox conditions that facilitate related sequestration reactions.	2, 4, 6	Assess literature and evaluate biogeochemistry related to iodine redox transformations. Identify links to potential sequestration processes.	L
Microbial oxidation process	Microbial oxidation of iodide to promote cycling of iodine to forms suitable for sequestration or reduced mobility.	5, 6	Assess literature and ongoing laboratory results to identify and evaluate the method for iodine and co-contaminants.	L
Physical Groundwater Flow Barrier	Use of a physical barrier (e.g., grout curtain, freeze wall) for plume containment or to direct groundwater flow.	2	Assess literature and evaluate either moving the technology to the screened-out list or retaining it for the screening evaluation.	L
Air Sparging	Injection of air into the aquifer to facilitate mass transfer from aqueous to gas phases + SVE capture.	2, 6	Assess literature and evaluate either moving the technology to the screened-out list or retaining it for the screening evaluation.	L

Technology	Brief Description	Status ^(a)	Initial Evaluation Information Needs	Near-Term Priority
Acid Induced Volatilization	Acidify to pH 3 or lower to form iodine gas + SVE capture.	6	Assess literature and evaluate either moving the technology to the screened-out list or retaining it for the screening evaluation.	L
Vacuum Induced Volatilization	Simple vacuum to induce volatilization from groundwater + SVE capture.	2, 6	Assess literature and evaluate either moving the technology to the screened-out list or retaining it for the screening evaluation.	L
Electrokinetic remediation (enhanced)	Subsurface electrodes promote iron precipitation, an acid front, contaminant desorption, and ion migration.	2, 3, 4, 5	Method has been tested for other contaminants. Improvements may be possible and could be quantified through a modeling study.	L
Extraction Wells (P&T)	Groundwater and dissolved contamination are extracted via wells, with aboveground treatment of the water.	1	Retain for the screening evaluation.	—
Horizontal wells	Variant of standard vertical extraction wells.	2	Assess literature and evaluate either moving the technology to the screened-out list or retaining it for the screening evaluation.	—
Targeted P&T + MNA for lower concentrations	Combination of P&T and MNA.	1, 2	Retain for the screening evaluation.	—

(a) Refer to Table 1 for a description of the status codes.
PRB = permeable reactive barrier; SVE = soil vapor extraction

Table 3. Aboveground treatment technologies for aqueous-, gas-, and solid-phase media.

Technology	Brief Description	Status ^(a)	Initial Evaluation Information Needs	Near-Term Priority
Adsorption from water	Capture of iodine from water onto solid-phase sorbent media (e.g., activated carbon, silver-impregnated carbon, zeolite, layered double hydroxides, organoclay, argentite, aerogels, SAMMS, carbon nanotubes, photocatalytic adsorption).	2, 3, 4, 5	Assess literature and identify list of adsorbents; perform laboratory studies to evaluate performance with respect to specific iodine species.	H
Ion Exchange	Mass transfer process where ions from solid phase media (e.g., commercial or ABEC resins) are exchanged for ions in solution.	2, 3, 4, 5	Assess literature and identify list of ion exchange resins; perform laboratory studies to evaluate the performance of candidate resins with respect to specific iodine species.	H
Microbial Enhanced Ion Exchange	Microbial facilitated iodine reduction to facilitate/enhance ion exchange.	2, 4	Literature review is needed to evaluate performance for achieving conditions that facilitate ion exchange.	H
Gas Phase Adsorption	Capture of iodine from gas on solid phase adsorbents (e.g., activated carbon, macroreticular resins, silver-impregnated alumina, silver exchanged mordenite, silver-loaded zeolite, silver impregnated silica-gel, bismuth-based sorbents, or silver-functionalized silica aerogels).	1, 2, 3, 4, 5	Established method for gas phase removal of iodine. Assess literature and identify list of adsorbents; perform laboratory studies to evaluate performance with respect to specific iodine species.	M
Membrane Separation – Reverse osmosis	Selective transmittal of water across a membrane due to hydrostatic pressure.	2, 3, 4, 5	Assess literature to evaluate the performance of the method for iodine species and co-contaminants.	M to L
Membrane Separation – Electrodialysis	Separation of ions from water by applying an electric current across a membrane.	2, 3, 4, 5	Assess literature to evaluate the performance of the method for iodine species and co-contaminants.	M to L
Electrochemical Separation – Capacitive Deionization	Current applied across porous activated or aerogel carbon electrodes captures ions in the electrodes.	2, 3, 4, 5	Assess literature to evaluate the performance of the method for iodine species and co-contaminants.	M to L

Technology	Brief Description	Status ^(a)	Initial Evaluation Information Needs	Near-Term Priority
Electrochemical Separation – Electrochemically Switched Ion Exchange	A switched electrode potential is used to capture ions by adsorption on an electroactive film at the electrode.	2, 3, 4, 5	Assess literature to evaluate the performance of the method for iodine species and co-contaminants.	M to L
Electrochemical Separation – Electrolysis	Uses electrolysis to oxidize halides.	4, 5	Method has been shown for bromide; assessment is needed to evaluate the performance of the method for iodine and co-contaminants.	M to L
Co-precipitation and Coagulation	Aqueous precipitation of iodine with an Ag, Cu, Hg, or Pb compound.	2, 4, 5	Demonstrated in the lab as part of an analytical technique; assess literature for applicability to remediation.	L
Gas Phase Absorber (Scrubber)	Preferential partitioning of iodine from gas phase to a liquid phase (e.g., caustic, mercuric nitrate-nitric acid, hyperazeotropic nitric acid, fluorocarbon, polymethylsiloxane, molten hydroxide).	1, 2, 3, 4, 5	Established method for gas phase removal of iodine.	L
Soil Washing	Ex situ scrubbing of soils using water-based solution, possibly with surfactants/additives.	2, 4, 5	Limited application to UP-1. Assess literature and evaluate either moving the technology to the screened-out list or retaining it for the screening evaluation.	L
Immobilization/ Encapsulation and Solidification/ Stabilization, cementitious waste forms	Encapsulation of iodine in a solid monolith with requisite leaching characteristics; cast stone/cementitious encapsulation.	2, 3, 4, 5	Targets secondary waste from aboveground treatment. Assess literature to evaluate the performance of the method for iodine and co-contaminants.	L
Glass Waste Form	Vitrification of solid phase to a glass waste form.	2, 3, 4, 5	Targets secondary waste from aboveground treatment. Assess literature to evaluate the performance of the method for iodine and co-contaminants.	L
Adsorption/ Vitrification	Capture iodine from gas onto nanoporous alumina, precipitate with Ag, Cu, or Na ₄ SiO ₄ then vitrify the alumina/iodine + glass formers to encapsulate the iodine.	3, 5	Targets secondary waste from aboveground treatment. Assess literature to evaluate the performance of the method for iodine and co-contaminants.	L

Technology	Brief Description	Status ^(a)	Initial Evaluation Information Needs	Near-Term Priority
Low-Temperature Vitrification	Iodine is captured on an adsorbent and is subsequently sequestered in low-temperature sintering glasses (e.g., bismuth-phosphate-zinc oxide, lead-boron-zinc).	3, 5	Targets secondary waste from aboveground treatment. Assess literature to evaluate the performance of the method for iodine and co-contaminants.	L
Encapsulation in Tin	Fusing iodide sorbed on silver-loaded sorbents with tin in a hot-pressing process to produce a consolidated mass.	3, 5	Targets secondary waste from aboveground treatment. Assess literature to evaluate the performance of the method for iodine and co-contaminants.	L

(a) Refer to Table 1 for a description of the status codes.

ABEC = aqueous biphasic extraction chromatography; SAMMS = self-assembled monolayers on mesoporous silica

Table 4. Vadose zone source remediation technologies (long-term ranking only; near-term, all are low priority).

