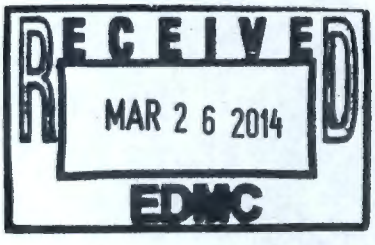
1223593

(2)

DOE/RL-2005-96
Addendum

Treatability Test Plan Addendum for 100-NR-2 Groundwater Operable Unit

Issued
April 2008



100-NR-2 Apatite Treatability Test Plan Implementation

Concurrence to proceed with the Treatability Test Plan addendum for high concentration injections at 100-NR-2 Groundwater Operable Unit.

Date 5/08/2008

K.M Thompson
DOE/RL

(TPA Project Mgr)

Date 5-8-2008

D. Goswami
Washington State Department of Ecology

1.0 Introduction

This addendum to the Strontium-90 Treatability Test Plan for 100-NR-2 Groundwater Operable Unit (DOE-RL-2005-96) describes the plan for conducting higher concentration injections for apatite formation at the 100-N Area Treatability Test site (see Figure 1-1). The injection solution consists of a mixture calcium, citrate, and phosphate (calcium chloride, trisodium citrate, sodium and ammonium phosphates, and a sodium bromide tracer). A low Ca-citrate-phosphate concentration solution for apatite formation was injected into the shallow aquifer in 10 injection wells shown in Figure 1-1 during FY06 and FY07 and performance monitoring is underway. The objective of the low concentration apatite solution injections was to stabilize the ^{90}Sr such that mobilization, and thus peak ^{90}Sr concentrations, are reduced during subsequent high concentration injections. The higher concentration formulation will be designed to provide for significant reductions in aqueous ^{90}Sr concentrations and long-term ^{90}Sr treatment. The Ca-citrate-phosphate solution causes temporary increases in the aqueous ^{90}Sr concentrations due to desorption of ^{90}Sr from the sediments which is controlled by the ionic strength of the solution, particularly the calcium concentrations. The two step process, low concentration injections followed by higher concentrations, was developed to minimize the increase in aqueous ^{90}Sr concentrations in the aquifer while providing for sufficient apatite for long-term ^{90}Sr treatment.

With the presentation of the *Evaluation of ^{90}Sr Treatment Technologies for the 100 NR-2 Groundwater Operable Unit* (Letter Report; Fluor/CH2M HILL, 2004) at the December 8, 2004, public meeting, U.S. Department of Energy (DOE), Fluor, Pacific Northwest National Laboratory (PNNL), and the Washington Department of Ecology (Ecology) agreed that a likely response scenario for groundwater remediation at 100-N is apatite sequestration as the primary treatment, followed by a secondary treatment, or polishing step, if necessary (most likely phytoremediation). Since that time, the agencies have worked together to identify which apatite sequestration technology has the greatest chance of reducing ^{90}Sr flux to the river, for a reasonable cost. In July 2005, aqueous injection, (i.e., the introduction of apatite-forming chemicals into the subsurface) was endorsed as the preferred method by the Innovative Treatment & Remediation Demonstration Program (ITRD) to undergo a Treatability Test under the Interim Record of Decision for 100-NR-2. Studies are in progress to assess the capability of aqueous injection to address both the vadose zone and the shallow aquifer along the 300 feet of shoreline where ^{90}Sr concentrations are highest.

The results of laboratory studies conducted with the Ca-citrate-phosphate solution and sediments from the 100-N Area are described in Szecsody et al. (2007). Laboratory experiments with higher concentration solutions are ongoing. An interim report on the 100-N Area treatability test site, field tests, and performance results to date for the low concentration Ca-citrate-phosphate injections conducted in 2006 and 2007 is currently being prepared and will be ready for public release in FY08.

Two pilot test sites at the east and west end of the treatability test site (see Figure 1-1), which are equipped with extensive monitoring well networks, were used for the initial low concentration formulation injections to develop the injection design for the remaining portions of the barrier. One (or both) of the pilot test sites will be used for the initial high concentration apatite injection to assess the side effects of the process prior to continuing with the remaining barrier well injections.

This addendum includes the following sections: the nominal design for field implementation for injections of the higher concentration solution, sampling and analysis plan, and schedule. Field test instructions will be developed prior to these high concentration injections that will incorporate results from ongoing laboratory experiments and design analysis and provide a detailed description of field test operational parameters and procedures.

2.0 Field Injections of High Concentration Ca-Citrate-PO4 Solution

The primary objective for development of the high concentration injection formulation is to maximize the amount of apatite formation providing long-term treatment while limiting the temporary increase in ^{90}Sr caused by the injection solution. The final low concentration injection solution used for barrier emplacement in 2007 is shown in Table 2.1. The nominal formulation for the high concentration injections is shown in Table 2.2. As indicated, the nominal reformulation concentrations are 4x that of the final low concentration formulation. The high-concentration formulation will be finalized prior to field deployment of the technology and documented in an injection specific field test instruction.

The final high-concentration formulation will be determined from the laboratory tests currently in progress. The field implementation approach is to first use the high-concentration formulation in an injection in one (or both) of the pilot-test sites with monitoring in the wells at the site up to two weeks following the injection. A rapid turn-around for gross beta analysis will be used to assess the ^{90}Sr increase at the site. After reviewing the early results, a decision will be made by DOE/RL and concurred with by Ecology on whether to proceed with the high-concentration formulation injections in the remaining treatability test wells. This schedule is compressed in order to take advantage of the limited high river stage period.

2.1 High Concentration Formulation

Three different low concentration formulations were tested at the 100-N Area pilot test sites during 2006 and 2007, with the objective of maximizing the amount of phosphate while minimizing the temporary increase in ^{90}Sr concentration. Based on preliminary performance monitoring data, the low concentration formulation shown in Table 2.1 (i.e., final Ca-citrate-PO4 formulation) resulted in a mean peak ^{90}Sr concentration increase, relative to mean baseline measurements at the pilot test sites, of 2.75 times at the pilot #1 site (range of 0.66 to 6.9 times) and 2.33 times at the pilot #2 site (range of 0.41 to 5.53 times). These data are shown in Tables 2.3 and 2.4 for Pilot test #1 and Pilot Test #2, respectively. Some of the reduction in observed peak ^{90}Sr during the second injection at the pilot test sites may be attributed to apatite formation and ^{90}Sr inclusion from the earlier injections at these sites.

The nominal high concentration injection formulation of four times the final low concentration formulation was developed using the following rationale:

- field measurements at the pilot test sites for ^{90}Sr peak concentrations
- estimated 50% decreasing in peak ^{90}Sr concentrations for sediment treated with the low concentration formulation (preliminary results from sequential Ca-citrate-PO4 injections, see Table 5.2 and 5.27 in Szecsody et al., 2007).

Laboratory studies are in progress using 100-N Area sediment treated with low concentration Ca-citrate-phosphate solution in January 2007, and then subjected to a range of high concentration solutions to determine the final composition of the high concentration Ca-citrate-phosphate solution. These studies are focused on initial short term aqueous Sr concentration increases during solution injection (< 24 h), subsequent Sr decrease over 30 day groundwater injection period, and the amount of apatite formation that occurs, for different formulations over the range of concentrations (PO4 from 20 mM to 60 mM) listed in Table 2-2. Some column experiments are also investigating the addition of fluoride to increase the apatite precipitation rate.

2.2 Injection Volumes and Rates

Field testing at the 100-N Area Apatite Treatability Test Site showed that the barrier can be subdivided into two portions based on the overall well capacity and contrast between the Hanford and Ringold hydraulic conductivities. The upstream portion, between injection wells 199-N-138 and 199-N-141 (see Figure 1-1), had relatively lower overall well specific capacity estimated from well development data, which was also reflected in observed well efficiencies during the low concentration injection operations, and a smaller contrast in hydraulic conductivity between the Hanford and Ringold Formation (based on injection tests at the Pilot #1 Test site [199-N-148]). The downstream portion, between injection wells 199-N-142 and 199-N-137, had overall higher well specific capacity and a larger hydraulic conductivity contrast between the Hanford and Ringold Formations (with the Hanford hydraulic conductivity values greater in the downstream portion than the upstream portion) based on the well development data and injection tests at the Pilot #2 Test site (199-N-147). The hydraulic conductivity contrast is important because it controls the radial extent of the injected reagent in the Hanford and Ringold Formation when using injection wells that are screened across both formations.

Based on the results of the Pilot #1 Test Site injections, an injection volume of ~120,000 gallons is required for the injection wells in the upstream portion of the barrier for sufficient overlapping coverage for the 30-ft injection well spacing. Since the contrast between the hydraulic conductivity between the Hanford and Ringold formations is low in this portion of the barrier, these wells should be injected during high river stage conditions to treat the uppermost portion of the unconfined aquifer while also providing adequate treatment in the Ringold treatment zone.

Results of the Pilot Test #2 site injection and other injection wells over the downstream portion of the barrier demonstrated the need for injection wells screened only in the Ringold portion of the treatment zone (see Section 2.5). Low river stage injections over this portion of the barrier that were targeted on the Ringold formation resulted in excessive regent loss to the Hanford formation, thus requiring very large injection volumes which were inefficient and in many cases may have still resulted in poor treatment coverage in the Ringold. Additionally, springs appeared at the shoreline near some of these wells during low river stage injections. Based on these observations, the spatial extent of treatment within the Ringold formation over this portion of the barrier is in question. To improve treatment efficiency, injection wells screened only across the contaminated upper portion of the Ringold formation are planned for installation along

the downstream portion of the barrier in the winter or early spring of 2008. Because these new wells should act to improve the spatial extent of treatment within the Ringold formation, peak ^{90}Sr concentrations associated with high concentration treatment may be higher than would be observed if this interval was first more effectively treated with the low concentration solution. However, it should be noted that baseline ^{90}Sr concentration depth profiles (from characterization well 199-N-121, N-122, and N-123) indicate that significantly more contamination resides within the Hanford portion of the profile, so limited pre-treatment of the Ringold formation sediments should have less impact to the overall ^{90}Sr mobilization during subsequent treatments than a similar limitation in the Hanford formation would be.

