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Richland, Washington 99352

0073863

AUG 3 1 2007

07-AMCP-0266

Ms. Jane A. Hedges, Program Manager
Nuclear Waste Program
State of Washington
Department of Ecology
3100 Port of Benton
Richland, Washington 99354

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EDMC

Dear Ms. Hedges:

COMPLETION OF HANFORD FEDERAL FACILITY AGREEMENT AND CONSENT ORDER (TRI-PARTY AGREEMENT) MILESTONE M-16-14A, "COMPLETE CONSTRUCTION OF A PERMEABLE REACTIVE BARRIER AT 100-N" AND COMPLETION OF CALENDAR YEAR 2007 CONSTRUCTION ACTIVITIES AT THE 100-N SEQUESTRATION BARRIER

The purpose of this letter is to formally notify the State of Washington Department of Ecology that the U.S. Department of Energy, Richland Operations Office completed Tri-Party Agreement Milestone M-16-14A, Complete Construction of a Permeable Reactive Barrier at 100-N. Completion of this milestone has previously been documented during the 100 Area Project Manager Meetings and the Central Plateau Tri-Party Agreement Milestone Reviews. Tri-Party Agreement Milestone M-16-14A required the U.S. Department of Energy, Richland Operations Office to complete the first set of low-concentration injections to emplace apatite along a 300 foot stretch of the Columbia River in accordance with the approved 100-NR-2 Treatability Test Plan, DOE/RL-2005-96, Revision 0, by May 31, 2007. The injection of apatite forming solutions in ten wells, forming the 300 foot apatite permeable reactive barrier, was completed on March 22, 2007, two months ahead of the milestone. Subsequent low-concentration injections were conduced in June 2007 targeting the aquifer in the Hanford Formation and underlying Ringold Formation. In accordance with the 100-NR-2 Treatability Test Plan, further injections utilizing higher-concentration apatite forming solutions will occur in Calendar Year 2008 to add robustness to the barrier.

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The 100-NR-2 Apatite Barrier Construction Completion Summary (attached), documents the full scope and supporting data for the barrier construction performed in Calendar Year 2007. Initial results indicate that the barrier was successfully emplaced and the technology shows promise in meeting the Strontium-90 reduction goals prescribed in the 100-NR-2 Treatability Test Plan.

If you have any questions, please contact me, or your staff may contact Briant Charboneau, of my staff, on (509) 373-6137.

Sincerely,

Matthew S. McCormick, Assistant Manager
for the Central Plateau

AMCP:KMT

Attachment

cc w/attach:
G. Bohnee, NPT
L. Buck, Wanapum
N. Ceto, EPA
L. J. Cusack, Ecology
R. H. Engelmann, EFSH
S. Harris, CTUIR
R. Jim, YN
S. L. Leckband, HAB
K. Niles, ODOE
R. E. Piippo, FHI
J. G. Vance, FFS
Administrative Record M-16-14A
Environmental Portal 100-NR-2

Title: **100-NR-2 Apatite Barrier Construction Completion Summary**

Author: R.J. Fabre, Fluor Hanford

Approval: J.V. Borghese, River Corridor Remedial Action Manager

Jane V Borghese 8/27/07
Signature Date

100-NR-2 Apatite Barrier Construction Completion Summary

Purpose

Efforts to reduce the flux of strontium-90 (^{90}Sr) to the Columbia River from past-practice liquid waste disposal sites have been underway since the early 1990s in the 100-N Area at the Hanford Site. Termination of all liquid discharges to the ground by 1993 was a major step toward meeting this goal. However, ^{90}Sr adsorbed on aquifer solids beneath the liquid waste disposal sites and extending to beneath the near-shore riverbed remains as a source of contaminates in the groundwater and the Columbia River.

The remedy specified by the framers of the *Interim Remedial Action Record of Decision for the 100-NR-1 and 100-NR-2 Operable Units of the Hanford 100-N Area* (Ecology, 1999) included operation of a pump-and-treat system as well as a requirement to evaluate alternative ^{90}Sr treatment technologies. It was recognized from the onset that pump-and-treat was unlikely to be an effective treatment method because of the geochemical characteristics of the ^{90}Sr, the primary contaminant of concern. Subsequent performance monitoring has confirmed that the pump-and-treat was not effective. Accordingly, the first Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) five-year review re-emphasized the need to aggressively pursue alternative methods to reduce impacts on the Columbia River.

With the presentation of the *Evaluation of ^{90}Sr Treatment Technologies for the 100-NR-2 Groundwater Operable Unit* (Letter Report) at the December 8, 2004 public meeting, DOE and Ecology agreed that the long term strategy for groundwater remediation at 100-N will include apatite sequestration as the primary treatment, followed by a secondary treatment or polishing step if necessary. Since that time the agencies have worked together to agree on 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 interim remedy and selected for field testing. Plans began 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 purpose of this construction summary report is to document the progress of the barrier construction in support of the *Strontium-90 Treatability Test Plan for 100-NR-2 Groundwater Operable Unit*, DOE/RL-2005-96, Rev. 0 (DOE-RL,2005), hereafter referred to as the TTP. The TTP supports the Federal Facility Agreement Consent Order, Milestone M-016-14A (Complete Construction on a 300 foot Permeable Reactive Barrier Utilizing Apatite Sequestration at 100-N as Described in "*Stontium-90 Treatability Test Plan for 100-NR-02 Groundwater Operable Unit*" DOE-RL-2005-96, Draft "A" (Ecology, EPA and DOE, 1889). These injections will mark completion of the initial treatment (low concentration only) of all ten wells forming the 300-ft apatite permeable reactive barrier.

Ringold Formation Pilot Tests and Treatment

Ringold Formation Treatments

The first pilot scale test, which was conducted in well 199-N-138 (Figure 1), involved injecting 96,000 gal of a dilute apatite-forming chemical solution (10 mM sodium citrate, 3.7 mM calcium chloride 2.4 mM sodium/disodium phosphate and 1 mM ammonium nitrate) into a single injection well at a pilot test site located on the upstream end of the proposed 300 ft apatite barrier. The first pilot injection test was conducted in June 2006, to demonstrate the strontium-90 sequestration process at a field scale and to assess any adverse water quality impacts (DOE-RL, 2005, page 4-18). This test was conducted during high river stage conditions to target both the upper Hanford Formation aquifer and underlying Ringold Formation aquifer.

The first pilot test was designed based on literature and laboratory testing in sediment columns at Pacific Northwest National Laboratory using NR-2 sediments collected at the test site. Preliminary results from the first field scale pilot test indicated that more calcium was present in aqueous solution in the test zone than was added, which was expected based on bench-scale testing results (i.e., Ca^{2+} desorbing from sediment). However, the amount of increase observed in the field experiment was greater than predicted from the laboratory studies, causing the mobilization of more adsorbed ^{90}Sr than was expected based on laboratory results. Subsequent laboratory tests were conducted to optimize the injection solution by minimizing the Na, Ca, and citrate concentrations in the treatment mixture and thereby minimize calcium and ^{90}Sr desorption.