Technology	Brief Description	Status ^(a)	Initial Evaluation Information Needs	Long-Term Priority
In Situ Reactive Gas	Introduction of reactive gas (e.g., ammonia) into the vadose zone to promote iodine sequestration or mobility reduction.	4, 6	Assess literature and evaluate geochemistry related to potential reactive gas sequestration processes based on approaches for uranium and ⁹⁹ Tc. Quantify conditions and rates of sequestration for flux control.	H
Microbial Facilitated Volatilization in Vadose Zone	Stimulation of microbes to promote iodine methylation + SVE capture of methyl iodide.	5, 6	Assess literature and perform laboratory studies to evaluate viability of potential remediation approaches for vadose zone application.	H
Permeable Reactive Barrier for Infiltration Flux Control at Water Table	Injected reagents promote sequestration or mobility reduction at the vadose zone-water table interface.	6	Assess literature and evaluate viability of potential sequestration approaches for water table application. Conduct modeling study to quantify conditions and rates of sequestration needed for flux control.	M (design study)
Reactive Liquid Reagent for Vadose Zone Treatment	Introduction of liquid reactive reagents for sequestration or mobility reduction within the vadose zone.	6	Assess literature and evaluate either moving the technology to the screened-out list or retaining it for the screening evaluation.	L

Technology	Brief Description	Status ^(a)	Initial Evaluation Information Needs	Long-Term Priority
Reactive Solid-Phase Amendments for Vadose Zone Treatment	Delivery of solid phase amendments for sequestration or mobility reduction in the vadose zone.	2, 6	Assess literature and evaluate viability of potential sequestration approaches for vadose zone application. Quantify conditions and rates of sequestration for flux control.	L
Microbial Reactions for Vadose Zone Treatment	Stimulation of microbial growth for transformation reactions or mobility reduction in the vadose zone.	5, 6	Assess literature and evaluate viability of potential for vadose zone application.	L
Surface Infiltration Control Barrier	Engineered cover comprised of asphalt, clay, and/or geo-membrane materials installed at the ground surface.	2	Retain for screening.	—
Horizontal Physical Barrier	Horizontal barrier installed in the subsurface (e.g., jet grouting or permeation grouting) to reduce contaminant mobility.	5	Assess literature and evaluate either moving the technology to the screened-out list or retaining it for the screening evaluation.	L
Lateral Desiccation Zone	Dry air injected into permeable zone creates a desiccated layer that slows contaminant flux towards groundwater.	5	Retain for screening	—
Deep Soil Mixing for Vadose Zone Treatment	Mechanical mixing of soil with addition of amendments for reaction or encapsulation.	5	Consider moving to screened-out list.	L
In Situ Encapsulation for Vadose Zone Treatment	Introduction of grout or similar materials (e.g., molten wax) to encapsulate contamination in the vadose zone.	5	Assess literature and evaluate either moving the technology to the screened-out list or retaining it for the screening evaluation.	L
Soil Vapor Extraction	Extraction of soil gas and volatile contamination from relatively permeable sediments by vapor extraction wells under vacuum.	2, 6	Assess literature and evaluate either moving the technology to the screened-out list or retaining it for the screening evaluation.	L
Thermally Induced Volatilization	Heating vadose zone soil (e.g., by resistive heating or hot air injection) to enhance contaminant volatilization + SVE capture.	2, 6	Assess literature and evaluate either moving the technology to the screened-out list or retaining it for the screening evaluation.	L
In Situ Vitrification	Soil is melted to encapsulate contamination + off-gas capture.	2, 6	Consider moving to screened-out list.	L

Technology	Brief Description	Status ^(a)	Initial Evaluation Information Needs	Long-Term Priority
Pore Water Extraction from Vadose Zone	Extraction of soil moisture/water (via high vacuum, wicking, electrokinetics, etc.) from the vadose zone, bringing with it contaminant mass.	2, 4, 5	Assess literature and evaluate either moving the technology to the screened-out list or retaining it for the screening evaluation.	L
In Situ Soil Flushing	Liquid flush of contamination out of vadose zone to the groundwater for in situ treatment or extraction well capture.	5	Assess literature and evaluate either moving the technology to the screened-out list or retaining it for the screening evaluation.	M to L
Deep Excavation of Vadose Zone	Removal of soil from the vadose zone (multiple approaches, including open pit & dragline; multiple wall support options).	—	Consider moving to screened-out list.	L
(a) Refer to Table 1 for a description of the status codes.				

4.4 Identification of Promising Technologies

The final step in the evaluation of remediation technologies was to identify promising technologies for further study. The list of promising technologies (Table 5) is comprised of in situ remediation technologies (Table 2) ranked “high” or “medium” priority and ex situ remediation technologies (Table 3) ranked “high” priority, with one exception discussed below. Because vadose zone remediation technologies all have a low near-term priority, as discussed in Section 4.3, they were not relevant to this selection process.

Table 5. Promising remediation technologies.

Technology	Status ^(a) & Priority	Initial Evaluation Information Needs
Monitored Natural Attenuation (MNA)	2, 3, 4, 5 High	Quantify natural transformation, sorption, and sequestration processes specific to UP-1 conditions. Evaluate iodine species distribution across the plume.
In Situ Sequestration by Calcite (iodate)	3 High	Quantify solubility of Ca-iodate precipitates in relation to Ca-carbonate precipitates. Evaluate mechanism to force carbonate precipitation in situ.
In Situ Sequestration by Apatite (iodate)	2, 3, 4, 5 High	Quantify 1) conditions and rates for iodate incorporation into apatite and 2) the solubility of iodate-substituted apatite.
In Situ Sequestration by Iron Oxides (iodate)	3, 4, 5, 6 Medium	Assess literature and evaluate geochemistry related to potential sequestration processes. Quantify 1) conditions and rates for iodate incorporation into iron oxide precipitates and 2) the solubility of precipitates incorporating iodate.
In Situ Sequestration by Organic Carbon	5, 6 Medium	Assess literature and evaluate biogeochemistry related to potential sequestration processes. Quantify 1) conditions and rates of iodate and/or iodide incorporation into soil organic matter and 2) the solubility of organic material incorporating iodine.
In Situ Sequestration by Bioaccumulation	5, 6 High	Assess literature and perform laboratory studies to identify and evaluate the performance and sequestration longevity of candidate microbes.
Microbial Facilitated Volatilization	5, 6 High	Assess literature and ongoing laboratory results to identify and evaluate the method for iodine and co-contaminants.
Enhanced Pump-and-Treat	2, 6 High	Assess literature to identify candidate enhancement chemicals and geochemistry related to iodine mobility enhancement and the impact on other aquifer constituents. Quantify iodine mobility enhancement and impact on other constituents for promising chemicals. Conduct a modeling study to evaluate various enhanced P&T configurations.
Ex Situ Aqueous Adsorption	2, 3, 4, 5 High	Assess literature and identify list of adsorbents; perform laboratory studies to evaluate performance with respect to specific iodine species.
Ex Situ Ion Exchange	2, 3, 4, 5 High	Assess literature and identify list of ion exchange resins; perform laboratory studies to evaluate the performance of candidate resins with respect to specific iodine species.
Microbial Enhanced Ex Situ Ion Exchange	2, 4 High	Literature review is needed to evaluate performance for achieving conditions that facilitate ion exchange.

(a) Refer to Table 1 for a description of the status codes.

5.0 Path Forward for Development of Promising Technologies

This section provides a summary of supporting literature for each of the promising technologies identified in Section 4.4 and briefly describes a conceptual approach for further evaluation of the technologies based on focused laboratory experiments and/or up-scaled evaluation through numerical simulation. The documented approach for each technology represents the recommended path forward for providing a more definitive determination of the technology's efficacy and implementability under Hanford Site conditions.

5.1 Monitored Natural Attenuation

Monitored Natural Attenuation (MNA) is a remedy defined by the EPA Office of Solid Waste and Emergency Response (OSWER) in *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites* (OSWER Directive 9200.4-17P; EPA 1999). The OSWER MNA Directive (EPA 1999) applies to soils and groundwater and defines natural attenuation processes included in an MNA approach as follows:

The “natural attenuation processes” that are at work in such a remediation approach [MNA] include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These in situ processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants.

Although the OSWER MNA Directive provides the overall structure for application of MNA at a site, the EPA has published technical protocols that provide more specific details for the process of evaluating and implementing MNA. These protocols are the functional processes that sites must follow for MNA remedies. Technical protocols for MNA assessment are available for inorganic and radionuclide contaminants in groundwater (EPA 2007a, b, 2010) and recent guidance (*Use of Monitored Natural Attenuation for Inorganic Contaminants in Groundwater at Superfund Sites*) has updated and clarified the approach to MNA for inorganic and radionuclide contaminants (EPA 2015). These protocol and guidance provide a useful structure from which to develop a suitable conceptual model of the site, identify and quantify natural attenuation processes, and estimate contaminant fate and transport relative to meeting remedial action objectives.