With this new well configuration over the downstream portion of the test site, it is estimated that injection volumes of approximately 60,000 gallons will be required during high river stage conditions to treat the Hanford formation. An estimated 60,000 gallon injection volume will also be required for each of the new Ringold-only injection wells in the downstream portion of the barrier. The injections in the Ringold-only wells can be conducted during any river stage condition; however periods with steep increases or decreases in river stage should be avoided due to the large hydraulic gradients generated during these times directed inland or towards the river.

Injection rates during the high Ca-citrate-phosphate injections should be approximately 40 gpm based on the results of the low concentration pilot test injections at the treatability test site. Higher injection rates in the upstream portion of the barrier caused large head build up in the Pilot #1 injection well with seeps appearing at the surface. Higher proportional injection rates may be possible for the injections in the downstream portion of the barrier targeting the Hanford Formation at high river stage. Lower injection rates may be required for treatment of the Ringold-only injection wells based on the results of specific capacity tests in the completed wells.

One additional field-implementation issue that will be explored prior to the high Ca-citrate-phosphate injections is the impact of density effects from this greater density solution. The relative importance of density effects is determined by both the fluid density contrast (reagent vs. ambient groundwater) and the formation permeability. Analysis of the potential impacts of density effects on the reagent plume will be conducted using the fluid densities in the range proposed for the high Ca-citrate-phosphate solution along with estimates of the hydraulic conductivities of the Hanford and Ringold Formation in the upstream and downstream portions of the site, as determined based on results from previous pilot-scale field tests at N-137 and N-138.

2.3 Field emplacement Approach

The schedule for field testing is constrained by the need to take advantage of high river stage conditions for most of the barrier well injections. Field testing with the final high concentration Ca-citrate-phosphate solution will first be conducted during high river stage conditions at one (or both) of the pilot test sites. Monitoring of the test site will be conducted for approximately two weeks after the injection to assess the ^{90}Sr concentration increases using this formulation. Gross beta analysis will be used for estimating ^{90}Sr concentrations to provide for quicker turn-around of

the analytical results. The decision on whether to proceed with injections in the remaining wells at the 100-N Area treatability test site will be made based on the analysis of these monitoring results from the pilot-scale testing.

If the decision is made to proceed with additional high concentration Ca-citrate-phosphate solution injections, the remaining wells will be injected in 2 or more stages. To prevent interference from adjacent injection wells, one half of the wells will be injected during a high river stage period and followed by a two-week reaction time period before injecting the remaining wells, also during high river stage conditions. The wells screened in only the Ringold Formation do not need to be injected during the high river stage period.

Multiple high-concentration injections, as shown in Table 2.2, may be required for each injection well to achieve the longevity required for long term treatment of ^{90}Sr. The design lifetime for the barrier is approximately 300 years to allow for radioactive decay of ^{90}Sr (i.e. ~10 half lives). The number of high-concentration injections is dependent on the final concentrations used and the efficiency of apatite formation and ^{90}Sr incorporation resulting from the field injection process. Laboratory experiments indicate 10% Sr substitution for Ca can be achieved, and given that assumption, a total of 90 mM PO4 needs to be precipitated as apatite to achieve 300 years of ^{90}Sr incorporation capacity.

Detailed field instructions will be prepared prior to the test that will include chemical mass, injection volumes, injection rates, sampling and analysis requirements, and the sequence of injections for the treatability test wells.

2.4 Barrier Performance Assessment

Barrier performance will be assessed through groundwater monitoring following the high concentration Ca-citrate-PO4 injections and from laboratory analysis of core samples collected from boreholes in the barrier. These analyses will assess the effectiveness in the reduction of aqueous ^{90}Sr concentrations in the barrier and the amount of apatite formation in the sediments in the barrier created by this process, which will be used to estimate the treatment longevity.

Performance monitoring will be conducted in the injection wells, compliance wells, pilot test monitoring wells, and aquifer tubes along the barrier. The performance monitoring will assess the reduction in ^{90}Sr concentrations and potential side effects from the injections by comparison with pre-injection values. Details on the analytes and sampling frequency are provided in Section 3.

Sediment samples will be collected from the barrier for apatite analysis in the laboratory from boreholes following the high-concentration injections. These samples will be collected at least 6 to 12 months following the injections to provide time for the amorphous Ca-phosphate phases to crystallize to hydroxyapatite. The sediment samples will be collected from the pilot test sites since these sites have the largest amount of monitoring data collected during the injections. Samples will be collected from multiple depths in both the Hanford and Ringold formations to assess the vertical variations in apatite formation. Laboratory experiments with the sediment will

include determination of the amount of apatite formed, the amount of Sr and ^{90}Sr incorporated, and the treatment capacity through a combination of batch and column experiments. Sequential extractions of Sr and ^{90}Sr from the sediment cores will be used to determine the amount in the aqueous phase, adsorbed to the sediment by ion exchange, and incorporated into apatite. The treatment capacity will be used to calculate the barrier longevity. Sediment samples are also planned to be collected during drilling at the barrier in the winter of 2008 for the Ringold-only injection wells for use in preliminary laboratory analysis of the apatite formation from the low concentration injections, sequential Sr and ^{90}Sr extractions, and development/testing of analysis techniques.

2.5 Ringold Formation Injection Well Installation

Previous injection experience indicated that six (6) additional wells completed in the Ringold formation would be required. The project location map and site map with the locations of the new wells are provided as Figures 2-1 and 2-2. Table 2-5 lists the well identification numbers and the well names. The wells will be drilled as a *Comprehensive Environmental Response, Compensation, and Liability Act of 1980* (CERCLA) activity and all waste generated during drilling will be managed as CERCLA investigation-derived waste.

Figure 2-3 presents the proposed well design and illustrates the construction details for the six new 100-NR-2 OU injection wells. The design of the wells must meet the minimum standards required in WAC 173-160 for construction of resource protection wells. All wells shall be 6-in. diameter and completed using Schedule 10 Type 304 or 316L stainless steel casing, with an end cap of the same material. The well screen will be 6-in., 0.020 in (20-slot), Type 304 or 316L stainless steel, V-wire, continuous wire-wrap screen and will be 7 ft in length. The filter pack will consist of 10-20 mesh Colorado silica sand. An environmentally compatible non-petroleum lubricant such as Jet-Lube Well Guard thread compound or equivalent may be used for lubricating the threads of the stainless steel while installing the casing. Table 2-6 provides a general summary of proposed well construction parameters for this well, including the estimated water level, well depth, screen interval, sand pack interval, bentonite seal intervals, and cement surface seal interval. Final well construction details will be confirmed by the BTR and/or FH field geologist/hydrogeologist prior to construction.

Final placement of the well screen will be at the direction of the BTR and/or FH field geologist/hydrogeologist. The well casing/screen string must be maintained in tension (i.e., the weight of the string is suspended from the top and not allowed to rest on the bottom of the borehole) to maintain straightness of the completed well. The filter pack will be placed from the bottom of the borehole to 1 ft above the top of screen. The filter pack will be composed of 10-20 mesh Colorado silica sand and will be settled by the dual surge block method and bailing technique per the well construction Statement of Work. This will be followed by a 3-ft layer of bentonite pellets placed immediately on top of the filter pack. A 3-ft layer of bentonite crumbles will follow the bentonite pellets. A cement grout seal will be placed immediately on top of the bentonite crumbles to ground surface. Accelerators may be used if excessive cement loss occurs.

Surface protection for each well will be a below-grade completion in accordance with WAC 173-160-420 (13) and GPR-EE-02-14.1, "Drilling, Remediating, and Decommissioning Resource Protection Wells and Geotechnical Soil Borings" with the following modifications:

- A metal flush-mount watertight monument shall be installed to enclose the top of each well below grade. This monument must include a removable cover equipped with a watertight gasket and securing bolts.
- The protective casing shall be a minimum of 2 in. larger in diameter than the permanent casing. This protective casing shall be made of Type 304 (or higher grade e.g., 304L, 316, or 316L) stainless steel. The protective casing shall rise to approximately 4 in. bgs in the groundwater monitoring wells. The protective casing on the groundwater monitoring wells will be capped with a watertight locking well cap.
- The permanent casing shall rise to approximately 8 in. bgs and shall be approximately 4 in. below the top of the protective casing in the groundwater monitoring wells. A concrete surface shall be installed to completely surround and secure the flush-mount monument of each well. The concrete surface must be sloped away from each well.
- A brass survey marker with the well identification number, well name, and completion date inscribed shall be installed on the north side of the sloped concrete surface that surrounds the flush-mount monument.

Final well development with a submersible pump will be performed on all wells after the wells are constructed. During final well development, water samples will be collected and analyzed for chemical parameters (pH, temperature, and specific conductivity) and turbidity using field instruments. A data logger will record pressure transducer water level measurements during drawdown and recovery phases of the final well development.
No sampling pumps will be installed in these wells.

3.0 Sampling and Analysis

Sampling and Analysis requirements for the high concentration apatite solution injections are organized into three periods with different analytes and frequencies. The three categories are: 1) initial pilot injection test(s), 2) barrier well injections, and 3) performance monitoring. The sampling and analysis for each of these periods is described below, and in Tables 3-1 and 3-2. Field test instructions will also be prepared prior to the injections that will include these sampling requirements along with a detailed set of operational parameters and procedures. Sampling will occur in a number of wells and aquifer tubes along the 100-N shoreline during all phases of treatment. The wells sampled during various phases are outlined in Table 3-3. Specifics on which wells will be sampled during pilot tests and barrier installation operations will be provided in activity specific field test instructions. All of the wells outlined in Table 3-3 will be sampled during pre-injection and performance monitoring.