Figure 1. Apatite Permeable Reactive Barrier (PRB) Treatability Test Well Location Map.

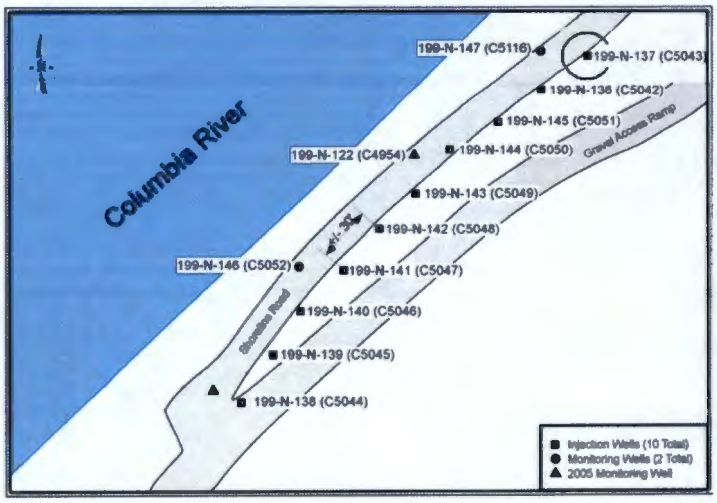
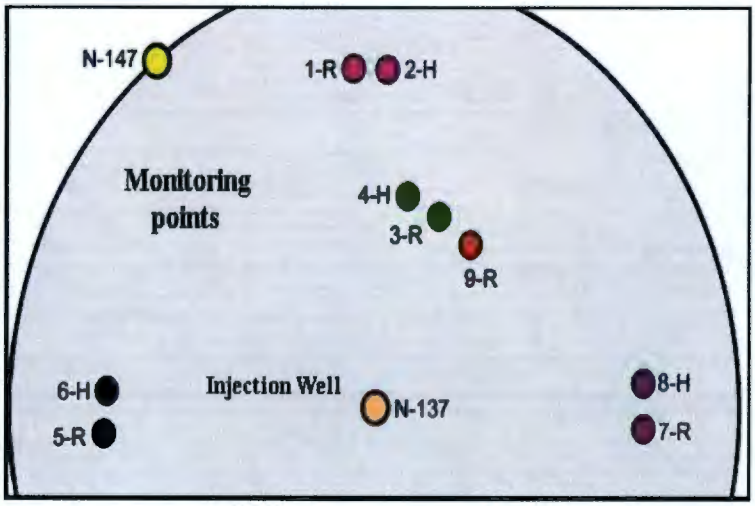


Figure 2. Injection and Monitoring points for Pilot Test Two (199-N-137)



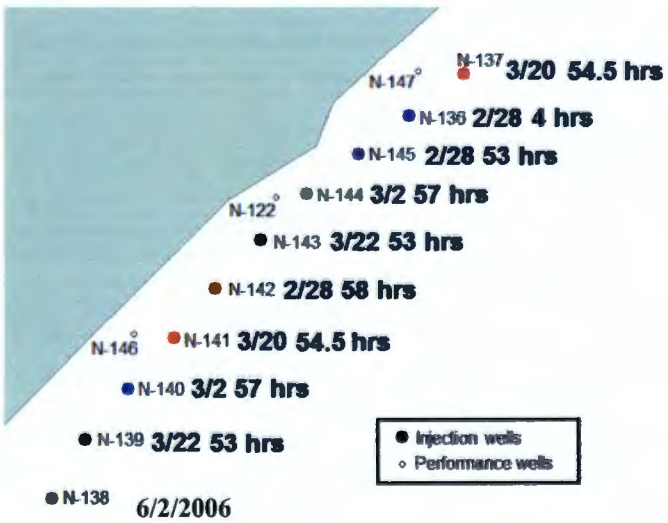
The objective of the second pilot test was to evaluate the performance of a modified apatite-forming solution. This test, which was conducted in well 199-N-137 (Figure 2) on September 27, 2006, was located at the far downstream end of the 300 ft barrier to avoid interference with the treatment zone from the first pilot test. The test array was similar to that used in the first pilot test. This test was conducted during low river stage conditions to target only the contaminated portion of the Ringold Formation. During the second pilot test, 60,000 gal of the modified formulation solution (5.0 mM sodium citrate, 2.0 mM calcium chloride, 2.4 mM diammonium phosphate, and 1 mM sodium bromide at pH 8.0) was injected. Following is a brief summary of the design modifications that were incorporated into the second pilot test and key findings based on pilot-scale field testing results:

- The injection design for Pilot test #2 was modified, in the following ways, based on results from the initial pilot test and subsequent bench scale testing
    - Apatite formulation was modified to account for Ca desorption from sediment and excess nitrogen (as nitrate) was removed to slow microbial degradation rate (some N still available for microbes from the ammonium).
    - Injection volume was reduced to account for anticipated lower river stage and subsequent reduction in treatment volume.
    - Treatment interval was comprised of ~ 3 m of Ringold Unit E and the lower portion of the Hanford formation (0.5 m static, 1 to 1.5 m under injection mounding conditions).
    - Maximize injection rate to overwhelm (i.e. minimize) PO_4 sorption kinetics and increase treatment at larger radial distances
- Initial injection rate was 80 gpm but reduced to 40 gpm after 3 hrs when, based on early arrivals in Hanford monitoring wells, it was determined that a disproportionate amount of flux was being lost to the Hanford formation. If continued, this would have resulted in ineffective treatment of the targeted Ringold interval
- It is likely that injection well inefficiency at the first pilot test helped to limit preferential flux into the higher permeability Hanford formation; this effect will be variable along the length of the barrier based on the efficiency of each injection well installation.

- Injection monitoring field parameter data indicate acceptable distribution of apatite forming chemicals during the second pilot test. However, future low water injections will require increased volume to account for loss to Hanford formation
- Indicators of microbial activity behind lagged relative to the first injection test, indicating that the removal of nitrate and reduction in citrate concentration in the new formulation, were effective in slowing the microbial degradation rate.
- Sr mobilization was significantly reduced by the modified injection recipe
    - Immediately following treatment at pilot test #1, ^{90}Sr concentrations increased on average by 10.5x within the treatment zone (ranged from no increase in the injection well to 25x)
    - Immediately following treatment at pilot test #2, ^{90}Sr concentrations increased on average by 3.3x within the treatment zone (ranged from no increase in the injection well to 6.2x)

Following the evaluation of bench- and field-scale results through completion of the second pilot-scale injection test, it was determined that additional bench-scale testing was required to develop a modified formulation that addressed treatment limitations identified for the formulation used in the second pilot test. Results from these laboratory tests indicated that the ratio of phosphate to calcium/citrate solution needed to be increased to a greater extent than the adjustment that was made to the formulation between the first and second pilot test. This new formulation was used during an initial barrier well treatment campaign which began on February 28, 2007 and ended on March 24, 2007. Ringold formation injection dates and durations are illustrated below (Figure 3). Injection in well 199-N-136 was halted after 4 hours when seeps were identified along the Columbia River bank. This was due, in part, to the high porosity of the Hanford formation. Specific conductivity increases in 199-N-136 during the injections in wells 199-N-137 and 199-N-145 indicated lateral movement of the chemical mixture through the lower portion of the barrier. This well (199-N-136) was again injected during the Hanford formation injection campaign for a full 48 hours.