The OSWER MNA Directive (EPA 1999) and the recent inorganic MNA guidance (EPA 2015) describe a progressive tiered approach to evaluating and implementing MNA. Initially, this information is useful to identify characterization objectives and associated data needs to enable MNA evaluation. Elements of site characterization include 1) hydrogeologic and contaminant distribution characterization, 2) determination of attenuation rates, 3) groundwater geochemistry characterization, 4) solid phase geochemical characterization, and 5) radionuclide considerations (EPA 2015). The recommended progression from characterization to evaluation of the suitability of MNA includes potential use of modeling analyses, but the protocol and guidance emphasize the need for collecting site-specific data to

evaluate attenuation and transport processes and provide information for model configuration (EPA 2015). MNA evaluation criteria use lines of evidence to defensibly determine whether MNA will meet remedial action objectives. Key elements focus on understanding of attenuation mechanisms. Categories of attenuation mechanisms for inorganic contaminants that need to be considered include 1) microbial degradation (direct and indirect), 2) chemical transformations/redox reactions, 3) sorption and precipitation processes, and 4) radioactive decay (EPA 2015).

Although MNA was included as a potential remedial alternative and evaluated in the 200-UP-1 OU feasibility study, additional information is needed to support re-evaluation of MNA in light of the updated conceptual site model (CSM) for the site. The updates to the CSM since the feasibility study include recognition that ^{129}I is present as multiple species in the groundwater and that there are transformation reactions and biogeochemical interactions that may lead to ^{129}I attenuation (Sections 2 and 3, Truex et al. 2016). This new information can now be used to initiate the progressive tiered process of evaluating MNA for ^{129}I . Initial activities include developing appropriate characterization objectives and aligning existing information and data gaps with these objectives. Laboratory experiments and associated updates to fate and transport modeling can then be used to provide the basis for evaluation of MNA.

5.2 In Situ Sequestration by Calcite

The interaction of iodine (I) with calcium carbonate minerals provides a possible mechanism for attenuation of iodine contamination in groundwater; this mechanism may have potential to contribute to the overall remedial approach under Hanford Site conditions. At first glance, the substitution of IO_3^- for CO_3^{2-} in calcite, or other calcium carbonate minerals, does not appear likely based on geometric grounds since lattice substitutions of like sized and like charged species occur most readily, and IO_3^- is different from CO_3^{2-} in both of these attributes. However, iodate has been found in calcite structures in natural settings, such as calcareous shells in marine settings (Lerouge et al. 2010) and in speleothems (Kuczumow et al. 2001; Wynn and Brocks 2014). Regarding naturally occurring Ca and I phases, multiple studies reference the mineral lauterite, $\text{Ca}(\text{IO}_3)_2$, (e.g., Lu et al. 2010; Zhang et al. 2013) as a naturally-occurring calcium-iodate phase that forms, for example, in the nitrate deposits of Chile (Ghose et al. 1978). The existence of this phase suggests that iodine association with calcite, especially as IO_3^- , is not unreasonable.

Previous testing (Claret et al. 2010; Kuczumow et al. 2001; Lerouge et al. 2010; Lu et al. 2010; Podder et al. 2015; Zhang et al. 2013) have also shown that iodine can be incorporated into the structure of CaCO_3 via substitution of IO_3^- for CO_3^{2-} (Lu et al. 2010; Podder et al. 2015). Research by Lu et al. (2010) found that iodate, but not iodide, could be incorporated into the structure of laboratory-grown calcite structures, and that increasing the amount of iodate in solution increased the I/Ca ratio in the calcite. Laboratory efforts aimed at determining the amount of iodine adsorbed to the surface of calcite and the amount that is incorporated into the structure were conducted by Podder et al. (2015). In these experiments, the researchers concluded that much of the iodate was likely adsorbed onto the surface, although some iodine was incorporated into the calcite structure.

Observations of iodine incorporation into calcite precipitates in groundwater samples taken from the Hanford Site, followed by laboratory testing to confirm the observations, determined that incorporation of iodine into the calcite structure is feasible and is already happening at the site (Zhang et al. 2013). The iodine associated with Hanford Site sediments was also evaluated in the study by Xu et al. (2015) and

2.9% to 39.4% of total iodine was reported incorporated into calcite. Sequential extraction experiments with sediments from the Hanford Site (Szecsody et al. 2017; Truex et al. 2017) have shown that the iodine released from the sediments is associated with the two sequential extraction steps intended to dissolve carbonates (sediments are first mixed with 1M Na-acetate [pH = 5] for 1 h to dissolve some carbonates, and then the sediments are mixed with acetic acid [pH = 2.3] for 5 days). The two carbonate extraction steps have indicated that most of the iodine (50% to 70%) is likely associated with or incorporated into carbonate minerals.

Other recent research efforts at PNNL have demonstrated a potential for iodate to become incorporated within the structure of calcite when present during precipitation. This co-precipitation offers a potentially significant remediation strategy to impede the transport of iodate. To further investigate this relationship, a series of batch experiments (Truex et al. 2016) were conducted to initiate calcite precipitation, using CaCl_2 and $(\text{NH}_4)_2\text{CO}_3$ solutions, in the presence of iodate under a variety of conditions. The variables that were manipulated included the concentration of the calcite-forming solutions (0.1M and 1M), presence of competing (and potentially charge balancing) co-precipitants likely to be encountered at the Hanford Site (e.g., Na^+ or CrO_4^-), concentrations of iodine and co-precipitants, time of iodine spike additions to determine whether incorporation or adsorption is taking place, and pH. Results demonstrated that iodate can be incorporated into the calcite structure, suggesting that calcite co-precipitation may be occurring at the Hanford Site. Significantly more IO_3^- was removed from solution when the IO_3^- was present during calcite precipitation compared to when IO_3^- was added to the experiment after the calcite had been precipitating for 1 to 2 days; this indicates that some of the IO_3^- is being incorporated into the calcite and not just adsorbed to the surface of the calcite. However, further experiments and modeling are needed to fully elucidate the mechanism of association.

To further assess the possibility for calcite-driven MNA, stability testing of the calcite precipitated in the presence of iodate is ongoing. It is currently unknown what effect incorporation of iodine will have on the stability of the calcite formed. Following the stability testing of calcite, the stability of the remaining calcium carbonate polymorphs, as well as the ability for these polymorphs (calcite, aragonite, vaterite, and amorphous calcium carbonate) to incorporate iodine, also needs to be evaluated.

Because there are many competing anions and cations present in Hanford Site groundwater, laboratory experiments evaluating the changes in iodate uptake and stability of the resulting calcium carbonates, combined with a computational study evaluating the energetics of iodate incorporation into calcite, versus other anions such as nitrate, sulfate, phosphate, or possibly even pertechnetate, could be of particular importance. For example, Mg is easily substituted for Ca in calcium carbonates and is present in the Hanford Site groundwater, but the effect this substitution may have on incorporation of iodine and/or the effect on stability of the mineral is currently unknown.

Additional informative tests, such as batch calcite, aragonite, vaterite, and amorphous calcium carbonate precipitation experiments using ^{129}I instead of ^{127}I and a wider range of iodine concentrations, as well as in the presence of different initial iodine species such as iodate, iodide, and organo-iodine, should be conducted. In addition, the effect of different sorbents, oxidants and reductants such as natural organic compounds of different types, Fe, Al and Mn oxides, phyllosilicates, etc., should also be evaluated. Experiments should be conducted to determine the effects of slow versus fast precipitation kinetics of calcium carbonate (i.e., the presence of sodium metasilicate may slow down precipitation of calcium carbonates and may therefore control the extent of iodate incorporation into calcium carbonate phases). Solid phase characterization, such as transmission electron microscopy, to confirm and quantify

incorporation of iodine (rather than just adsorption) is also needed to better inform the conceptual model and to determine the role that iodine incorporation may have on MNA under Hanford Site conditions.

5.3 In Situ Sequestration by Apatite

Implementation of an apatite permeable reactive barrier (PRB) technology for in situ sequestration of strontium-90 (^{90}Sr) has been previously demonstrated on the Hanford Site (Vermeul et al. 2014). Full-field-scale application of this technology as a remedial alternative addressing a groundwater contaminant plume beneath the Hanford 100-N Area provides some advantages to this technology over other less well-developed technologies, because currently available technical expertise and regulatory/stakeholder familiarity with the apatite technology can be leveraged.