3.1 Pilot Test Sampling and Analysis

Pre-Injection- 1 time the week before injection

- Analytes → major cations, anions, gross beta, Sr-90

Injection – Every 4 hours during injection in all monitoring wells, adjacent injection wells and nearby compliance wells. Sample the injection stream three times during injection (start/middle/end). Routinely measure injection stream field parameters (except DO, ~ once per hour). Sample aquifer tubes as necessary; to be determined in the field.

- Analytes → major cations, anions, citrate

Post-Injection – Daily sampling for 1 week, starting immediately after injection completion. Sample every other day during 2nd week. Then collect 1 sample per week for 4 weeks.

- Analytes → major cations, anions, citrate, gross beta

Other Monitoring – Pressures in injection well and all wells within 30 ft. Monitor all chemical flow rates at injection skid.

3.2 Barrier Installation Sampling and Analysis

Pre-Injection – 1 time the week before injection

- Analytes → major cations, anions, gross beta, Sr-90

Injection – Sample the injection stream three times during injection (start/middle/end). Routinely measure injection stream field parameters (except DO,~ once per hour). Collect sample near the end of injection from adjacent injection wells and available monitoring wells and compliance wells.

- Analytes → major cations, anions, citrate

Post-Injection – Daily sampling for 1 week, starting immediately after injection completion. Sample every other day during 2nd week. Then collect 1 sample per week for 4 weeks.

- Analytes → major cations, anions, citrate, gross beta

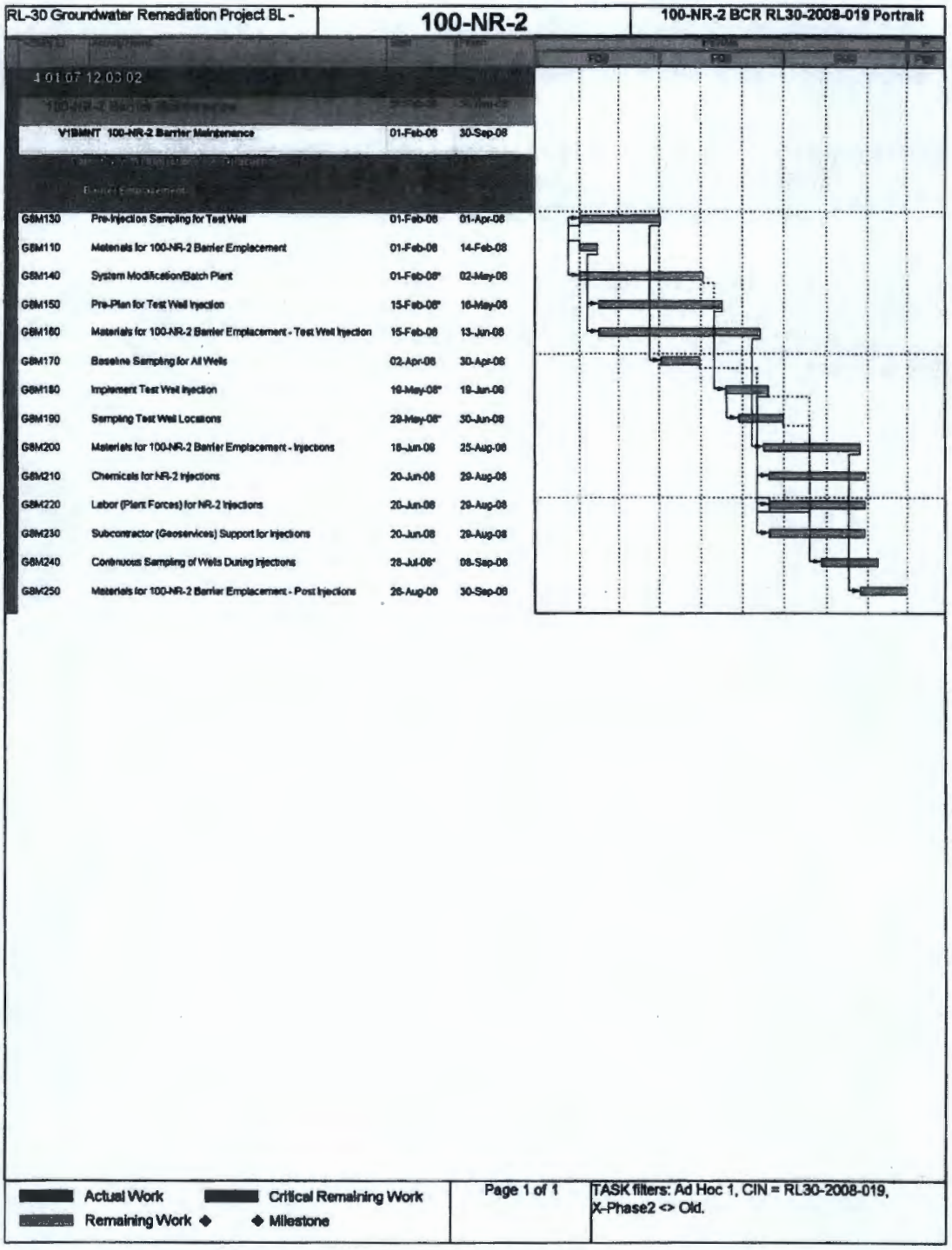
Other Monitoring – Pressures in injection well and all wells within 30 ft. Monitor all chemical flow rates at injection skid.

3.3 Performance Monitoring Sampling and Analysis

Bi-monthly monitoring of barrier wells, pilot-test monitoring wells, and compliance wells for 2 years following barrier emplacement. Analyze for all analytes. Continued monitoring needs determined after 2 years.

- Analytes → major cations, anions, gross beta, periodic sample splits for Sr-90 analyses

4.0 Schedule


RL-30 Groundwater Remediation Project BL -
100-NR-2
100-NR-2 BCR RL30-2008-019 Portrait
4 01 07 12 03 02
V1BMNT 100-NR-2 Barrier Maintenance 01-Feb-08 30-Sep-08
G8M130 Pre-Injection Sampling for Test Well 01-Feb-08 01-Apr-08
G8M110 Materials for 100-NR-2 Barrier Emplacement 01-Feb-08 14-Feb-08
G8M140 System Modification/Batch Plant 01-Feb-08* 02-May-08
G8M150 Pre-Plan for Test Well Injection 15-Feb-08* 16-May-08
G8M160 Materials for 100-NR-2 Barrier Emplacement - Test Well Injection 15-Feb-08 13-Jun-08
G8M170 Baseline Sampling for All Wells 02-Apr-08 30-Apr-08
G8M180 Implement Test Well Injection 16-May-08* 19-Jun-08
G8M190 Sampling Test Well Locations 29-May-08* 30-Jun-08
G8M200 Materials for 100-NR-2 Barrier Emplacement - Injections 18-Jun-08 25-Aug-08
G8M210 Chemicals for NR-2 Injections 20-Jun-08 29-Aug-08
G8M220 Labor (Plant Forces) for NR-2 Injections 20-Jun-08 29-Aug-08
G8M230 Subcontractor (Geoservices) Support for Injections 20-Jun-08 29-Aug-08
G8M240 Continuous Sampling of Wells During Injections 28-Jul-08* 08-Sep-08
G8M250 Materials for 100-NR-2 Barrier Emplacement - Post Injections 26-Aug-08 30-Sep-08
Actual Work
Critical Remaining Work
Remaining Work
Milestone
Page 1 of 1
TASK filters: Ad Hoc 1, CIN = RL30-2008-019, X-Phase2 <> Old.

5.0 References

DOE-RL-2005-96 – Original TTP

Fluor/CH2M HILL. 2004. Evaluation of Strontium-90 Treatment Technologies for the 100-NR-2 Groundwater Operable Unit. Letter Report. (http://www.washingtonclosure.com/projects/endstate/risk_library.html#narea).

Szecsody JE, CA Burns, RC Moore, JS Fruchter, VR Vermeul, MD Williams, MJ Truex, DC Girvin, and JL Phillips. 2007. *Hanford 100N Area Apatite Emplacement: Laboratory Results of Ca-Citrate-PO4 Solution Injection and Sr-90 Immobilization in 100N Sediments*. PNNL-16891, Pacific Northwest National Laboratory, Richland, WA.

Table 2-1. Final Low Concentration Ca-citrate-phosphate Injection Formulation used in 2007

1.0 mM calcium chloride
2.5 mM trisodium citrate
10 mM phosphate (mixture of sodium phosphate, disodiumphosphate, and diammmonium phosphate, pH 7.8)
1.0 mM sodium bromide

Table 2-2. Nominal High Concentration Ca-citrate-phosphate Injection Formulation (4x low concentration injection solution) and chemical weights for 120,000 gal. injection volume.

Component	Nominal Concentration	Chemical Weights
calcium chloride	3.6 mM	399 lbs
trisodium citrate	9.0 mM	2645 lbs
phosphate (mixture of sodium phosphate, di-sodium phosphate, and di-ammonium phosphate for pH buffering)	40 mM	4596 lbs Na_2HPO_4 671 lbs NaH_2PO_4 264 lbs $(NH_4)_2HPO_4$
sodium bromide (tracer)	1.0 mM	103 lbs

Table 2-3. Baseline and Peak ^{90}Sr Concentrations at the Pilot #1 Test Site.