Figure 3. Ringold Injections dates and Durations



Ringold Injection Construction Design

The following description provides details on the injection design that was used for conducting the initial apatite treatment of the Ringold formation at the 8 additional injection well locations. FH conducted these injections using the same approach followed during the two previous pilot tests, with modifications/amendments to the approach as indicated below.

Each of the 8 injection locations consists of a central 6-in diameter injection well and additional monitoring wells at several locations (i.e., adjacent to the pilot test site locations and where compliance monitoring wells are available). Water level transducers and sampling pumps for collection of groundwater samples were placed in the two adjacent injection wells, and where available, in the adjacent monitoring wells, to monitor water levels during injection and to collect water samples for determining when the apatite solution arrives at surrounding locations.

The Ringold injections were conducted during the low water period of the year and required less injected solution than during high water conditions.

To prevent impacting adjacent treatment zones before the apatite forming solutions have had sufficient time to fully react, the eight injections were conducted in phases, with each phase made up of alternating injection well locations along the length of the barrier. In addition, timing of the two injection phases insured a minimum of two weeks of reaction time between adjacent injections. The phased injection approach of the 8 injections wells (with the re-treatment of 199-N-137) and order of injection is summarized below:

	1st Injection	2nd Injection	3rd Injection
February 28	199-N-136	199-N-142	199-N-145
March 2	199-N-144	199-N-140	
March 20	199-N-137	199-N-141	
March 22	199-N-139	199-N-143	

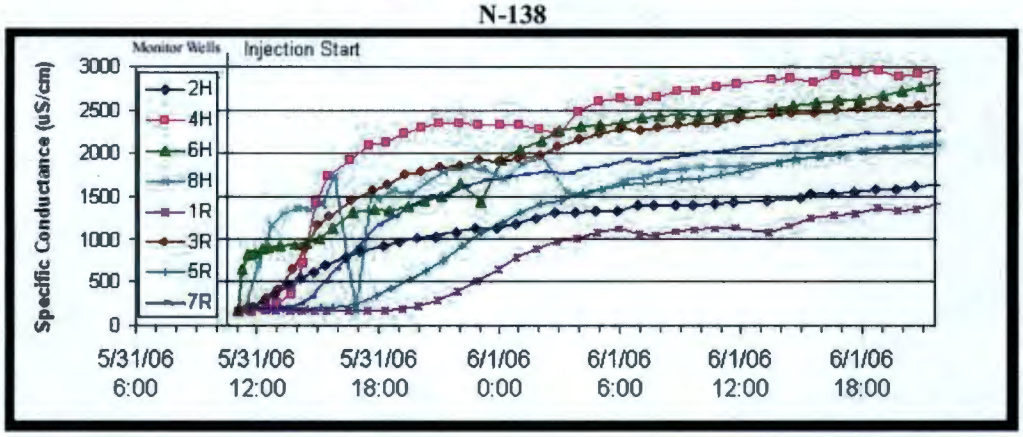
Well's 199-N-141, 199-N-137, 199-N-139, and 199-N -143 were treated on March 20 & 22, 2007 when the river stage reached and elevation 119.737 meters above sea level. The injection rates were adjusted and total chemical volume increased to compensate for the porosity of the Hanford formation. This adjustment was designed to treat both the Ringold and the Hanford formation. Since the river was not expected to reach the 119.737 meter level for the remainder of the year (2007), it would not prove beneficial to retreat these wells during the Hanford Injection campaign. The single injection will provide initial treatment with the remaining one meter of the Hanford formation to be treated during future injections or during the Apatite Infiltration Gallery work.

Injection Solution Specific Conductance

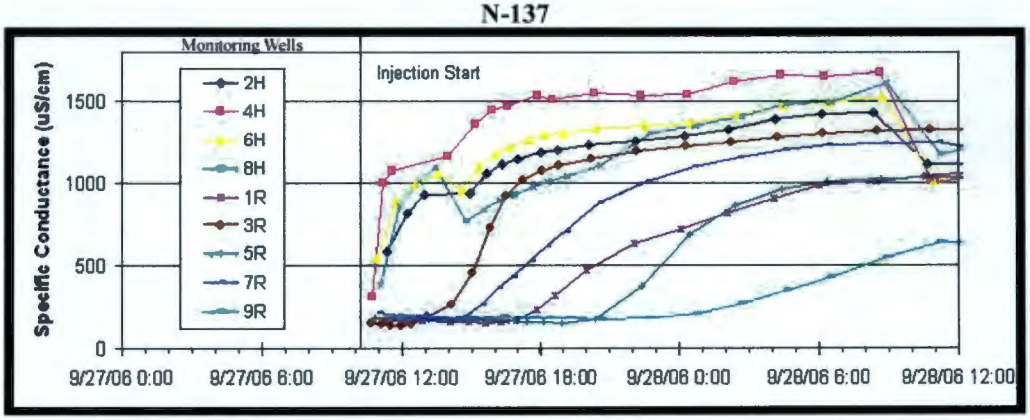
Specific conductance provides an effective parameter for monitoring the injection solution concentration. Based on laboratory studies, the specific conductance for the chemical mix used in these injections is to be 2520 µS/cm. An acceptable range for this is ± 50 µS/cm, (or 2470 to 2570 µS/cm). Changes in the conductance measurements in the groundwater at adjacent monitoring wells is also an effective method to determine solution arrival since the phosphate and calcium changes the electrolyte concentration, an increase readings indicates the infusion of the chemical mixture in the aquifer formation. The charts below show the specific conductance in the wells adjacent to the injections points. The adjacent well locations are denoted in the left side of the charts along with the specific conductivity. The increase value indicates arrival of the chemical solution. Normal average specific conductivity for the Columbia River is approximately 250 µS/cm. Beginning conductivity which is greater than the normal average readings are attributed to previous injections and residual solution which has not precipitated. As demonstrated by the graphs in Figure 4 the specific conductivity in the adjacent monitoring wells did increase during the course of the injections indicating the arrival of the chemical mixture in the required 20 foot area of impact.