Development of the apatite PRB concept began in the early 2000s. Initial efforts focused on development of an amendment formulation that would allow for in situ formation of apatite through injection of amendment solutions. The developed approach relies on injection of a two-part amendment solution, one containing a Ca-citrate complex and the other a Na-phosphate solution (Moore et al. 2004). This initial development effort was followed by a series of bench-scale laboratory studies (Szecsody et al. 2007, 2009) that demonstrated, using site-specific sediments and groundwater, that ^{90}Sr contamination in groundwater could be irreversibly sequestered through sorption and subsequent incorporation into the apatite structure. Results from these laboratory-scale experiments were used to design a series of pilot- and treatability-scale field experiments (Williams et al. 2008; Vermeul et al. 2010, 2014) that demonstrated the field-scale efficacy of the technology. Based on barrier performance assessment monitoring data generated by these field demonstrations, it was determined that the apatite PRB was meeting remedial objectives and thus the technology received support from the regulatory and stakeholder community for expansion of the barrier footprint in subsequent years (Lee et al. 2015).

Researchers have also evaluated apatite as an approach for sequestering uranium in situ (Szecsody et al. 2016). In this study, bench-scale laboratory experiments were conducted using sediments and groundwater from the Old Rifle Site in Rifle, Colorado, a former vanadium and uranium ore-processing facility located adjacent to the Colorado River. These studies were focused on evaluating the apatite technology under Rifle site conditions and using two different remedial design configurations (PRB and direct source treatment). Treatment-related uranium mobility change was evaluated by 1) comparing uranium leaching in treated and untreated sediments, 2) comparing uranium present in multiple surface phases for treated and untreated sediments using a series of six sequential extractions and 3) surface phase analysis of the phosphate mineral phases formed. Based on these measures, it was demonstrated that with a sufficient amount of phosphate amendment and apatite mineral formation, apatite can be used as a viable remediation strategy for source area treatment of uranium. It was also demonstrated that under the right conditions (e.g., high apatite loading and/or low uranium contaminant flux), emplacement of apatite to form a PRB may also be a viable remedial approach, although in many cases the amount of apatite loading required could be cost prohibitive.

Others have conducted laboratory studies to evaluate the use of apatite as an approach for sequestering radioactive iodine. Research has focused on methods to incorporate both the iodate anion (Campayo et al. 2011) into the apatite structure or iodide into lead-vanadate/phosphate structure (Guy et al. 2001). Although these studies did not focus on in situ formation of iodine-substituted apatite as a groundwater remediation approach, the results do indicate that there is potential for iodate to be

incorporated into the apatite structure when favorable conditions are present. Because the initial work on iodate substitution used a relatively high aqueous iodate to phosphate ratio (i.e., fairly high iodate concentration) and was conducted at a relatively high pH without the presence of other solution ions, additional bench-scale studies are needed to evaluate the efficiency of the technology under anticipated field conditions (i.e., lower iodate concentration, more neutral pH, sub-oxic conditions with Ca, Mg-carbonate groundwater). The initial work did demonstrate that iodate-substituted hydroxyapatite can occur under relatively low temperature conditions. Incorporation of iodate into the mineral structure, not just adsorption on the hydroxyapatite surface, was also confirmed by solid phase X-ray diffraction and nuclear magnetic resonance analysis (Campayo et al. 2011). In contrast, although iodide substitution can occur in lead vanadate/phosphate (i.e., $\text{Pb}_{10}(\text{VO}_4)_{4.8}(\text{PO}_4)_{1.2}\text{I}_2$) (Guy et al. 2001), the compounds used to form this precipitate would not occur in an in situ system (i.e., PbI_2), so this approach would not be practical as an in situ technology.

Additional bench-scale experiments are needed to support a quantitative assessment of the efficacy and implementability for treating iodine contaminated groundwater in the 200-UP-1 OU. Recent experiments show that biotic and abiotic iodate reduction can occur in sediments (Truex et al. 2016; Szecsody et al. 2017). The purpose of the additional experiments would be to a) evaluate iodate substitution under a range of relevant geochemical conditions, and b) maximize iodate incorporation mass and rate under Hanford groundwater relevant geochemical conditions. The first series of experiments would include a) iodate substitution fraction under a range of iodate/phosphate/calcium conditions (i.e., varying iodate concentration), b) varying pH conditions, and c) an evaluation of stability and fraction incorporation of the iodate-substituted apatite. The fraction of iodate substitution would be determined by a) sequential ion exchange then acid dissolution of the precipitate and elemental analysis (I, P, Ca, other metals), and b) electron microprobe analysis to evaluate the crystallinity, morphology, and iodate distribution in the precipitate. Experiments needed to maximize the incorporation mass and rate of iodate substitution in Hanford groundwater would include a) varying Ca, PO_4 , and F (keeping iodate constant at a relevant field-scale concentration), b) varying pH and oxidation/reduction potential (i.e., dissolved oxygen), and c) varying phosphate technology (i.e., Ca-citrate- PO_4 or Na-polyphosphate). All experiments would be conducted using Hanford groundwater and Hanford subsurface sediments.

If preliminary batch iodate substitution experiments were successful, 1-D column experiments would then be needed to evaluate the injection of aqueous reactants into Hanford sediment and the efficiency of iodate substitution. While previous studies show iodate sorption is low (and varied) in Hanford sediments (i.e., K_d of 0.8 to 7.6 L/kg) (Xu et al. 2015), injection of Ca-citrate-phosphate or Na-polyphosphate reagents may act to mobilize some iodate. The use of the phosphate injection technology would need to be evaluated as both a source area treatment (i.e., phosphate injection to treat iodate in the injection area) and a PRB. A series of 1-D column experiments would be conducted to evaluate the effectiveness of direct treatment of contaminated sediments and the potential for longer-term treatment of iodate being advected (i.e., from upgradient) into an apatite-laden sediment.

5.4 In Situ Sequestration by Iron Oxides

The sorption or co-precipitation of iodine with iron oxides minerals could provide possible mechanisms for immobilization of iodine in contaminated groundwater. Iron oxides play an important role in sorption of anionic species in natural environments as a result of high zero points of charge and high surface area (Wang and Anderko 2001; Nagata and Fukushima 2010; Li et al. 2016). For iodine, previous studies (Ticknor and Cho 1990; Yu et al. 1996; Dai et al. 2004, 2009; Nagata et al. 2009, 2010) have shown that iodine can be removed from groundwater or pore water through adsorption on iron oxides. For example, Yu et al. (1996) found that iodate can be removed from solution quickly by ferrihydrite. Ticknor and Cho (1990) reported adsorption of iodate on hematite and goethite in diluted synthetic groundwater. Similarly, in near-neutral conditions, Couture and Seitz (1983) reported iodate and iodide sorption by hematite (Fe_3O_4). Dai et al. (2004, 2009) found that the amount of iodate adsorbed in soils was greatly dependent on the soil iron oxide content. Through column experiments, Hakimi (1996) showed that the soil with positively charged goethite at pH 4.5-6 was able to remove 97% of influent iodate. These findings indicate that sorption or co-precipitation of iodine with iron oxides could be a potentially effective iodine sequestration method to remediate the 200-UP-1 OU iodine groundwater plume.

Bench-scale experiments are needed to support a quantitative assessment of the efficacy and implementability of iron-oxide-based geochemical sequestration of iodine as a remediation approach. The bench-scale testing would primarily be intended to quantify sequestration efficiency (i.e., decrease in aqueous iodine concentration) and longevity of precipitated or immobilized phases containing iodine. Additionally, information regarding implementability with respect to emplacement on a large scale and advection in the subsurface and potential issues, such as interferences from co-contaminants or altering mobility of co-contaminants or broader system implications (e.g., downgradient effects or impact on P&T operations), would be important outcomes of the testing.

Bench-scale experiments would cover a range of materials and conditions to determine the most promising options and to address the abovementioned information needs. Multiple iron oxide minerals (e.g., 2-line ferrihydrite, magnetite, hematite, goethite) should be evaluated under a range of pH conditions and iodine concentrations. Laboratory synthesis of iron oxides of controlled particle sizes could be of particular importance in assessing the effects of iron oxide particle sizes on iodine adsorption or co-precipitation because adsorption capacity of iron oxide is proportional to its surface area. Tests would evaluate iodine sequestration when an iron-mineral-forming solution is added to an artificial groundwater containing iodate or iodide. The in-place formation of iron mineral precipitates would be evaluated both in the initial presence of iodate or iodide and with the iodine species added after iron mineral precipitate formation. Additional tests would examine iron-mineral-forming solution and iodine sequestration in the presence of sediment from the 200-UP-1 OU.