	Baseline		5/31/06 N-138 Inject Formula 1 (4,10,2.4) Post Inj Peak		6/8/2007 N-138 Inject Formula 3 (1,2.5,10) Post Inj Peak		Ratios			
Well	Sr pCi/L	Date	Sr pCi/L	Date	Sr pCi/L	Date	Formula 1 Peak / Mean Baseline	Formula 1 Peak / Baseline	Formula 3 Peak / Mean Baseline	Formula 3 Peak / Baseline
N-138	811	4/26/2006	801	6/2/2006	480	10/19/2007	1.10	0.99	0.66	0.59
N-123	1,040	4/12/2006	2,720	8/8/2006	1,480	9/7/2007[a]	3.75	2.62	2.04	1.42
APT-1	877	4/26/2006	3,400	10/9/2006	1,400	7/13/2007	4.68	3.88	1.93	1.60
P-1-R	570	4/26/2006	6,696	6/2/2006	2,500	7/8/2007	9.22	11.75	3.44	4.39
P-2-H	574	4/26/2006	3,735	6/2/2006	1,400	6/20/2007	5.14	6.51	1.93	2.44
P-3-R	314	4/26/2006	7,829	6/2/2006	1,600	10/19/2007	10.78	24.93	2.20	5.10
P-4-H	895	4/26/2006	7,365	6/2/2006	2,600	7/13/2007	10.14	8.23	3.58	2.91
P-5-R			11,000	6/28/2006	5,000	10/19/2007	15.15		6.88	
P-6-H	729	4/26/2006	9,482	6/16/2006	1,400	7/8/2007	13.06	13.01	1.93	1.92
P-7-R			12,000	7/17/2006	3,000	11/14/2007	16.52		4.13	
P-8-H			2,100	7/24/2006	1,100	7/8/2007	2.89		1.51	
Mean	726		6,103		1,996		8.40	8.99	2.75	2.54

Color Key
Sr-90
WSCF - Total beta radiostrontium
[a]Data flagged with Q qualifier

Table 2-4. Baseline and Peak ^{90}Sr Concentrations at the Pilot #2 Test Site.

	Baseline		9/27/06 N-137 Inject Formula 2 (2,5,2.4) Post Inj Peak		3/20/2007 N-137 Inject Formula 3 (1,2.5,10) Post Inj Peak		Ratios			
Well	Sr pCi/L	Date	Sr pCi/L	Date	Sr pCi/L	Date	Formula 2 Peak / Mean Baseline	Forumla 2 Peak / Baseline	Formula 3 Peak / Mean Baseline	Formula 3 Peak / Baseline
N-137	1,842	9/25/2006	4,002	10/27/2006	500	8/10/2007	3.25	2.17	0.41	0.27
N-147	1,220	9/18/2006	942	2/15/2007	3,000	3/23/2007	0.77	0.77	2.44	2.46
APT-5	932	9/25/2006	2,657	10/5/2006	1,100	10/19/2007	2.16	2.85	0.89	1.18
P2-1-R	1,857	9/27/2006	11,320	9/28/2006	6,800	4/6/2007[a]	9.20	6.10	5.53	3.66
P2-2-H	605	9/27/2006	1,804	9/28/2006			1.47	2.98		
P2-3-R	1,900	9/25/2006	8,800	10/19/2006	3,800	3/23/2007	7.16	4.63	3.09	2.00
P2-4-H	867	9/27/2006	1,768	9/28/2006			1.44	2.04		
P2-5-R	728	9/25/2006	4,574	10/13/2006	2,600	3/26/2007	3.72	6.28	2.11	3.57
P2-6-H			5,050	9/28/2006			4.11			
P2-7-R	1,295	9/25/2006	4,330	9/28/2006	2,200	8/23/2007	3.52	3.34	1.79	1.70
P2-8-H			3,535	9/28/2006			2.87			
P2-9-R	1,053	9/25/2006	6,721	10/13/2006	2,900	8/23/2007	5.46	6.38	2.36	2.75
Mean	1,230		4,625		2,863		3.76	3.76	2.33	2.20

Color Key
Sr-90
WSCF - Total beta radiostrontium
[a]Data Flagged with F Qualifier

Table 2-5. Well Identification Numbers and Well Names.

Well ID	Well Name
C6177	199-N-159
C6178	199-N-160
C6179	199-N-161
C6180	199-N-162
C6181	199-N-163
C6182	199-N-164

Table 1-6. Proposed Well Construction for NR-2 Operable Unit Wells.

Estimated Depth to Water (ft)[1]	Planned Total Depth (ft)[2]	Screen and Casing Diameter (in.)	Screen Slot Size	Screen Length[2] (ft)/ Interval (ft bgs)	Filter Pack Mesh/ Interval (ft bgs)	Bentonite Seal Interval (ft bgs)	Bentonite crumbles Interval (ft bgs)	Cement Seal Interval (ft bgs)
8-10	25	6	20	7/ 24'-17	10-20/ TD – 16	16-13	13-10	10- 0

Notes:

[1] Estimated depth to water taken from previously drilled wells and depends upon river stage.

[2] Information presented on table are estimates. Final position of well screen, filter pack interval, and bentonite seal intervals will be determined based upon actual borehole conditions

bgs = below ground surface

TD = total depth

Table 3-1. Apatite Pilot Test Sampling Requirements (Primary analytes shaded)

Parameter	Media/ Matrix	Sampling Frequency	Volume / Container	Preservation	Hold Time
Major Cations/metals: Al, As, B, Ba, Bi, Ca, Co, Fe, K, Mg, Mn, Ni, Zn, Zr, P, Sr, U, Si, S, Sb	Water	See sections 3.1, 3.2, and 3.3 for pilot test, barrier installation, and performance monitoring requirements, respectively	20 ml plastic vial	Filtered (0.45 µm), HNO_3 to pH <2	60 DAYS
Anions: Cl^-, Br, SO_4^{2-}, PO_4^{3-}, NO_2^-, NO_3^-	Water	See sections 3.1, 3.2, and 3.3 for pilot test, barrier installation, and performance monitoring requirements, respectively	20 ml plastic vial	Cool 4^0C	45 DAYS
Small Molecular Weight Organic Acids: Citrate, Formate	Water	See sections 3.1, 3.2, and 3.3 for pilot test, barrier installation, and performance monitoring requirements, respectively	20 ml plastic via	Filtered (0.22 µm), Sodium Azide, or freeze	20 Days
Sr-90 – PNNL Lab	Water	See sections 3.1, 3.2, and 3.3 for pilot test, barrier installation, and performance monitoring requirements, respectively	1 L plastic bottle	Filtered (0.45 µm), HNO_3 TO PH <2	60 Days
Gross Beta	Water	See sections 3.1, 3.2, and 3.3 for pilot test, barrier installation, and performance monitoring requirements, respectively	1 L plastic bottle	Filtered (0.45 µm), HNO_3 TO PH <2	60 Days
pH	Water	With every water sample, and as needed	Field Measurement	n/a	n/a
Specific Conductance	Water	With every water sample, and as needed	Field Measurement	n/a	n/a
Dissolved oxygen[a]	Water	With every water sample, and as needed	Field Measurement	n/a	n/a
Oxidation-Reduction Potential	Water	With every water sample, and as needed	Field Measurement	n/a	n/a
Temperature	Water	With every water sample, and as needed	Field Measurement	n/a	n/a
(a) Dissolved oxygen measured in monitoring well samples only. Not required for injection solution.					

Table 3-2. Analytical Requirements (Primary analytes shaded)

Parameter	Analysis Method	Detection Limit or (Range)	Typical Precision/Accuracy	QC Requirements
Major Cations / metals: [redacted], Fe, K, Mg, P, [redacted], Si, S Al, B, Ba, Bi, Ni, Zn, Zr, Sr	ICP-OES, EPA Method 6010B or equivalent	1 mg/L 0.1 mg/L	±10%	Daily calibration; blanks and duplicates and matrix spikes at 10% level per batch of 20.
Anions: Cl^-, [redacted], SO_4^{2-}, [redacted], NO_2^-, NO_3^-	Ion Chromatography, EPA Method 300.0A.or equivalent	1 mg/L	±15%	Daily Calibration; Blanks And Duplicates At 10% Level Per Batch Of 20.
Small molecular weight organic acids: [redacted] and formate	Ion Chromatography, AGG-IC-001 (Based on EPA Method 300.0A.)	1 mg/L	±15%	Daily Calibration; Blanks And Duplicates At 10% Level Per Batch Of 20.
Sr-90 – PNNL Lab	separation followed by gross alpha/beta via liquid scintillation	75 pCi/L	±15%	Daily Calibration; Blanks And Duplicates At 10% Level Per Batch Of 20.
Gross Beta	Liquid Scintillation	5 pCi/L	±20%	Daily Calibration
pH	pH electrode	(2 to 12 units)	± 0.2 pH unit	User calibrate per manufacturer directions
Specific conductance	Electrode	(0 to 100 mS/cm)	± 1% of reading	User calibrate per manufacturer directions
Dissolved oxygen	Membrane electrode	(0 to 20 mg/L)	± 0.2 mg/L	User calibrate per manufacturer directions
Oxidation-Reduction Potential	Electrode	(-999 to 999 mV)	± 20 mV	User calibrate per manufacturer directions
Temperature	Thermocouple	(-5 to 50 °C)	± 0.2°C	Factory calibration

Table 3-3 Wells sampled during pre-injection, injection and performance monitoring. Field test instructions will specify monitoring requirements during injection operations.