Figure 4. Specific Conductivity in Barrier Wells

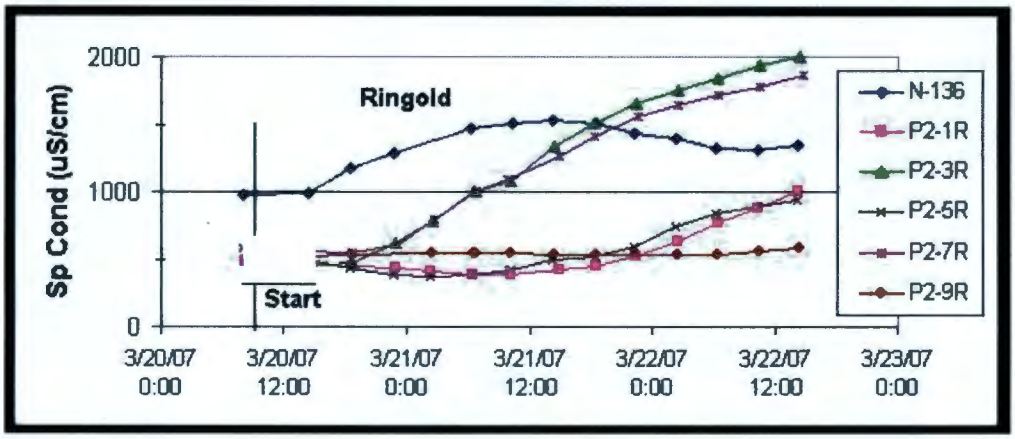
Pilot Test One Results
N-138

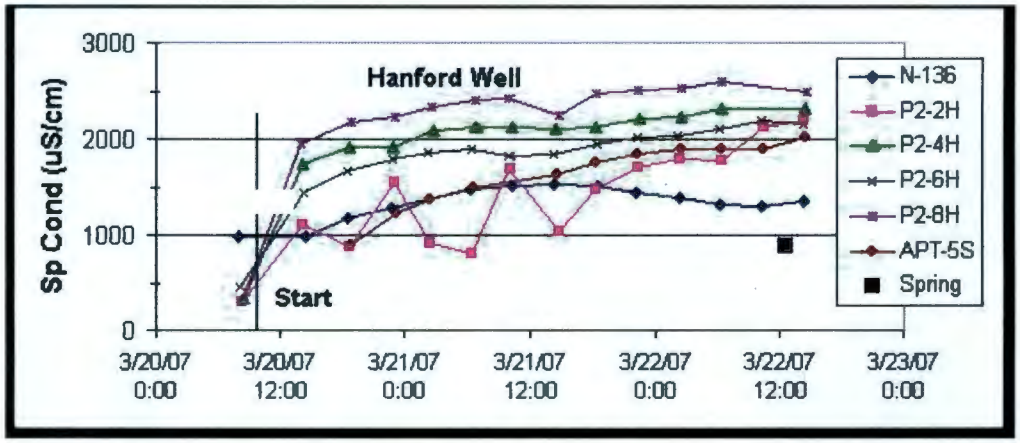


Pilot Test Two Results
N-137

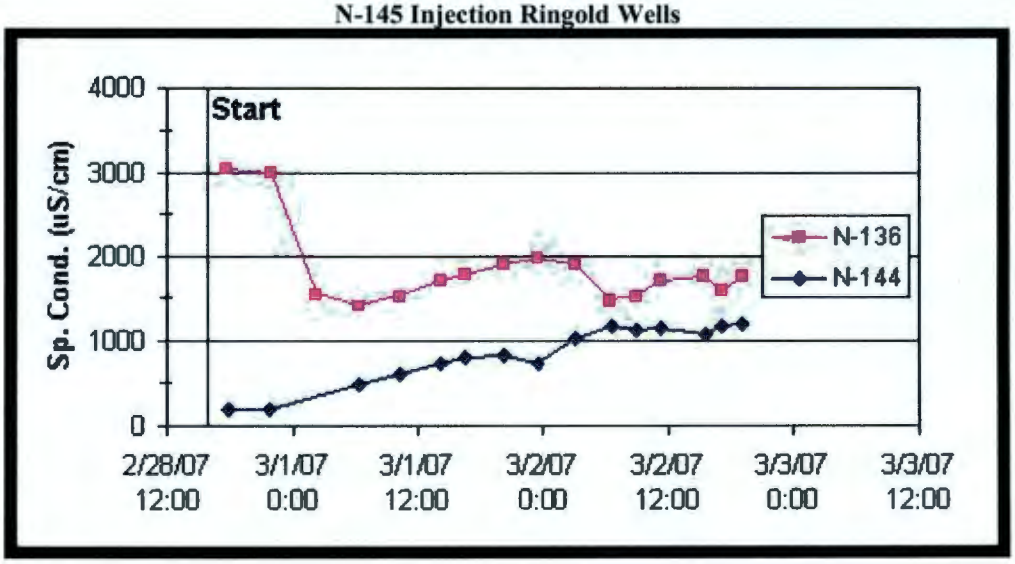


N-137 Injection Ringold Wells

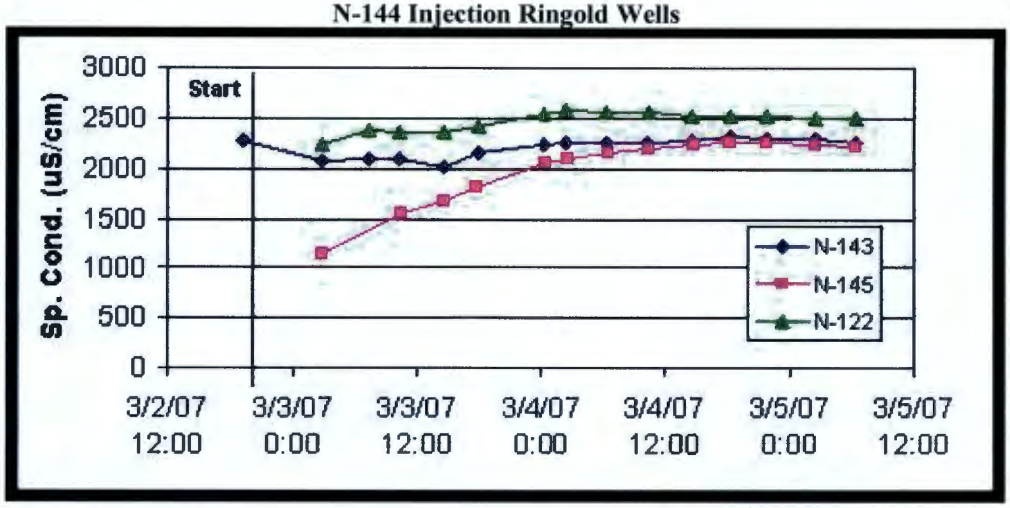




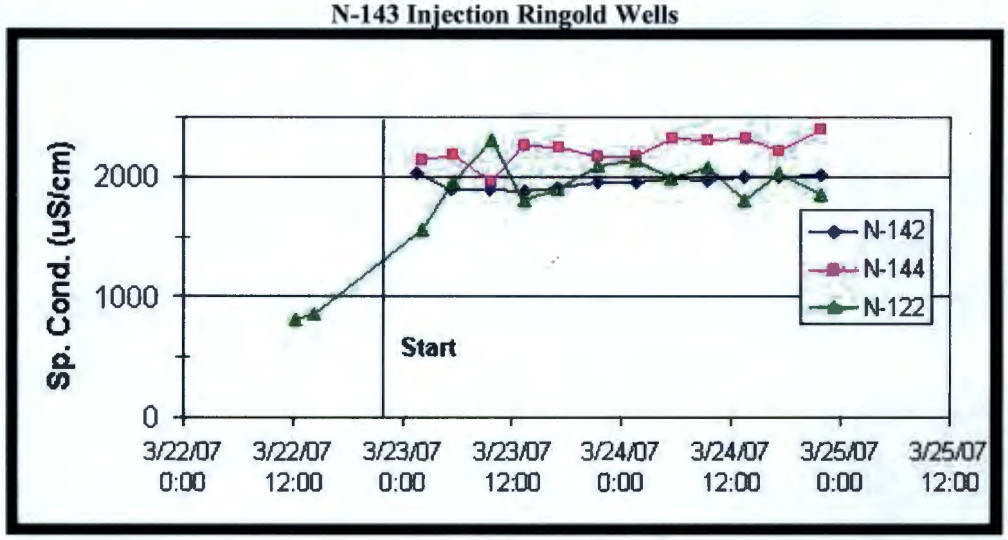
N-145 Injection Ringold Wells



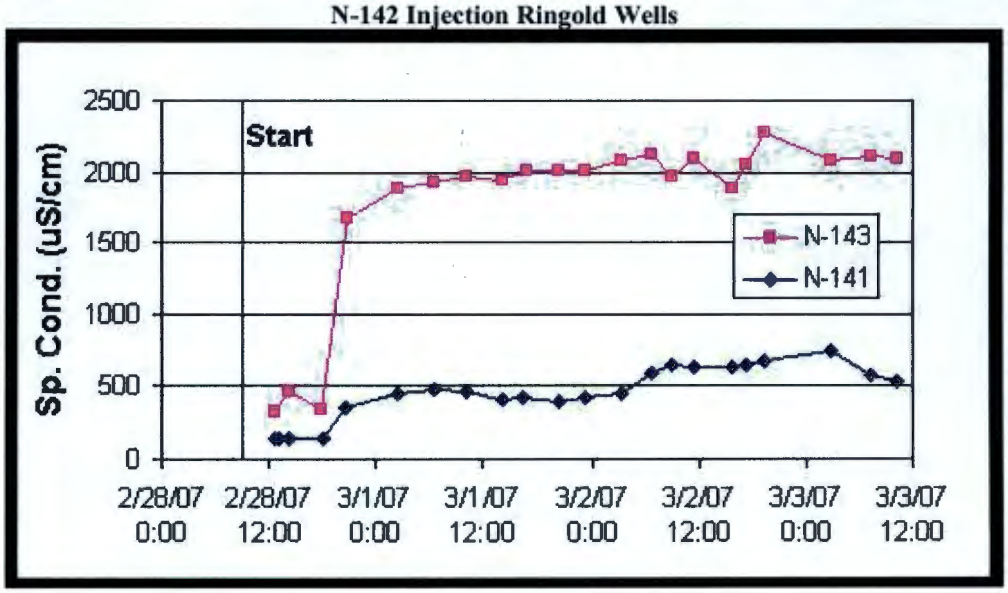
N-144 Injection Ringold Wells



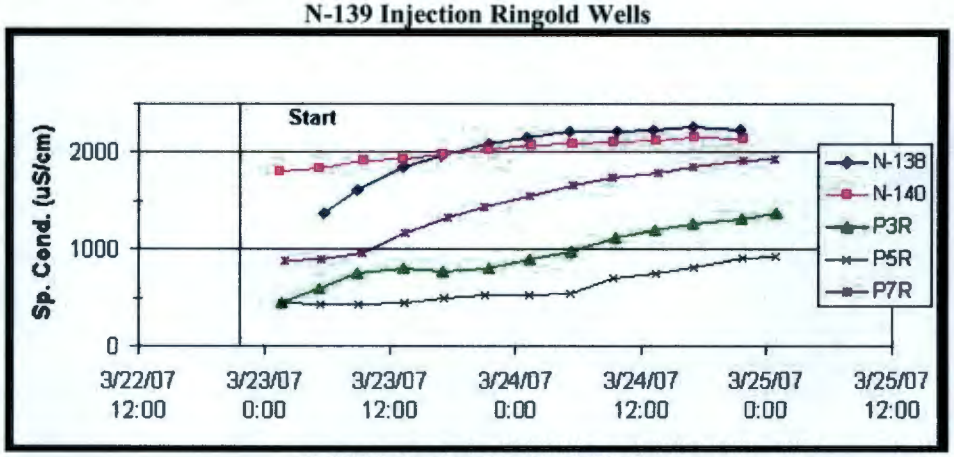
N-143 Injection Ringold Wells



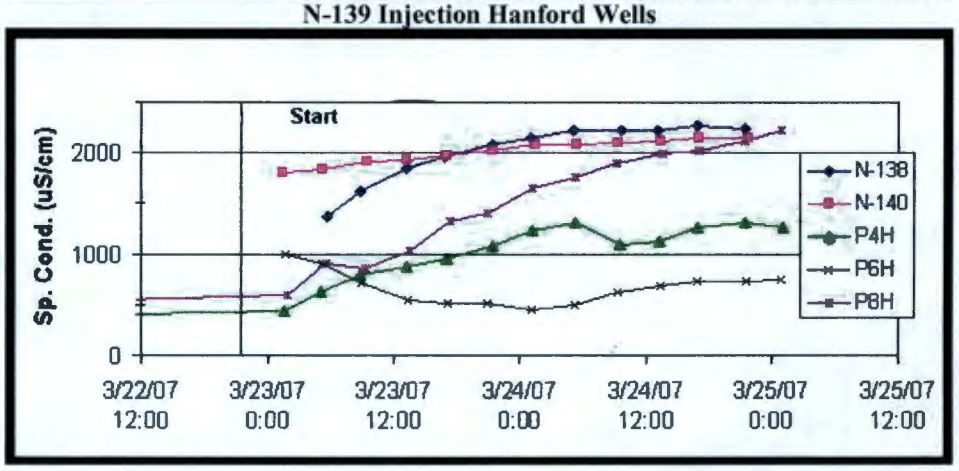
N-142 Injection Ringold Wells



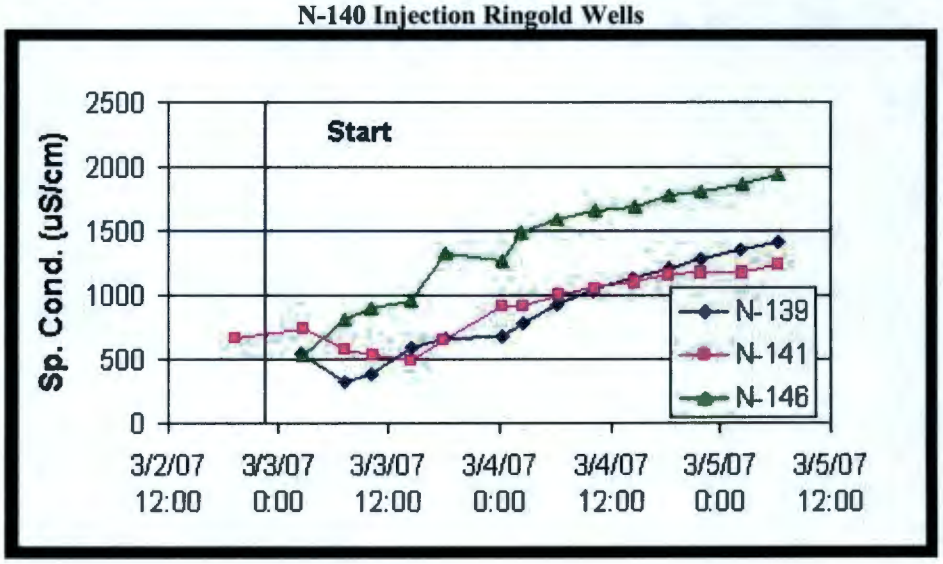
N-139 Injection Ringold Wells

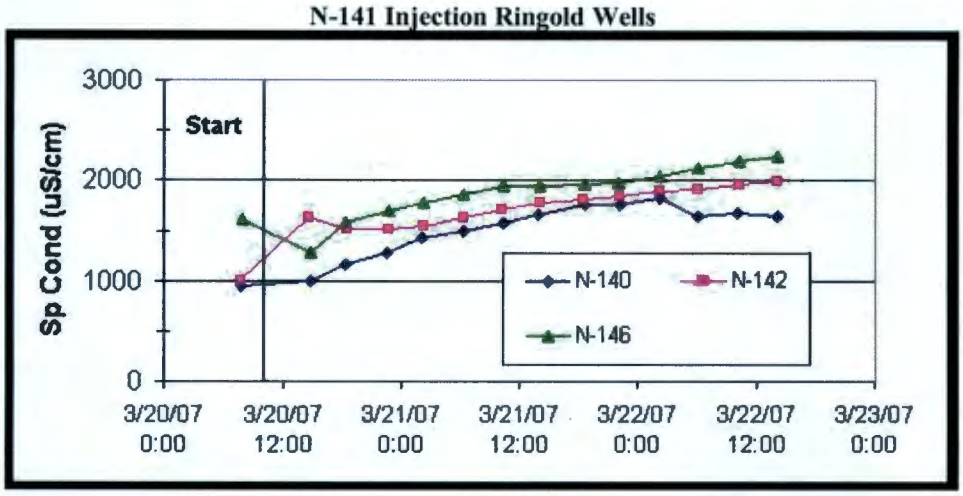


N-139 Injection Hanford Wells



N-140 Injection Ringold Wells





Hanford Formation Injection Design

The following description provides details on the injection design for conducting the full-scale Hanford formation treatment injection at wells 199-N-136, 199-N-138, 199-N-140, 199-N-142, 199-N-144, 199-N-145. These injections were conducted in three phases; three wells, one well and then two wells.