5.5 In Situ Sequestration by Organic Carbon

Soil organic matter (SOM) has been shown to be the primary control on iodine sorption in shallow soils (Assemi and Erten 1994; Bird and Schwartz 1997; Emerson et al. 2014; Fukui et al. 1996; Kaplan 2003; Neal and Truesdale 1976; Sheppard and Thibault 1991; Whitehead 1974; Yoshida et al. 1992; Yu et al. 1996). Approximately 90% of the total iodine in 26 soils and sediments with varying SOM content tested was shown to be present as organic iodine, while inorganic species became important in low SOM

sediments (Hu et al. 2009). In addition, soil redox has been shown to affect adsorption of iodine on soils. Oxic sediments with high SOM showed greater sorption than anoxic high SOM sediments (Ashworth and Shaw 2006; Ashworth et al. 2003; Maillant et al. 2007; Sheppard and Hawkins 1995; Whitehead 1974). Iodine has also been shown to be released from anoxic sediments, where iodate was the dominant form under non-flooded oxic conditions, while iodide was dominant under anoxic flooded conditions (Yuita 1992). Laboratory column studies using Savannah River Site sediments under oxidizing and reducing conditions showed lower K_d values when either iodide or iodate was added to sediments tested in reducing conditions (Emerson et al. 2014). These studies indicate that the oxic conditions at Hanford may allow increased adsorption of ^{129}I , if natural organic matter, such as humic and fulvic acid, were used as a remedial alternative.

Bench-scale experiments are needed to support a quantitative assessment of the efficacy and implementability of sequestration of iodine by organic carbon as a remediation approach. The bench-scale testing would primarily be intended to quantify sequestration efficiency (i.e., decrease in aqueous iodine concentration) and longevity of precipitated or immobilized phases containing iodine. Additionally, information regarding implementability with respect to emplacement on a large scale and advection in the subsurface and potential issues, such as interferences from co-contaminants or altering mobility of co-contaminants or broader system implications (e.g., downgradient effects or impact on P&T operations), would be important outcomes of the testing.

Bench-scale tests would assess the effects of candidate forms of organic carbon (e.g., chitin, lignin, humic acid, fulvic acid) on sequestration of iodate and iodide. A matrix of treatments including different concentrations of iodate, iodide, and candidate organic carbon sorbents under sorption and then desorption conditions would provide screening information to assess whether interactions would provide suitable mitigation of iodine migration.

5.6 In Situ Sequestration by Bioaccumulation

Iodine is an element that accumulates in biological material, including vertebrates, algae, coral, sponges, lobworms, and shellfish. Accumulation of iodine is significant from a health perspective because radioiodine concentrates in the thyroid gland in mammals. Most studies of iodine accumulation have been performed on thyroid tissue and in brown algae. More recently, iodine accumulation by bacteria, as well as other phototrophs, has been studied.

Laminaria digitata is a brown algae (kelp) that has been shown to accumulate iodine to levels ranging from 0.4% to 4.7% of the organism's dry weight, depending on the stage of growth (Küpper et al. 1998). This yields an accumulation of 30,000 times the iodine levels found in seawater (Colin et al. 2003; Küpper et al. 1998). X-ray absorption spectroscopy studies have shown that the accumulated form of iodine in *L. digitata* is iodide and that the purpose of iodide in this organism is to act as an inorganic antioxidant (Küpper et al. 2008). In this function, iodide scavenges reactive oxygen species, leading to efflux of the iodide into the external environment in the form of iodide and volatile iodocarbons. Iodine uptake and formation of iodo-organic compounds has been shown to be catalyzed by vanadium-dependent haloperoxidases, specifically iodoperoxidases (Colin et al. 2003; La Barre et al. 2010). These enzymes oxidize iodide to iodine (I_2), which spontaneously oxidizes to hypoiodous acid (HIO) and is then taken up into the cell, where it spontaneously reverts to iodide and can be associated with cellular material (Verhaeghe et al. 2008).

Accumulation of iodine in other algal species and diatoms has also been demonstrated (Manley 2009; Osterc and Stibilj 2012; Shimura et al. 2012; Thorenz et al. 2014; van Bergeijk et al. 2013). Regardless of the species, uptake appears to occur through the mechanism of a haloperoxidase, with or without hydrogen peroxide.

Until recently, only a few instances of bacterial accumulation of iodine could be found. More recently, a number of aerobic bacteria have been found that are able to accumulate iodine (Amachi et al. 2005a, b; Fournier et al. 2014; Li et al. 2011; MacLean et al. 2004). Similar uptake of iodine has not been demonstrated in anaerobic bacteria, indicating that iodide uptake in bacteria may occur through oxidative processes. A vanadium iodoperoxidase from *Zobella galactanivorans* has been demonstrated (Fournier et al. 2014). Amachi et al. (2005a) demonstrated iodine uptake in a number of bacteria common to marine and terrestrial environments. One bacterium, *Arenibacter troitsensis* strain C-21, was able to accumulate 80% of a 0.1- μ M iodide solution. Uptake by this bacterium appeared to be catalyzed by hydrogen peroxide produced by a glucose oxidase enzyme (Amachi et al. 2007a); a proposed haloperoxidase enzyme then oxidizes the iodide using hydrogen peroxide as the oxidant, yielding iodine or hypiodous acid, which then diffuses into the cell. The two species of bacteria discussed in this paragraph are of particular interest because they are both members of the family *Flavobacteriaceae*, which have been found in groundwater at Hanford. Iodine accumulation by bacteria is more pertinent to the subsurface of Hanford, where bacteria are the dominant organism that may possess this ability.

For bioaccumulation to be feasible for application to the 200-UP-1 or other iodine plumes in the Hanford Site Central Plateau, methods of emplacing and stimulating microbes would be required. While adsorption to the surface of microbes can take place, typically uptake into bacteria requires conversion of ionic species that can be transported across the bacterial cell wall and then, in the cell, be converted back into iodine that would associate with cellular material. Some type of reactive zone would need to be established where indigenous microbial communities are stimulated, or exogenous bacteria are added to intercept the ^{129}I plume. Experiments would be required to determine the effect of bacterial cell density on accumulation, followed by experiments in Hanford sediments using columns experiments to look at accumulation under field-relevant conditions.

Determining the feasibility of this approach would require running experiments to quantify adsorption or uptake of iodine during biotransformation. While iodate, organo-iodine, and iodide are present in the groundwater, hypiodous acid, which is a short-lived intermediate, is the reactive form that usually leads to uptake into bacteria. Experiments performed to date indicate there may be effects of bacterial cell density, as well as activity of the bacteria present. Experiments using ^{125}I would facilitate quantifying uptake and accumulation by bacterial cells. These experiments should include different cell densities, with the activity of ^{125}I determined in the media, as well as in the cell pellet from the experiments. Initial experiments can focus on use of bacteria with known iodine transformation abilities, and then similar experiments could be conducted with Hanford communities. Once iodine uptake is better understood, additional experiments can be designed and conducted to determine the short- and long-term stability of the accumulated iodine.

5.7 Microbial Facilitated Volatilization

One aspect of iodine cycling that has not been studied at the Hanford Site is volatilization of iodine, which could potentially allow for recovery of volatilized ^{129}I using technologies such as soil vapor extraction. This technology could also be applicable to the current P&T system, where fluidized bed biofilm reactors (FBBRs) are being used for nitrate removal from Hanford groundwater. Volatilization of organo-iodine species in the FBBR would allow for capture on activated carbon, which could be regenerated or disposed.

Methyl iodide is a volatile iodine compound that plays a large role in carrying iodine from terrestrial and marine environments to the atmosphere. Many examples of iodine volatilization come from looking at the activity of algae and microalgae in oceans and other freshwater bodies of water (Baker et al. 2001; Bravo-Linares et al. 2010; Hepach et al. 2016; Huang et al. 2010, Hughes et al. 2011; Karlsson et al. 2008; La Barre et al. 2010; Manley 2002; Ohsawa et al. 2001; Osterc and Stibilj 2012; Smythe-Wright et al. 2006; Stemmler et al. 2014, Thorenz et al. 2014; Toda and Itoh 2011). Likewise, some terrestrial environments harbor bacteria that catalyze methylation of iodide, yielding volatile iodine species (Amachi et al. 2001, 2003). As mentioned previously, organic iodine compounds are commonly produced during the oxidation of iodide to iodine, while in other bacteria, iodide is directly methylated by the enzymatic activity of microbes. During oxidation of iodide to iodine (I_2), a range of organic compounds are produced, whereas direct methylation produces methyl iodide. Once in the atmosphere, methyl iodide is broken down by sunlight and the iodine produced is deposited back to terrestrial or marine environments with precipitation. While there is potential for volatilization of iodine in the subsurface, photolysis would not be expected.