Barrier Wells	Compliance Wells	Other Monitoring Wells	Aquifer Tubes
N-136	N-122	N-126 (P1-1R)	APT1 (C5269)
N-137	N-123	N-127 (P1-2H)	APT5 (C5386)
N-138	N-146	N-128 (P1-3R)	Array 2A (C5256)
N-139	N-147	N-129 (P1-4H)	Array 3A (C5257)
N-140		N-130 (P1-5R)	Array 4A (C5258)
N-141		N-131 (P1-6H)	Array 6A (C5259)
N-142		N-132 (P1-7R)	Array 7A (C5260)
N-143		N-133 (P1-8H)	NVP2-116.0 (C5251)
N-144		N-148 (P2-1R)	
N-145		N-149 (P2-2H)	
		N-150 (P2-4H)	
		N-151 (P2-3R)	
		N-152 (P2-9R)	
		N-153 (P2-8H)	
		N-154 (P2-7R)	
		N-155 (P2-6H)	
		N-156 (P2-5R)	

Figure 1-1. 100-N Area Apatite Treatability Test Plan Site Map

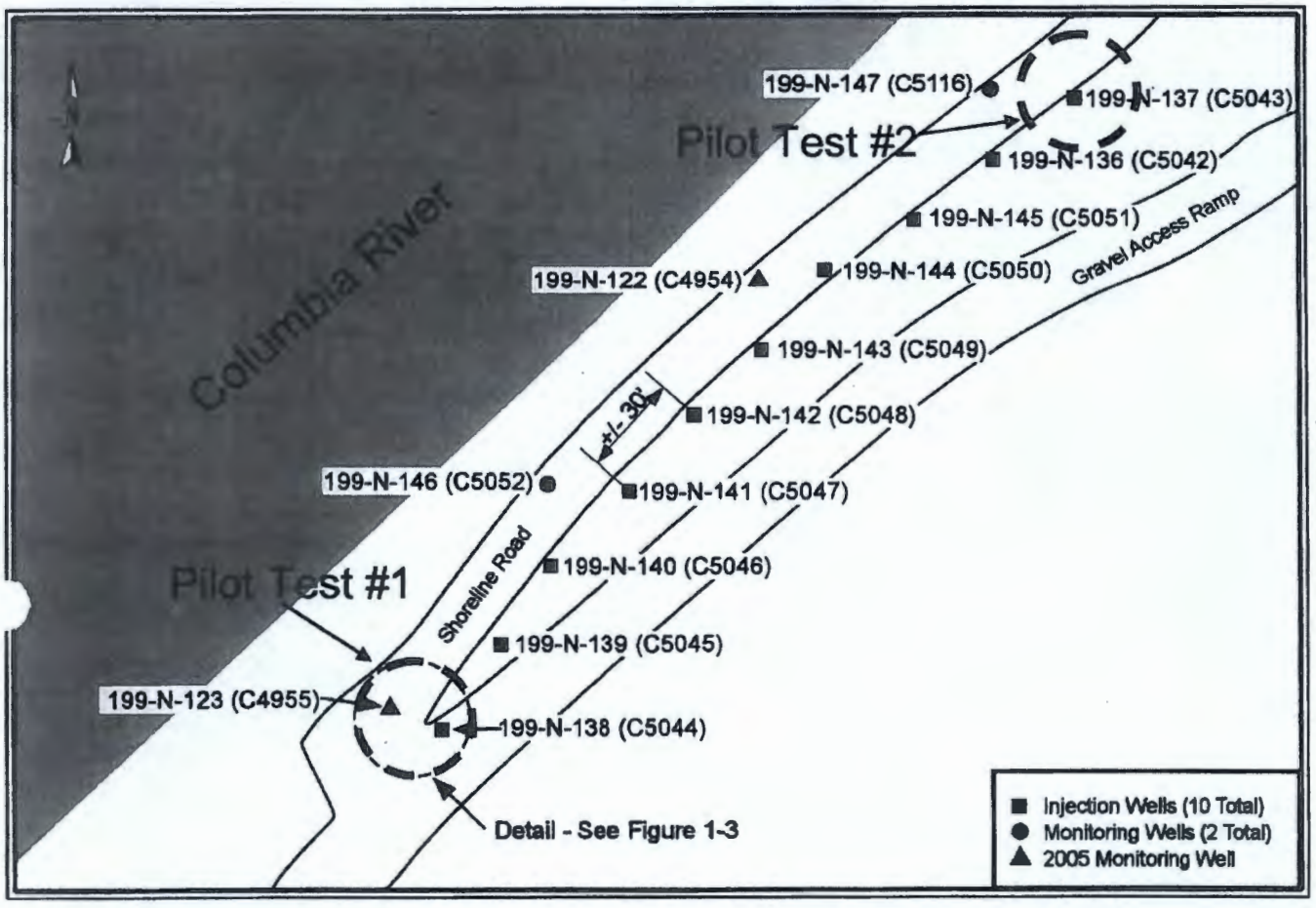


Figure 2-1. Location Map for the 100-NR-2 Operable Unit.

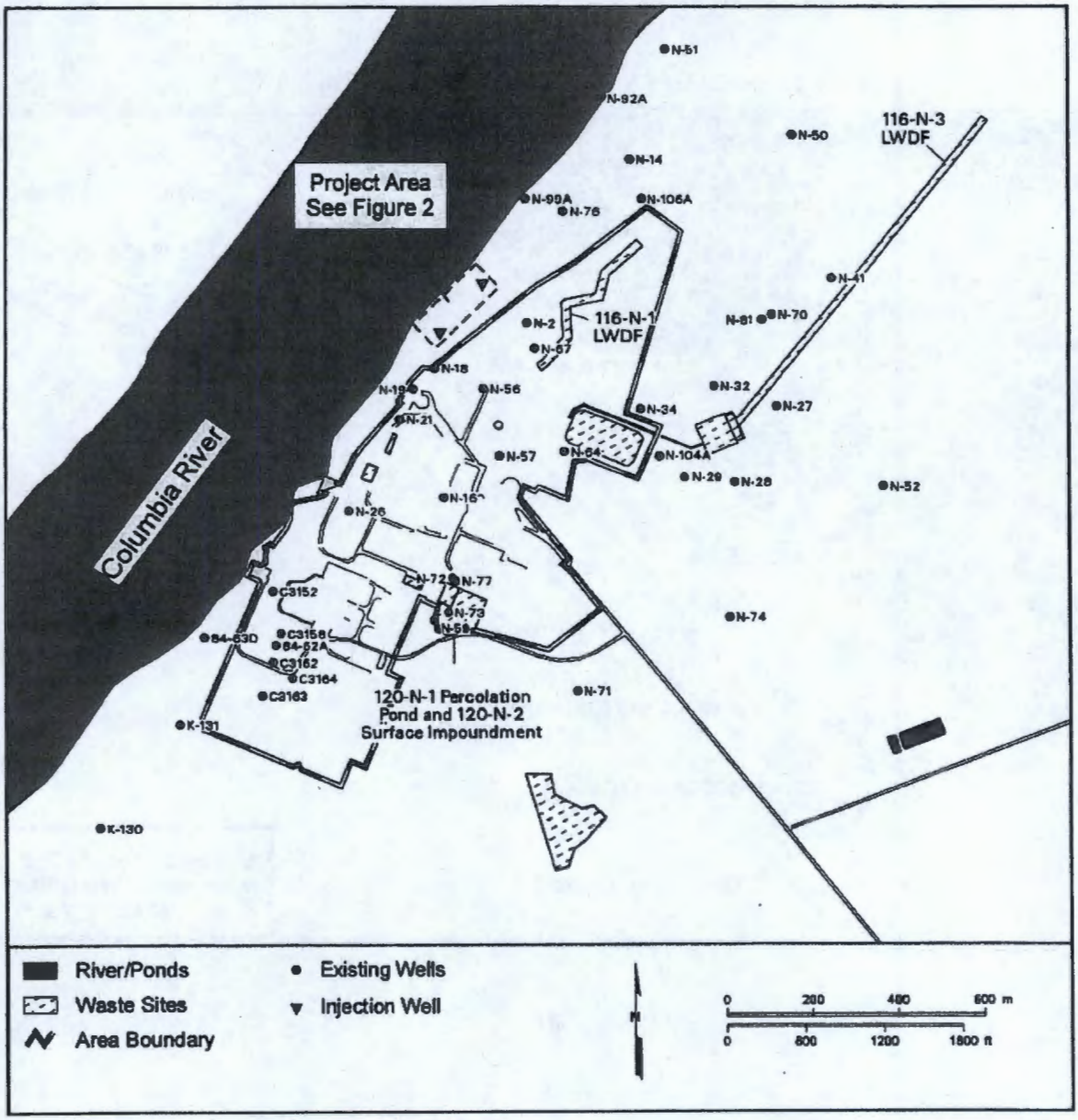


Figure 2-2. Well Locations.