It should be noted that these injections were still part of the technology development phase of the project and the information developed will be used to establish the protocol for future barrier expansion injections and higher concentration chemical injections.

Based on the injection design analysis conducted to date, injection volumes were established at either 60,000 or 100,000 gallons of apatite forming chemical solution. The different specified total injection volumes result from two distinct zones along the barrier length which demonstrated different aquifer porosity properties in earlier tests and injections. These volumes would provide sufficient amendment to reach the targeted radial extent of 20 ft in the Hanford formation. The volume was determined by evaluating results from previous barrier injections, projected river stage conditions and model analysis. The solution injection rate was specified to be 40 gpm.

Solution Composition

The final version of the apatite forming chemical containing; 2.5 mM trisodium citrate, 1.0 mM calcium chloride, 8.1 mM disodium hydrogenphosphate, 0.5 mM diammonium hydrogenphosphate, 1.0 mM sodium bromide was developed from observations made during the two pilot injections and bench scale tests. It was used during the three phase injections.

Order of Treatment

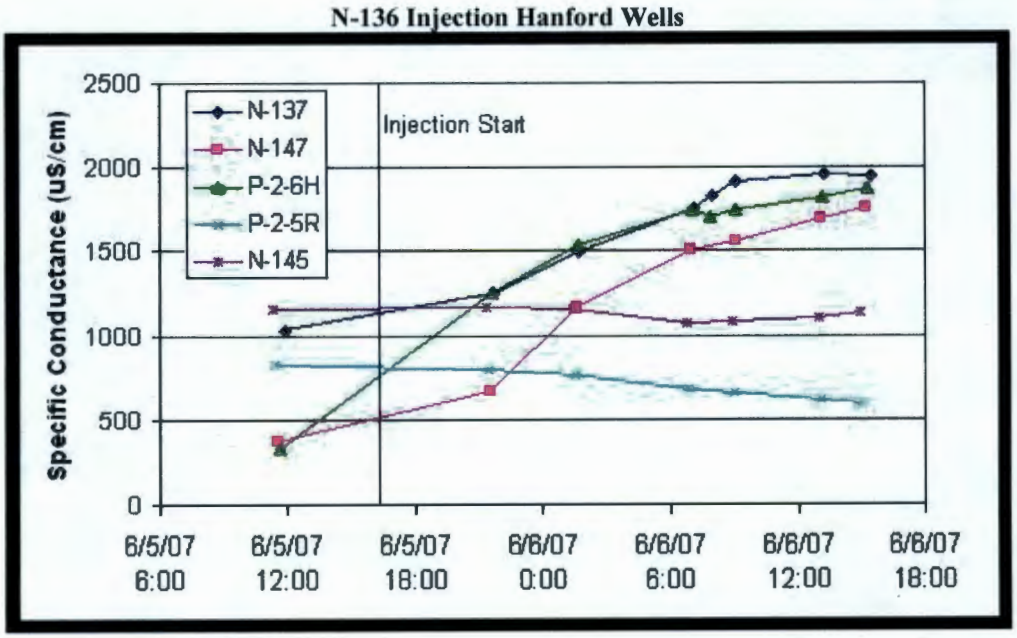
To prevent impacting adjacent treatment zones before the apatite forming solutions have had sufficient time to fully react, the six injections were conducted in three phases, with each phase made up of alternating injection well locations along the length of the barrier. In addition, timing of the phased injections assured that a minimum of two weeks of reaction time between adjacent injections. The phased injection approach and order of injection is summarized below:

	1st Injection	2nd Injection	3rd Injection
June 5	199-N-142	199-N-136	199-N-144
June 8	199-N-138		
July 10	199-N-140	199-N-145	