In-depth analysis of bacterial involvement in volatilization of iodine from soil was part of a study looking at cycling of iodine in rice paddy soil (Muramatsu et al. 1996). Likewise, volatile iodine production was noted in soil, seawater, and bacterial cell suspensions (Amachi et al. 2000). Analysis of volatile fractions recovered in silver mesh or granular activated carbon indicated that volatile species were primarily organo-iodine, rather than volatile I_2 .

Involvement of soil bacteria in the volatilization of iodine was further supported in a study comparing iodine emissions from rice paddy, upland field, forest, and wetland soil (Amachi et al. 2003). This microbial catalysis of volatile iodine species was further supported when iodine emissions ceased after soils were autoclaved or when antibiotics were added to inhibit bacterial activity. Interestingly, iodine emission was not affected when fungal inhibitors were added, showing the prevalence of bacteria in iodine volatilization from soils. Molecular characterization of bacteria isolated from the soil showed that iodine-volatilizing bacteria are widespread and not confined to a specific group of bacteria. Bacteria were distributed in Proteobacteria (α , β , and γ subdivisions), *Cytophaga-Flexibacter-Bacteriodes* (CFB) Group, and high G+C Gram-positive bacteria. CH_3I was the primary volatile iodine species found during these studies.

A similar study was performed using samples of seawater to determine whether bacteria were involved in volatilization of iodine in marine environments (Amachi et al. 2004). Similar groups of bacteria, α - and γ -Proteobacteria, and the CFB group were isolated and shown to volatilize iodide to CH_3I . Experiments also showed that iodate was not converted to CH_3I . When samples were autoclaved, filtered to remove bacteria, or antibiotics were added, little volatilization of iodide was shown. One of the

bacteria isolated during these experiments was able to volatilize up to 2% of the total iodine added to the growth medium to CH₃I.

Bacteria isolated from brackish water were shown to methylate a range of halides, including iodide (Fujimori et al. 2012). Five genetically distinct species belonging to the genera *Erythrobacter* or *Pseudomonas* were able to produce CH₃I when grown in the presence of iodide. These bacteria represent species of α - and γ -Proteobacteria. Analysis of the headspace of the vials showed primarily CH₃I and not other iodinated volatiles.

Recent research has shown that a wide variety of marine and terrestrial bacteria also volatilize iodine through the methylation of iodide (Amachi et al. 2001). Six out of ten terrestrial bacteria tested were shown to methylate iodide, while seven out of ten marine bacteria were shown to methylate iodide. In these same studies, anaerobic bacteria (*Clostridia* and methanogens) did not appear to methylate iodide. The cell extract from a *Rhizobium* species was shown to methylate iodide when S-adenosyl methionine (SAM) was used as the methyl donor, indicating that bacteria may use a mechanism similar to that used by phototrophs. Preliminary studies with *Shewanella oneidensis* MR1, a bacterium capable of radionuclide transformation, indicate that iodomethane may be formed during the reduction of iodate (Szecsody et al. 2017).

Along with CH₃I, a number of other volatile organo-iodine compounds can be formed during oxidation of iodide. Two bacterial species isolated from marine samples and which are closely related to *Roseovarius tolerans* were able to produce CH₂I₂ and CH₂CI from constituents in the growth medium (Fuse et al. 2003). Molecular iodine was also a product of iodide oxidation by these bacteria. Bacteria that produced the volatile organic compounds were grown in media containing yeast extract and peptone.

Volatilization of iodine has been shown to be linked to iodide oxidation, so this process may occur in Hanford groundwater. Formation of volatile organo-iodine species during the iodide oxidation process should be tested. Experiments would use groundwater from the 200-UP-1 ¹²⁹I plume to understand formation of volatile compounds under natural cycling conditions and biostimulation (i.e., addition of carbon source) conditions. Experiments should also be performed in the presence of Ringold Formation sediments, which would allow determination of the effects of mineral phases on the process. These experiments would provide rates of formation for volatile organo-iodine species, as well as rates of changes in inorganic speciation.

5.8 Enhanced Pump-and-Treat

Enhanced P&T is an extension of the standard P&T approach, whereby remedial amendments are added to injected water or otherwise directly injected into a groundwater plume to increase mobility of target contaminants, which here consists of iodine (primarily in the form of iodate and organo-iodine as discussed in Section 2). If contaminant desorption/mobility can be increased and the groundwater extraction system is configured to capture the mobilized contaminant mass, then P&T efficiency and overall effectiveness can be enhanced.

There are many factors that influence the speciation and transport properties of iodine, including geochemical reactions (e.g., oxidation/reduction transformations) and physical interactions (e.g., sorption). Although iodine is generally considered a relatively mobile radionuclide, predominantly as aqueous iodate with a smaller fraction as aqueous iodide, previous studies have shown that a significant

fraction of the iodine mass can be strongly bound to sediments. Xu et al. (2015) performed sequential extractions on Hanford sediment samples and showed that substantial fractions of sediment-associated iodine, with the majority associated with sediment organic carbon and calcite, iron oxides, or other mineral phases. Enhanced mobility of aqueous species, as well as these more strongly bound fractions, would be the target of an enhanced P&T system.

5.8.1 Reductant Solution Addition (Sodium Dithionite)

Recent laboratory experiments (Xu et al. 2015; Truex et al. 2017; Szecsody et al. 2017) have shown that iodate sorption is about 4 times greater than iodide sorption. Laboratory experiments injecting iodate and iodide into Hanford 200 Area water-saturated sediments have shown that when iodate is reduced to iodide, nearly all iodine mass is advected out of the sediment within a few pore volumes. Sodium dithionite is well established to dissolve and reduce some ferric oxides in Hanford sediments (Szecsody et al. 2004), so if some iodine mass is associated with iron oxides, this will also be mobilized. Therefore, one minimal enhanced P&T option is to inject a low concentration of an aqueous reductant, such as sodium dithionite or a carbon source, to stimulate microbial iron reduction, into the aquifer to form reducing conditions. This option would need to be investigated to evaluate potential side effects (such as changing the mobility of other co-located contaminants). Extensive studies of chemical reduction of 100-D Area Hanford sediments (Szecsody et al. 2005a, b) showed that Fe, Mn, and As were more mobile in reducing environments (although other contaminants of concern were not investigated). Uranium, technetium, and chromate mobility are all expected to decrease in a reducing environment.

5.8.2 Carbonate Solution Addition

Geochemical manipulation of the subsurface to selectively dissolve some sediment surface phases that may have incorporated iodate (i.e., carbonates) could also be investigated. Methods have been developed based on sequential extraction techniques, for determining the fraction of solid-phase metals and radionuclides in sediments (Gleyzes et al. 2002; Lerner et al. 2006; Kohler et al. 2004). These methodologies use sequential extractions to partition the adsorbed species into four operationally defined geochemical fractions: 1) exchangeable, 2) carbonate associated, 3) iron- and manganese-oxide associated, and 4) the residual fraction comprised of organic carbon and primary/secondary minerals containing metals within the crystalline lattice structure. More specifically, extraction of iodate from carbonates could involve a) carbonate exchange (i.e., injection of a high- CO_3 solution to increase the rate of carbonate dissolution/precipitation, freeing up some iodate) or b) net carbonate dissolution by injecting acidic pore water.