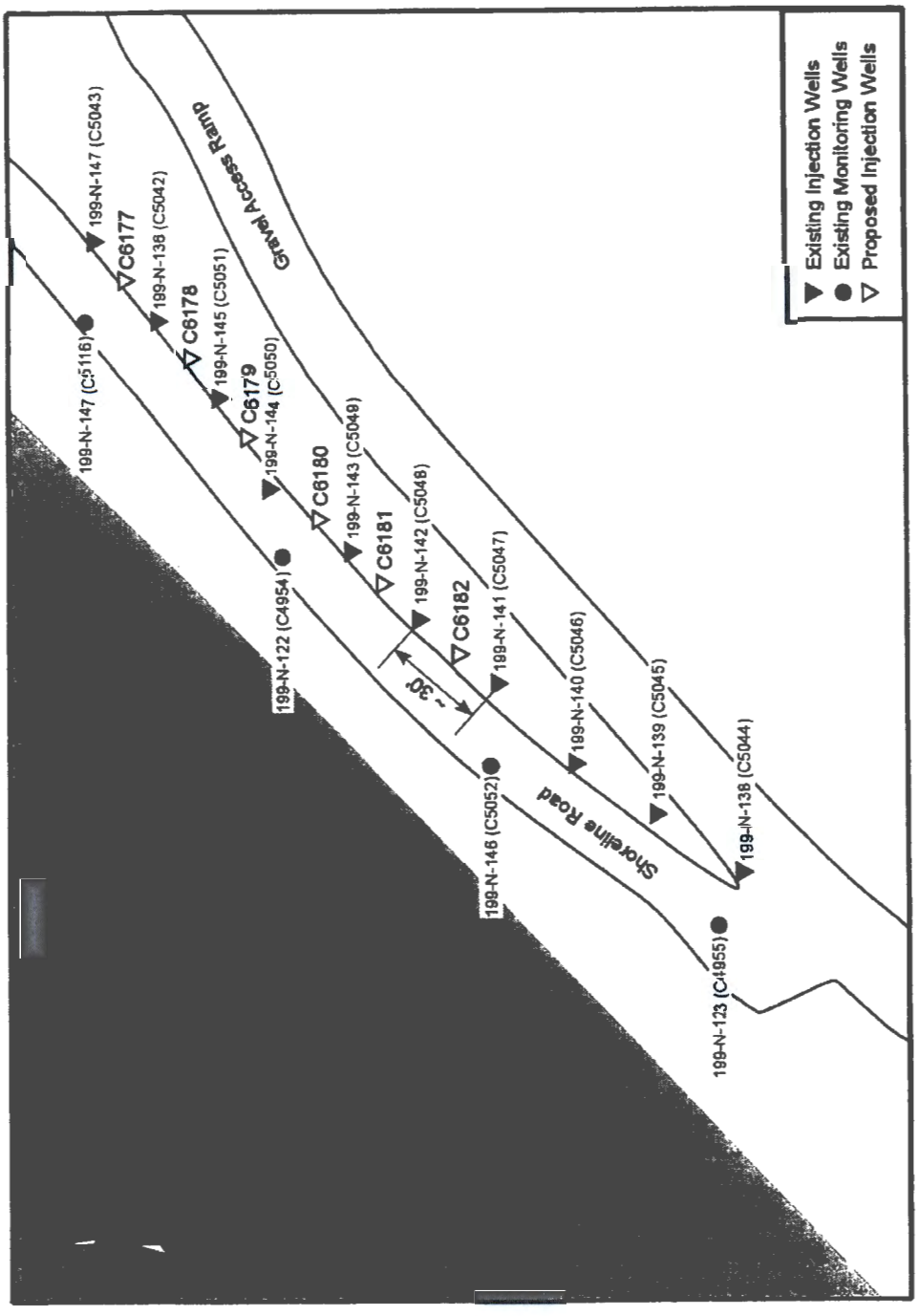
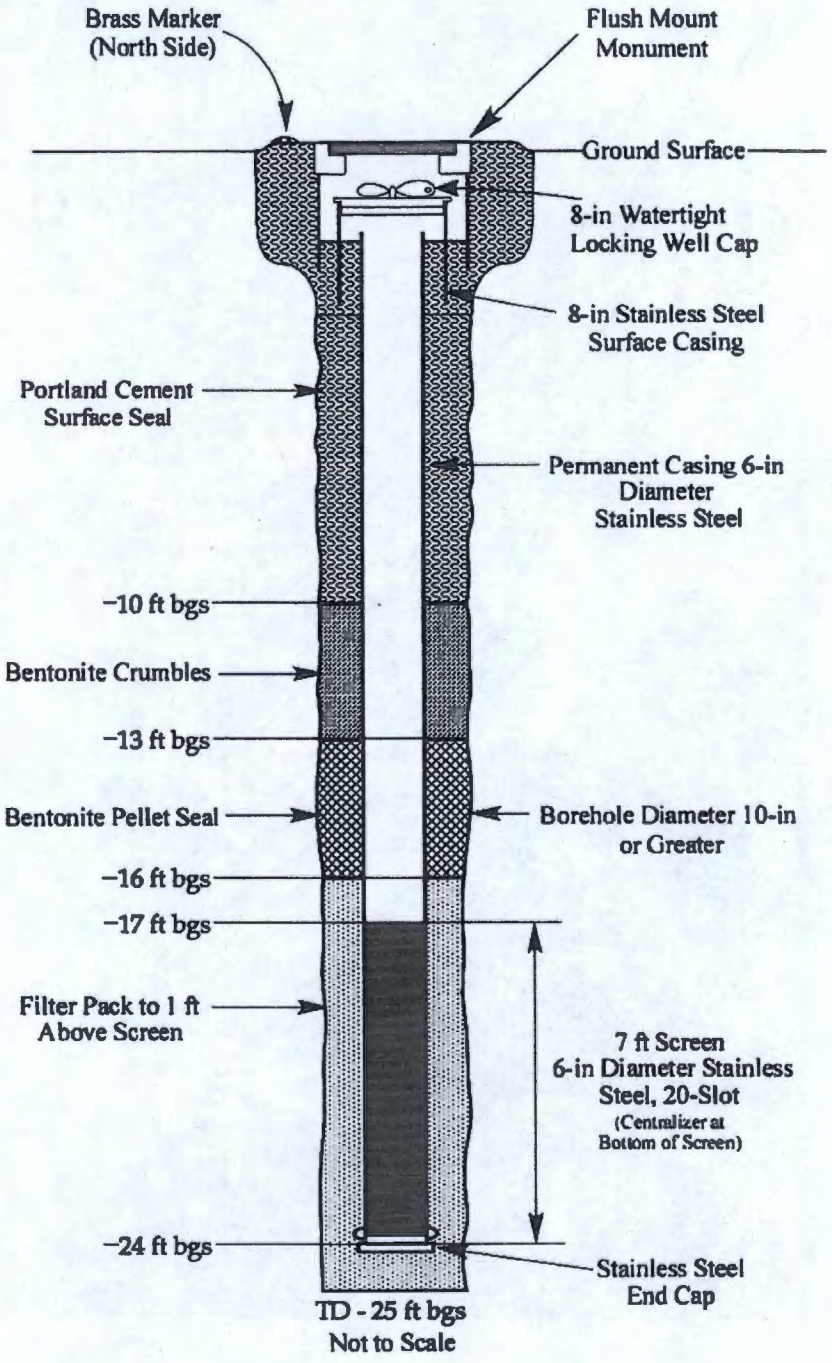


Figure 2-3. Well Completion Design for 100-NR-2 Injection Wells.



(2)

Field Test Instruction

100-NR-2 Apatite PRB Treatability Test for Sequestration of Sr-90

High Concentration Pilot-scale Injection Testing

Purpose

The objective of this field test instruction is to provide technical guidance for conducting high concentration pilot-scale field tests in support of the 100-NR-2 Treatability Test Plan Addendum, DOE/RL-2005-96, Rev 0, hereafter referred to as the TTP. The TTP supports the Federal Facility Agreement Consent Order, Milestone M-16-06-01 ("Complete Construction of a Permeable Reactive Barrier at 100-N"). These injections will occur at both the upstream (199-N-138) and downstream pilot test site locations (199-N-137 and 199-N-159). Results from these injection testing activities will be used to develop an injection design for high concentration chemical treatment of the 300-ft apatite permeable reactive barrier.

Summary

Field testing at the 100-N Area Apatite Treatability Test Site showed that the barrier can be categorized by two general hydrologic conceptual models based on the overall well capacity and contrast between the Hanford and Ringold hydraulic conductivities. The upstream portion, between injection wells 199-N-138 and 199-N-141 (Figure 1), was characterized by relatively low overall well specific capacity estimated from well development data and a lower contrast in hydraulic conductivity between the Hanford and Ringold. The downstream portion, between injection wells 199-N-142 and 199-N-137, was characterized by generally higher well specific capacity and a larger hydraulic conductivity contrast between the Hanford and Ringold Formations (with the Hanford hydraulic conductivity values greater in the downstream portion than the upstream portion). The implication of this is that injections in the downstream portion of the barrier have to be done in two phases- one to treat the Ringold Formation, and one to treat the Hanford formation. On the upstream portion, adequate treatment can be achieved by injecting in a single well screened across both formations. For this reason, the pilot test outlined in this field test instruction will be conducted as three distinct injections. Treatment of the Hanford and Ringold formations will occur during a single injection operation at the upstream pilot test site (199-N-138). The Ringold Formation will be treated concurrently through a separate injection at a newly installed Ringold-only injection well at the downstream pilot test site location (199-N-159). At the conclusion of these two injections, treatment of the Hanford formation will occur at the downstream pilot test site location using well 199-N-137. The remainder of this test instruction provides details for conducting these injections.

Injection Design

The following description provides details on the injection design for conducting the pilot-scale apatite injection testing for the high concentration formulation. It should be emphasized that these pilot-scale tests are a scoping effort that will be used to establish the protocol for future barrier injections. Accordingly, conditions for the test may be changed or adjusted as the pilot tests proceeds, depending on input from on-going laboratory work and modeling, and the judgment of the PNNL and FH technical project leads. Thus detailed instructions for conducting the pilot scale injection tests will not be available beforehand, nor should they be expected.

The pilot test sites both consist of a central 6-in diameter injection well surrounded by small diameter monitoring wells as well as downgradient aquifer tubes to provide additional monitoring points (Figure 1). Water level transducers and sampling pumps for collection of groundwater samples will be placed in the monitoring wells to monitor water level during injection and to collect water samples (used to determine when the apatite solution arrives at the monitoring wells). Based on injection well hydraulic performance observed during previous barrier treatment operations, an injection rate of 40 gpm will be specified during treatment of the upstream portion of the barrier and during Hanford formation targeted treatment of the downstream portion of the barrier. However, injection rates may need to be reduced in the newly installed Ringold-only injection wells, depending on the hydraulic performance of these wells.