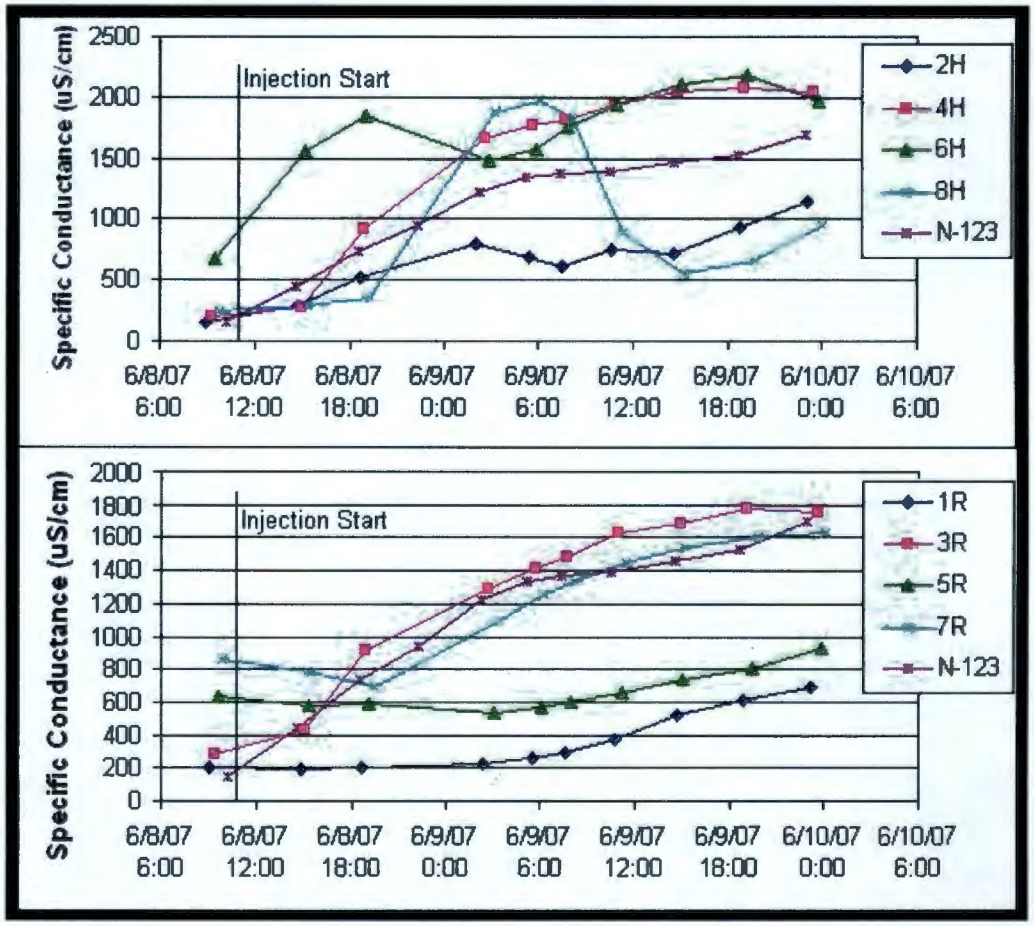
Injection Solution Specific Conductance

Specific conductivity using field instruments was used as an indicator of chemical arrival in the adjacent monitoring well. The results for the Hanford injections are graphed and summaries below (figure 5):

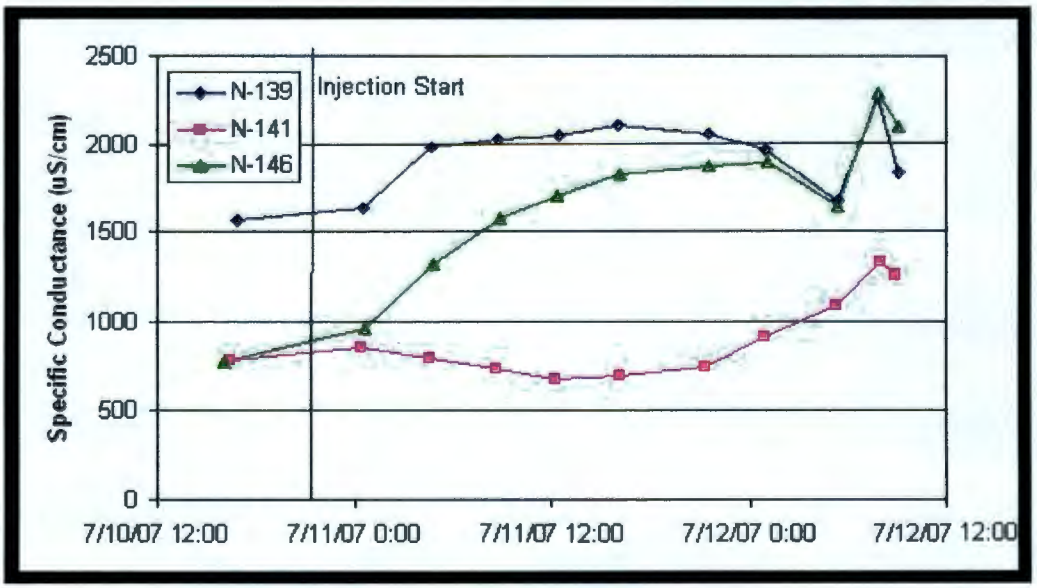
Figure 5. Specific Conductance for Hanford Injections