The treatment of uranium co-precipitated in carbonates, and the ability to extract this uranium, has been demonstrated (Kohler et al. 2004). So, this approach could potentially be applied for iodate-substituted carbonate. This involves using a high concentration carbonate solution that would be injected into the aquifer. This solution is typically kept in contact with uranium-laden sediments for 1000 h, and has been found to extract as much uranium from the uranium-substituted carbonate as more aggressive acidic solutions, without mobilizing significant concentrations of other metals that occur by acidifying the groundwater (Kohler et al. 2004). Although acidifying injection water is not recommended, laboratory experiments can be conducted comparing iodine species mobility in a) groundwater (i.e., no treatment), b) high pH carbonate water (i.e., carbonate exchange treatment), c) pH 5.0 acetate buffered solution (i.e., extraction solution designed to dissolve a portion of carbonates), d) pH 2.3 acetic acid (i.e., extraction

solution designed to dissolve all carbonates, and e) 8M nitric acid (i.e., extraction solution designed to dissolve phosphates, silicates, and oxides, that may also contain iodine species).

In the characterization of vadose zone cores (Truex et al. 2017; Szecsody et al. 2017) and aquifer cores (Lee et al. 2017), a series of six sequential extractions (including the four solutions indicated above) were conducted to quantify the iodine mass that was extracted at each stage in the sequence. The extractions indicate that 50% to 80% of the total iodine mass associated with the sediment is extractable with a pH 5 Na-acetate and pH 2.3 acetic acid extractions. These extractions dissolve carbonates, but may also dissolve amorphous and/or some crystalline iron oxides. Therefore, while extraction data indicates significant iodine mass is associated with a solid phase (or phases) that is dissolved by acetate extractions, calcite has not been positively identified as containing the iodine mass, but it would be consistent with current laboratory results that this iodine mass may be iodate associated with carbonate precipitates (Truex et al. 2016). The existing P&T system in the Hanford 100-K Area also offers some insight into the effects of injecting pH 5.0 to 6.5 water into the Hanford aquifer (DOE 2016). There is significant carbonate dissolution occurring near the 100-K Area injection wells, with downgradient carbonate precipitation (i.e., as the pH is neutralized by dissolving carbonate, the carbonate solution is now supersaturated and some carbonate precipitates). This also caused increased mobilization of ^{90}Sr (some ^{90}Sr was incorporated into carbonates) and ^{14}C (possibly incorporated into carbonates, but not proven) in the 100-K Area. This host of co-contaminant mobilization issues associated with injection of acidic water in the slightly alkaline Hanford aquifer demonstrates why careful selection of enhanced P&T solutions should be initially evaluated in laboratory experiments.

Enhanced P&T solutions that should be evaluated include a) slight reductant (sodium dithionite), and b) high pH carbonate solution to promote carbonate exchange. A series of sequential extractions that include ion exchange and progressively more acidic solutions (described above) could be used to evaluate the fraction of iodine species that is mobilized by the different recommended injection solutions. Results from these laboratory-scale experiments would then help identify promising mobility-enhancing amendments, and determine the reaction rate information needed to parameterize numerical flow and transport models. Multiple models would be developed to test various amendment addition strategies and pumping configuration strategies. Based on these simulation results, the most favorable remedial schemes could be identified and an evaluation performed to determine the expected increase in efficiency/recovery for enhanced P&T relative to the baseline technology.

5.9 Ex Situ Aqueous Adsorption

Groundwater beneath the 200 West OUs is currently being treated ex situ to remove ^{99}Tc , uranium, nitrate, chromium, and the chlorinated solvents. However, the accepted remedy for ^{129}I groundwater contamination is hydraulic containment. To move beyond hydraulic containment to actual aboveground treatment of ^{129}I requires an ex situ technology capable of capturing the iodine. A wide variety of materials have potential or have been used in industry for iodine adsorption (capture), but the effectiveness depends on multiple factors, including the iodine speciation. As discussed in Section 2, iodine speciation in groundwater samples from the 200 West Area is dominated by iodate, which, on average, accounts for greater than 70% of the total iodine present, while iodide accounts for less than 5% of the total iodine present. Therefore, ex situ adsorption technology must either be effective for capture of iodate, or the iodate must be converted to iodide to improve performance.

Adsorption involves the interphase accumulation or concentration of substances at a surface of a solid. Adsorption of iodine from the aqueous phase involves the mass transfer of iodine onto a solid that typically has high surface area and active sites with an affinity for one or more iodine species. Adsorption therefore concentrates iodine onto a solid-phase material from a more dilute aqueous concentration. The solids with sorbed iodine require either further processing (e.g., regeneration to give a reusable solid and a concentrated liquid) and/or disposal as a solid waste. The effectiveness of the adsorption is a function of the form of iodine present in the water, the sorption media, pH/alkalinity conditions, and temperature.

There are a plethora of potential adsorbents, both natural and synthetic, including activated carbon (e.g., Hoskins et al. 2002; Parker et al. 2014; Kosaka et al. 2012; Ikari et al. 2015), zeolites (e.g., Li et al. 2014), layered double hydroxides (e.g., Kentjono et al. 2010; Theiss et al. 2014), organoclays (e.g., Li et al. 2014), argentite (e.g., Li et al. 2014; Kaplan et al. 2000; Mattigod et al. 2007), aerogels (e.g., Sánchez-Polo et al. 2006, 2007), self-assembled monolayers on mesoporous silica (SAMMS) (e.g., Mattigod et al. 2007; Kaplan et al. 2000), carbon nanotubes (e.g., Pishko et al. 2013), and a number of other materials. Some of these adsorbents include silver impregnation (doping) to promote iodine capture and formation of immobile silver iodide when adsorbed. Several studies (Kaplan et al. 2000; Mattigod et al. 2003, 2007, Pierce et al. 2010, Li et al. 2014) have assessed the relative effectiveness of adsorbents to determine the most appropriate material to use. Pierce et al. (2010) in particular has a significant list of “getter” materials for adsorption of iodine species. A broad list of information is also available for gas-phase adsorption (e.g., Riley et al. 2016), some of which may translate to aqueous phase adsorption, though the removal efficiency could be expected to be lower than for the gas phase.

Further information is needed regarding specific adsorbents for removal of, preferably, iodate (or a sequence that converts iodate to iodide and then removes iodide). Such work would assess the literature and identify a list of adsorbents, which would then undergo laboratory studies to evaluate performance with respect to specific iodine species. Loading efficiency, ease of adsorbent regeneration, and disposal of secondary waste would all be aspects that the laboratory studies should help quantify.

5.10 Ex Situ Ion Exchange

Ion exchange is a process technology in which ions that are held by electrostatic forces to charged functional groups on the surface of a solid treatment medium are exchanged for ions of similar charge in a solution. Ion exchange is classified as a sorption process because the ion exchange involves mass transfer from the liquid phase to the solid phase (where the charged functional groups are located). The effectiveness of the ion exchange treatment can be affected by the aqueous speciation of iodine in water and depends on the design/nature of the ion exchange resin. Ion exchange media must be regenerated (resulting in a concentrated liquid waste containing the iodine) and/or sent to treatment/disposal. The radioactivity of the sorbed iodine is not mitigated in the adsorption process, so suitable handling and final disposition are required.

Groundwater beneath the Central Plateau at Hanford is contaminated with co-mingled ⁹⁹Tc, uranium, nitrate, ¹²⁹I, chromium, and chlorinated solvents, such as carbon tetrachloride and trichloroethene. Groundwater beneath the 200 West OUs is currently being treated ex situ to remove ⁹⁹Tc, uranium, nitrate, chromium, and the chlorinated solvents. ¹²⁹I migration is currently being controlled using hydraulic containment as the accepted remedy. As discussed in Section 2, iodine speciation in

groundwater samples from the 200 West Area is dominated by iodate, which, on average, accounts for greater than 70% of the total iodine present, while iodide accounts for less than 5% of the total iodine present.

A variety of synthetic ion exchange media, with differing degrees of effectiveness and aqueous pH applicability, are commercially available. These include Dowex 1 and Dowex 21K (The Dow Chemical Company); resins PFA600, A-530E, and A-532E (The Purolite Company); and SIR-700 and SIR-1200 (ResinTech, Inc.). Aqueous biphasic extraction chromatography (ABEC) resins are another class of materials that selectively extract iodide (and pertechnetate) anions from alkaline radioactive wastes. ABEC resin development for large-scale chromatographic equipment has been undertaken (Bond et al. 1999; Alexandratos 2009). Batch testing (Parker et al. 2014) of ion exchange on synthetic resin media for iodine treatment has shown adsorption rates similar to those for certain activated carbon media, on the order of 1.7 µg iodine per gram of resin. Reduction of iodine to iodide in the testing by Parker et al. (2014) was found to more than double the loading capacity of most resins (except Dowex 21K and SIR-700).