Based on chemical arrival responses observed during previous barrier treatment operations, an injection volume of 120,000 gallons of apatite forming chemical solution will be specified, which should provide sufficient volume to meet injection design criteria at the targeted radial extent of 20 ft. Over the upstream portion of the barrier, a single 120,000 gallon injection will be conducted to treat the Hanford and Ringold formations simultaneously. Over the downstream portion of the barrier, two separate injection operations of approximately 60,000 gallons each will be required for targeted treatment of the Hanford and Ringold formations. Both the upstream portion of the barrier and the Hanford interval over the downstream portion of the barrier needs to be treated during high Columbia River stage conditions to treat as high in the Hanford formation profile as possible. Treatment of the Ringold-only injection wells can be conducted during any river stage condition; however periods with steep increases or decreases in river stage should be avoided due to the large hydraulic gradients generated during these times directed inland or towards the river.

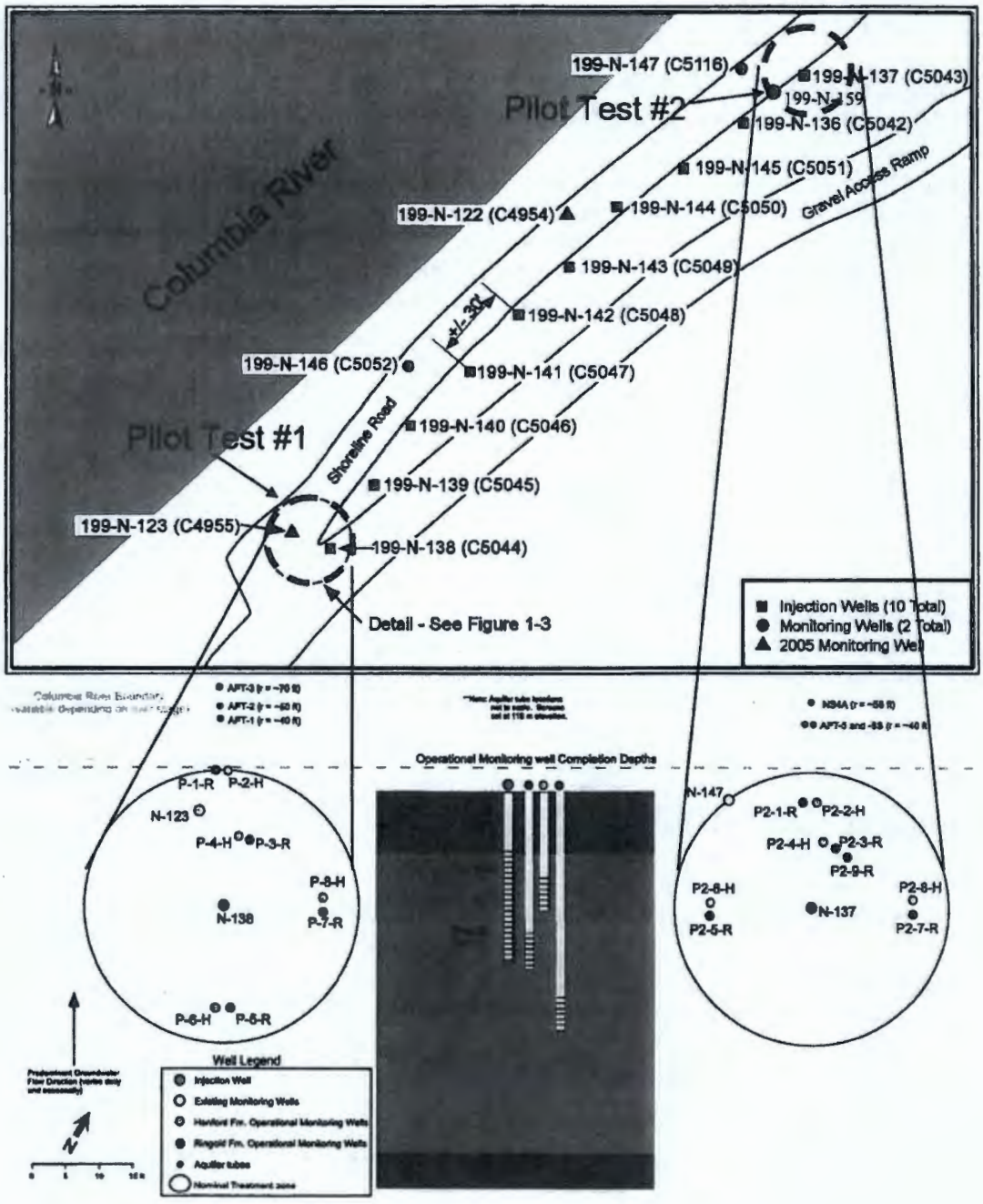


Figure 1. Apatite PRB Treatability Test Well Location Map.

Chemical Formulation

Solution Composition

Following is the recipe for the high concentration apatite injection solution:

9.0 mM trisodium citrate [HOC(COONa)(CH2COONa)2*2H2O] FW 294.1 g/mol
- also called sodium citrate dihydrate, ACS registry **6132-04-3**
- granular is more soluble than powdered
- reagent grade (quality) or equivalent for the citrate: USP/FCC (lower grades contain up to 5 ppm heavy metals)

3.6 mM calcium chloride, [$CaCl_2$], FW 110.98 g/mol
- reagent grade (quality) or equivalent: certified ACS, ACS registry **10043-52-4** (lower grades can contain 20 ppm lead)

32.4 mM disodium hydrogenphosphate [Na_2HPO_4], FW 141.96 g/mol
- also called disodium phosphate, anhydrous
- reagent grade (quality) or equivalent: certified ACS, ACS registry **7558-79-4** (lower grades can contain extra NaOH, which is only a small problem, changes pH and ionic strength)

5.6 mM sodium dihydrogenphosphate [NaH_2PO_4], FW 119.98 g/mol
- also called monosodium phosphate, anhydrous
- reagent grade or equivalent: certified ACS grade, ACS registry **7558-80-7** (lower grades can contain 8 ppm arsenic and 10 ppm heavy metals)

2.0 mM diammonium hydrogenphosphate [$(NH_4)_2HPO_4$], FW 132.1 g/mol
- also called diammonium phosphate
- granular is more soluble than powdered
- reagent grade (quality) or equivalent: certified ACS, ACS registry **7783-28-0**

1.0 mM sodium bromide [NaBr], FW 102.90 g/mol
- reagent grade (quality) or equivalent: certified ACS, ACS registry **7647-15-6**

At these molar concentrations, a 120,000 gal injection volume will consist of the following dry chemical weights:

Mix #1: (Ca/citrate in deionized water, minimum solution volume of 10,000 gallons)
2645 lbs of trisodium citrate
399 lbs of calcium chloride

Mix #2: (PO4/Br in deionized water, minimum solution volume of 10,000 gallons)
4596 lbs of Disodium hydrogenphosphate
671 lbs of Sodium dihydrogenphosphate
264 lbs of Diammonium hydrogenphosphate
103 lbs of Sodium bromide

Because we are relying on microbial degradation of the citrate for apatite formation to occur, make up water for these solutions should not contain residual chlorine or any other form of bactericide. Make up water will be from the Columbia River immediately upstream of the injection site.

Solution Stability Concerns

Solubility limits for each of the apatite solution components, based on laboratory evaluation and relevant solubility limits reported in the literature, are provided in Table 1. Minimum delivery volumes indicated above (10,000 gal) shall be maintained to avoid chemical precipitation during transport.

Mix #1 (trisodium citrate and calcium chloride) should be mixed up by completely dissolving the trisodium citrate first, then adding the calcium chloride. When making up Mix #2, disodium hydrogenphosphate, (FW 141.96) is soluble in 8 parts of water and hence should be added first in, at a minimum, 8 times the volume of water to mass of chemical used. Next diammonium hydrogenphosphate should be added (solubility 1g/1.7 mL water) followed by sodium bromide (1g/1.1 mL water) and finally sodium dihydrogenphosphate which is freely soluble. The criteria provided in Table 1 will result in a solution that is stable at both room temperature and 5°C for > 3 days (this solution is thermodynamically stable and should not form a precipitate).

Table 1. Solution Stability Criteria.

Apatite Solution Components	Max Conc. (mM)
trisodium citrate	120
calcium chloride	48
disodium hydrogenphosphate	526.5
sodium dihydrogenphosphate	91
diammonium hydrogenphosphate	32.5
sodium bromide	65

Another stability concern is the potential for biodegradation of the citrate solution during transport. Potential mitigation approaches include, but are not limited to, steam cleaning or some other sterilization approach of dissolving/mixing equipment, using distilled make-up water, filter sterilization (0.2 micron) of make-up water, UV sterilization of make-up water, and chilling the solution for transport. The approach should follow industry standards for citrate solution transport that assures the citrate solution will not be appreciably degraded during transport or during the 48 to 60 hrs it takes to inject the solution.

Order of Treatment

The first two phases of this pilot test will occur simultaneously. These phases will include treatment at the upstream pilot test site and treatment of the Ringold Formation at the downstream pilot test site. There should be no hydraulic interferences between the

two injections as the injection wells are 300 foot apart. The third phase of the test will be treatment of the Hanford formation at pilot site 2.

Materials and Equipment.

The minimum requirements for equipment and materials as specified in the Engineering Design Criteria together with additional sampling related materials and equipment are listed as follows.

- Generator
- Pumps, fire hose, flow meters and shutoff/control valves
- Makeup water source (river water)
- Apatite solution delivered to site in tanker trucks. Exact weights and chemical formulation will be provided to the vendor in a supplemental SOW.
- 600-gallon purge water containment tank
- Coolers and/or refrigerator for sample storage
- Sample trailer and monitoring equipment (QED flow through cell with pH, ORP, DO, T, EC), HACH kit for field screening phosphate measurement.
- Submersible or peristaltic sample pumps and 1000 ft of ¼ or 1/8 inch poly tubing
- Pressure transducers
- Personnel safety equipment and materials (gloves, eye wear, eye wash, etc.)

Test Monitoring

- The chemical delivery system will be monitored on a regular basis to maintain appropriate flow rates. Measurements of system readings (flow, pressure) will be made on an hourly basis (nominally). Additionally, measurements of temperature, specific conductance (EC), pH and oxidation reduction potential (ORP) of the injection stream will be measured and recorded on an hourly basis.
- Pressure will be monitored in the injection well and as many surrounding monitoring wells as possible. Routine visual inspection of surface seal will be performed during the injection.
- An inflatable packer will be used to allow for an acceptable injection rate
- Primary monitoring of apatite solution arrival/distribution during the injection test will be through the collection of aqueous samples
    - Samples will be collected from the injection stream every four hours
        - Field parameters (EC, T, pH, ORP, DO) will be measured for each sample
        - Aqueous samples will be collected and submitted for IC (anions) and ICP-OES (major cations), and citrate (PNNL lab) analysis
        - At least 1 set of tanker samples will be submitted for IC, ICP-OES, and citrate analysis for each individual tanker truck.
    - Samples will be collected from monitoring wells and aquifer tubes on a routine basis, beginning with a baseline sampling event prior to chemical

injection. The sampling frequency will vary depending on solution arrival dynamics, and will be adjusted during the test. For example, the wells closer to the injection well will be monitored more frequently initially, then less frequently once the EC indicates complete arrival of the injection solution. Nominally, a sampling frequency of once every four hours will be used until sufficient evidence for a change is obtained.

- For each sample, field parameters will be recorded for each sample (EC, T, pH, ORP, DO).
- Aqueous samples will be collected and submitted for IC (anions) and ICP-OES (major cations), and citrate (PNNL lab) analysis

- Primary performance monitoring will be through the collection of aqueous samples (Fluor Hanford responsibility).
  - Field parameters (EC, T, pH, ORP, DO) will be measured for each sample collected.
  - Aqueous samples will be submitted for the following analysis:
    - IC – anions and small molecular weight organic acids
    - ICP-OES – major cations
    - Gross Beta

Sampling and Analysis

Water will be pumped from the wells at a nominal rate of 1 gpm. Based on an assumption that 50 ft of sample tubing running from each well to a sampling manifold located in a sample trailer, approximately 2 minutes of purge time will be sufficient time for parameter stabilization prior to each sample collection event. This is consistent with previous pilot tests.

Once field parameters (pH, EC, DO , ORP, and T) have stabilized, indicating that representative groundwater samples can be collected, parameter values will be recorded manually on data sheets which will be copied for distribution. The original data sheets will be pasted into a bound (FH controlled) field notebook at the earliest convenience following the test. Calibration of field probes will occur once (immediately prior to the test) and will follow the manufacturer's instructions using standard calibration solutions provided by the vendor or as prepared under standard laboratory practice in the GRP 200 Area Field lab or PNNL laboratories.

The sample stream will be discharged to a purgewater containment tank(s). Routine purgewater collection and disposal will be required throughout these planned field activities.

Sample collection and analysis for the planned apatite injections will be performed according to the guidelines set forth in Tables 1 through 3. It should be noted that the operational and performance monitoring approach and sampling requirements described in this section may be altered based on the results of ongoing bench-scale studies and observations made during other injection operations. This test instruction applies

treatment and the sampling immediately following treatment. For long-term monitoring instructions, refer to the addendum to the Strontium-90 Treatability Test Plan for 100-NR-2 Groundwater Operable Unit (DOE-RL-2005-96).

Pumping Rates and Pressures

The Apatite solution will be injected until the total design volume (not to exceed 120,000 gallons) has been injected into the test well. Thus, it is anticipated that ~50 hours of continuous pumping will be needed to inject the entire volume. Actual volumes and test duration shall be at the discretion of the PNNL field task lead in accordance with roles and responsibilities specified in Reference 1.

Data Management

All operational, monitoring, and field parameter probe calibration data will be recorded manually on data sheets which will be copied for distribution to FH and PNNL personnel. The original data sheets will be pasted into a bound (FH controlled) field notebook at the earliest convenience following the test. All samples submitted to analytical laboratories will be accompanied by an appropriately filled out chain of custody form.

Health and Safety

All work performed on site will be conducted in accordance with the apatite treatability study Health and Safety plan and any applicable task specific JSA (FH developed documents). Gloves and eye protection are needed while handling chemicals and during sample collection. A portable eye wash station will be present during the sample collection and tracer mixing process. Spillage and drops of sample media will be absorbed on tissue and kept in a separate bag for RCT survey/release at the end of the test.

Table 1. Apatite Pilot Test Sampling Requirements (Primary analytes shaded)

Parameter	Media/ Matrix	Sampling Frequency	Volume/ Container	Preservation	Holding Time
Major Cations/metals: Al, As, B, Ba, Bi, [redacted] Co, Fe, K, Mg, Mn, Ni, Zn, Zr, P, Sr, [redacted], Si, S, Sb	Water	See Table 2	20 ml plastic vial	Filtered (0.45 µm), HNO_3 to pH <2	60 DAYS
Anions: Cl^-, [redacted], SO_4^{2-}, [redacted], NO_2^-, NO_3^-	Water	See Table 2	20 ml plastic vial	Cool 4°C	45 DAYS
Small Molecular Weight Organic Acids: [redacted], Formate	Water	See Table 2	20 ml plastic via	Filtered (0.22 µm), Sodium Azide, or freeze	20 Days
Sr-90 – PNNL Lab	Water	See Table 2	1 L plastic bottle	Filtered (0.45 µm), HNO_3 TO PH <2	60 Days
Gross Beta	Water	See Table 2	1 L plastic bottle	Filtered (0.45 µm), HNO_3 TO PH <2	60 Days
Field Parameters (pH, Specific Conductance, Dissolved Oxygen [a], Oxidation-Reduction Potential, Temperature)	Water	With every water sample, and as deemed necessary during injection. See Table 2	Field Measurement	None	n/a
(a) Dissolved oxygen measured in monitoring wells only. Not required for measurements of injection stream.					

Table 2. Sampling Locations and Frequencies

Sample Purpose	Sampling Locations	Sampling Frequency	Analytes	Responsible Contractor
Baseline Monitoring	Injection Wells, monitoring wells, compliance wells	1 time prior to treatment	Cations, Anions, gross beta, Sr-90, field parameters	FH
Injection Monitoring	Injection stream, monitoring wells, adjacent injection wells, compliance wells, aquifer tubes	Nominally once every four hours. Aquifer tubes only near end of injection	Cations, Anions, organic acids, field parameters	PNNL
Performance Monitoring	Injection Wells, monitoring wells, compliance wells	Daily for 1st week, every other day for 2nd week, 1x per week for one month.	Cations, Anions, organic acids, gross beta, field parameters, Sr-90 splits immediately after and one month after treatment	FH
Injection Wells: N-137 and N-138 Injection Stream: sampled at injection skid Monitoring Wells: P-1-R, P-2-H, P-3-R, P-4-H, P-5-R, P-6-H, P-7-R, P-8-H, P2-1-R, P2-2-H, P2-3-R, P2-4-H, P2-5-R, P2-6-H, P2-7-R, P2-8-H, P2-9-R Adjacent Injection Wells: N-136 and N-139 Compliance Wells: N-123 and N-147 Aquifer Tubes: APT-1, APT-5				

Table 3. Analytical Requirements (Primary analytes shaded)

Parameter	Analysis Method	Detection Limit or (Range)	Typical Precision/Accuracy	QC Requirements
Major Cations / metals: Ca, Fe, K, Mg, P, Sr, Si, S,Al, B, Ba, Bi, Ni, Zn, Zr, Sr	ICP-OES, EPA Method 6010B or equivalent	1 mg/L 0.1 mg/L	±10%	Daily calibration; blanks and duplicates and matrix spikes at 10% level per batch of 20.
Anions: Cl^-, Br^-, SO_4^{2-}, PO_4^{3-}, NO_2^-, NO_3^-	Ion Chromatography, EPA Method 300.0A.or equivalent	1 mg/L	±15%	Daily Calibration; Blanks And Duplicates At 10% Level Per Batch Of 20.
Small molecular weight organic acids: Citrate and formate	Ion Chromatography, AGG-IC-001 (Based on EPA Method 300.0A.)	1 mg/L	±15%	Daily Calibration; Blanks And Duplicates At 10% Level Per Batch Of 20.
Sr-90 – PNNL Lab	separation followed by gross alpha/beta via liquid scintillation	75 pCi/L	±15%	Daily Calibration; Blanks And Duplicates At 10% Level Per Batch Of 20.
Gross Beta	Liquid Scintillation	5 pCi/L	±20%	Daily Calibration
pH	pH electrode	(2 to 12 units)	± 0.2 pH unit	User calibrate, follow manufacturer recommendations
Specific conductance	Electrode	(0 to 100 mS/cm)	± 1% of reading	User calibrate, follow manufacturer recommendations
Dissolved oxygen	Membrane electrode	(0 to 20 mg/L)	± 0.2 mg/L	User calibrate, follow manufacturer recommendations
Oxidation-Reduction Potential	Electrode	(-999 to 999 mV)	±20 mV	User calibrate, follow manufacturer recommendations
Temperature	Thermocouple	(-5 to 50 °C)	± 0.2°C	Factory calibration

Summary of Test Instructions

- Collect baseline samples prior to chemical injection
  - Field parameters and performance monitoring samples
- Begin chemical injection
  - 1 gal/min each chemical
  - 38 gal/min water
  - 40 gal/min total solution injection rate
- Measure field parameters in available site monitoring wells
- Measure field parameters on skid every hour
- Collect aqueous samples for analysis with each field parameter measurement
- Conduct performance monitoring post injection (FH samplers)