Technologies such as ion exchange have been shown to be effective for iodide and less effective for iodate. Thus, applying ion exchange for treatment of the ^{129}I in the 200-UP-1 OU groundwater using the P&T system will require the development and/or testing of either ion exchange resins that are effective for iodate, or methods for conversion of iodate to iodide (which would allow use of currently available ion exchange technologies).

Further information is needed regarding specific ion exchange resins for removal of iodate (or a multi-part process that converts iodate to iodide and then removes iodide). Such work would assess the literature and identify a list of resins, which would then undergo laboratory studies to evaluate performance with respect to specific iodine species. Loading efficiency, ease of adsorbent regeneration, and disposal of secondary waste would all be aspects that the laboratory studies should help quantify.

5.11 Microbial Enhanced Ex Situ Ion Exchange

As described in Section 5.10, treatment of the ^{129}I in the 200-UP-1 OU groundwater using the P&T system will require the development and/or testing of new ion exchange resins that are effective for iodate, or methods to convert iodate to iodide, thereby allowing currently available ion exchange resins to be applied. One such approach for converting iodate to iodide is via microbial activity, which gives rise to this combined process of microbial enhanced ion exchange.

Iodate can be used as an alternate electron acceptor for bacterial growth, and is converted to iodide under anaerobic or microaerobic conditions. To date, nitrate-reducing, iron-reducing, and sulfate-reducing bacteria have been found to reduce iodate. Likewise, a number of phototrophs, such as diatoms and algae, have been shown to reduce iodate (Bluhm et al. 2010; Chance et al. 2007, 2009; Hung et al. 2005). Amachi et al. (2007b) demonstrated the dissimilatory iodate reduction by *Pseudomonas* sp. SCT, isolated from marine sediment slurry, in the presence of nitrate under anaerobic conditions. During these experiments, cells pre-grown without iodate did not reduce it, nor could they reduce iodate aerobically (Amachi et al. 2007b). The iodate-reducing enzyme, which was called an iodate reductase, was found in the periplasmic space, which is located between the inner and outer membranes of this bacterium.

Tsunogai and Sase (1969) reported several marine laboratory strains of nitrate-reducing bacteria could reduce iodate aerobically, concluding that iodate is reduced in a coupled mechanism by nitrate reductases. Other studies have shown microbial reduction of iodate with anaerobic cell suspensions of *Desulfovibrio desulfuricans* and marine bacterium *Shewanella putrefaciens* (Councell et al. 1997). In addition to these two bacterial species being able to directly reduce iodate to iodine, soluble ferrous iron and sulfide, as well as iron monosulfide produced by the metabolism of these microbes, were shown to abiotically reduce iodate to iodide. Likewise, *S. putrefaciens* strain MR-4 was shown to reduce iodate to iodide (Farrenkopf et al. 1997).

Reduction of iodate has also been demonstrated by the perchlorate respiring bacterium strain GR1 (Kengen et al. 1999). An enzyme that was isolated from the periplasm of this bacterium was shown to reduce perchlorate, chlorate, nitrate, iodate, and bromate.

Sediments from traps incubated in iodine-contaminated groundwater at the Hanford Site have yielded a number of bacterial isolates that can oxidize or reduce different iodine species. Because the dominant iodine species in 200-UP-1 groundwater has been shown to be iodate, experiments were performed to determine the ability of various Hanford isolates to reduce iodate in the presence of nitrate, a common co-contaminant in the 200-UP-1 groundwater. One isolate, designated *Agrobacterium* DVZ35, has been shown to reduce iodate to iodide in the presence of nitrate (Lee et al. in review). Nitrate was also reduced, but no nitrite was measured during the experiment, indicating conversion to nitric oxide. Iodate reduction occurred under both anaerobic and microaerobic conditions. When the culture was spiked with nitrate, iodate concentrations continued to decrease in the culture medium.

A number of *Shewanella* species have shown the ability to reduce iodate under anoxic conditions (Mok et al. in review). Preliminary results from these experiments indicate that iodate reduction is accomplished using proteins implicated in ferric iron reduction by these bacteria. In experiments performed with *S. oneidensis* MR1, less than 5% of the supplied iodate was converted to iodide, indicating other mechanisms for iodate transformation, such as volatilization or accumulation (Szecsody et al. 2017). In contrast to *Agrobacterium* DVZ35, *S. oneidensis* MR1 was able to reduce iodate in the absence of nitrate (Lee et al. in review).

These results indicate that FBBR systems similar to those used in existing P&T systems could be used to convert iodate to iodide, which could then be absorbed into biomass or the activated carbon carrier used in the reactors. Alternately, a denitrification reactor could be set up prior to the ion exchange building (RAD building) at the 200 West P&T facility, with extraction wells from the 200-UP-1 ¹²⁹I plume pumping to this reactor and the effluent, containing iodide, being fed into ion exchange beds.

The feasibility of the above approach would require performance of laboratory-scale reactor experiments. Samples of the biological support used in the FBBR could be taken and reactors set up and operated using parameters currently applied in the full-scale system. The feasibility of using the process as a pretreatment for ion exchange could be tested by enriching bacteria from the FBBR support material and then treating iodate contaminated simulated groundwater. Effluent from the reactor could then be treated using different ion exchange resins. Initial resins tested would be the Purolite resin currently used for ⁹⁹Tc removal.

6.0 Quality Assurance

The PNNL QA Program is based upon the requirements defined in DOE Order 414.1D, *Quality Assurance*, and 10 CFR 830, “Energy/Nuclear Safety Management,” Subpart A, Quality Assurance Requirements. PNNL has chosen to implement the following consensus standards in a graded approach:

- ASME NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, Part 1, Requirements for Quality Assurance Programs for Nuclear Facilities.
- ASME NQA-1-2000, Part II, Subpart 2.7, Quality Assurance Requirements for Computer Software for Nuclear Facility Applications, including problem reporting and corrective action.
- ASME NQA-1-2000, Part IV, Subpart 4.2, Guidance on Graded Application of Quality Assurance (QA) for Nuclear-Related Research and Development.

The procedures necessary to implement the requirements are documented through PNNL’s “How Do I...? (HDI), a system for managing the delivery of laboratory-level policies, requirements, and procedures.

The *DVZ-AFRI Quality Assurance Plan* (QA-DVZ-AFRI-001) was applied as the applicable QA document for this work under the NQA-1 QA program. This QA plan conforms to the QA requirements of DOE Order 414.1D and 10 CFR 830, Subpart A. This effort is subject to the *Price Anderson Amendments Act*.

The implementation of the Deep Vadose Zone – Applied Field Research Initiative QA program is graded in accordance with NQA-1-2000, Part IV, Subpart 4.2, Guidance on Graded Application of Quality Assurance (QA) for Nuclear-Related Research and Development. The technology level defined for this effort is Basic Research, which consists of research tasks that are conducted to acquire and disseminate new scientific knowledge. During Basic Research, maximum flexibility is desired in order to allow the researcher the necessary latitude to conduct the research. Therefore, any graphs or data presented in this document are “For Information Only;” no evaluation was performed as to the accuracy of presented data.

7.0 Summary and Conclusions

¹²⁹I is present in several large, though dilute, plumes in the groundwater, including the plume in the 200-UP-1 OU at the (DOE) Hanford Site. ¹²⁹I is an uncommon contaminant and mature remediation technologies are limited. In this study, available information was compiled and used to categorize potential remediation technologies, culminating in a recommendation of 11 promising technologies for further evaluation (listed below). Approaches to improve the technical information about promising technologies were also recommended so that a subsequent evaluation of potential remediation alternatives can assess these technologies.

Promising ¹²⁹I Remediation Technologies Needing Further Evaluation:

Monitored Natural Attenuation (MNA)	Microbial Facilitated Volatilization
In Situ Sequestration by Calcite (iodate)	Enhanced Pump-and-Treat
In Situ Sequestration by Apatite (iodate)	Ex Situ Aqueous Adsorption
In Situ Sequestration by Iron Oxides (iodate)	Ex Situ Ion Exchange
In Situ Sequestration by Organic Carbon	Microbial Enhanced Ex Situ Ion Exchange
In Situ Sequestration by Bioaccumulation	

This report provides the technology screening identified as a step in the *UP-1 Evaluation Plan for Iodine* (DOE 2015, Draft A). Based on this screening, further work will be conducted to evaluate the promising technologies and determine technologies for which treatability testing is warranted.

8.0 References

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