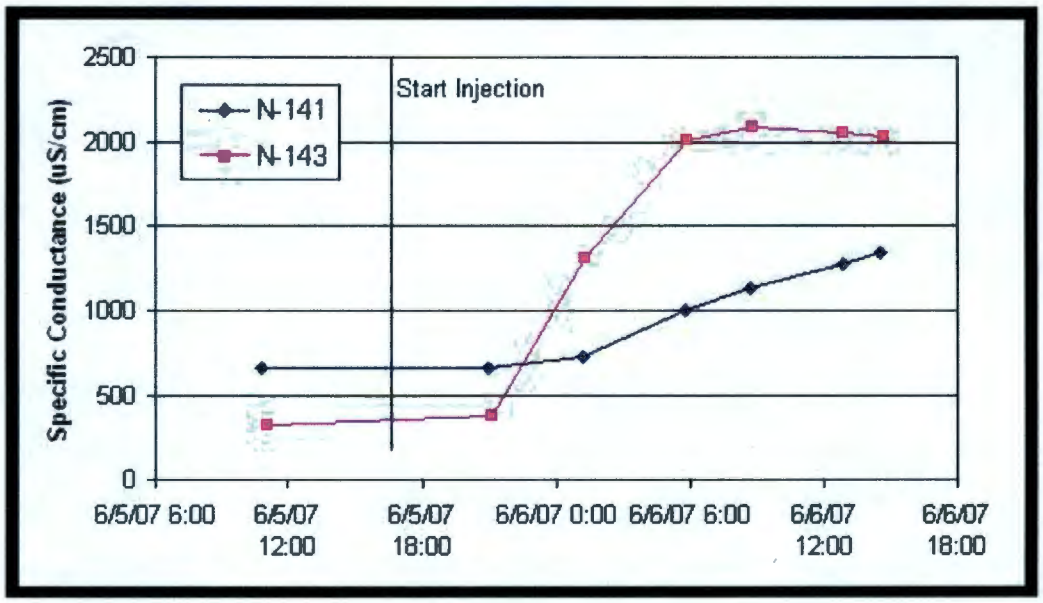
N-138 Injection Hanford Wells



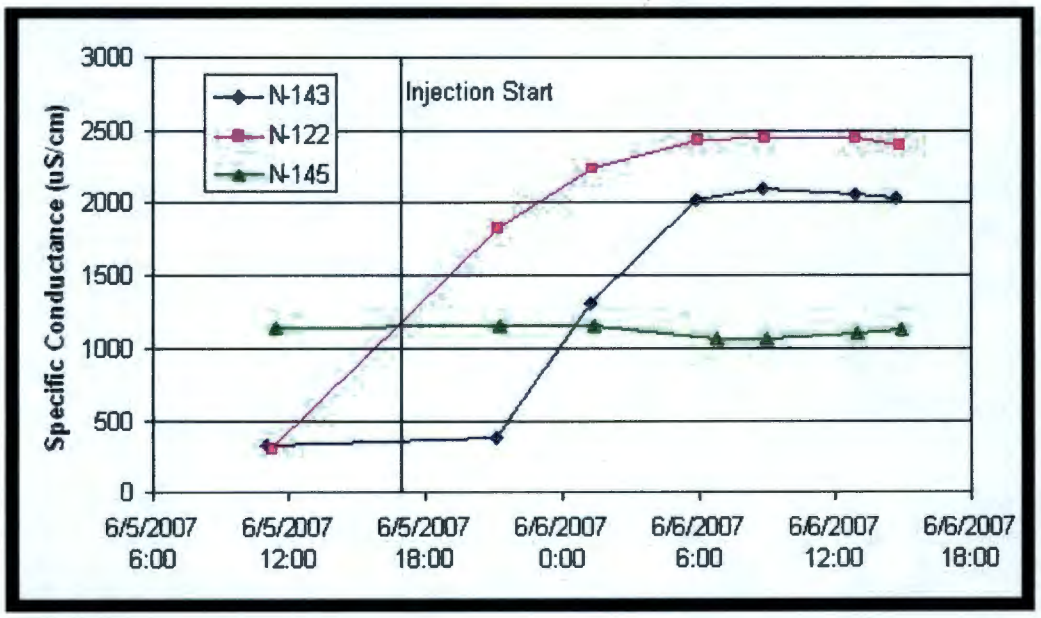
N-140 Injection Hanford Wells



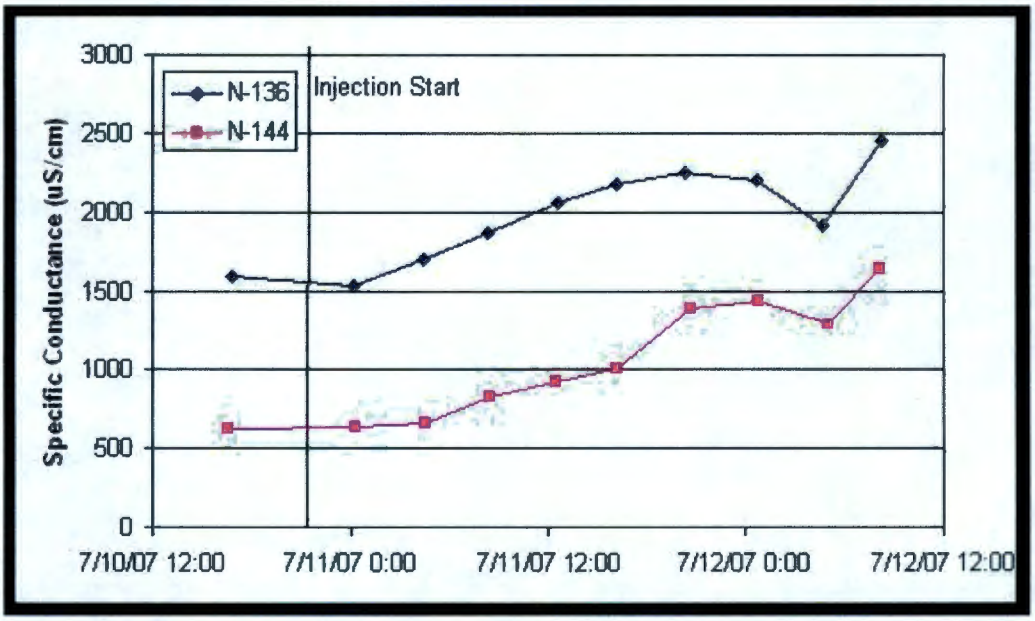
N-142 Injection Hanford Wells



N-144 Injection Hanford wells



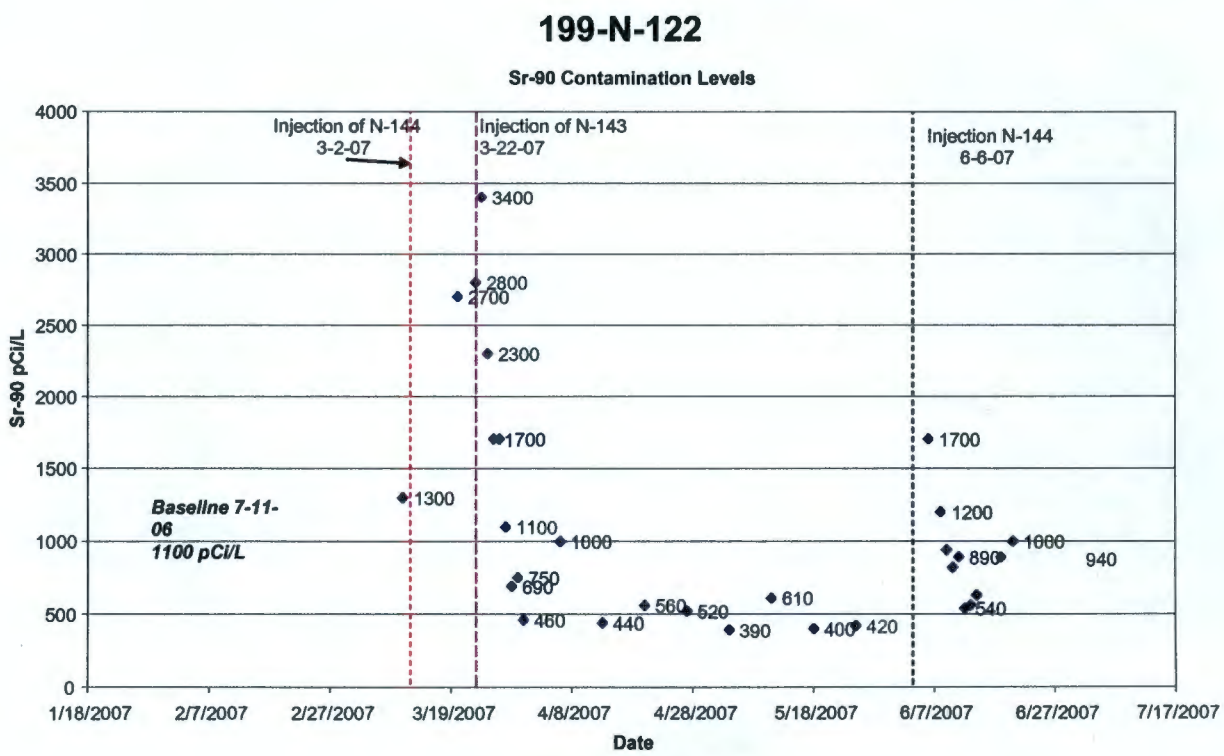
N-145 Injection Hanford Wells



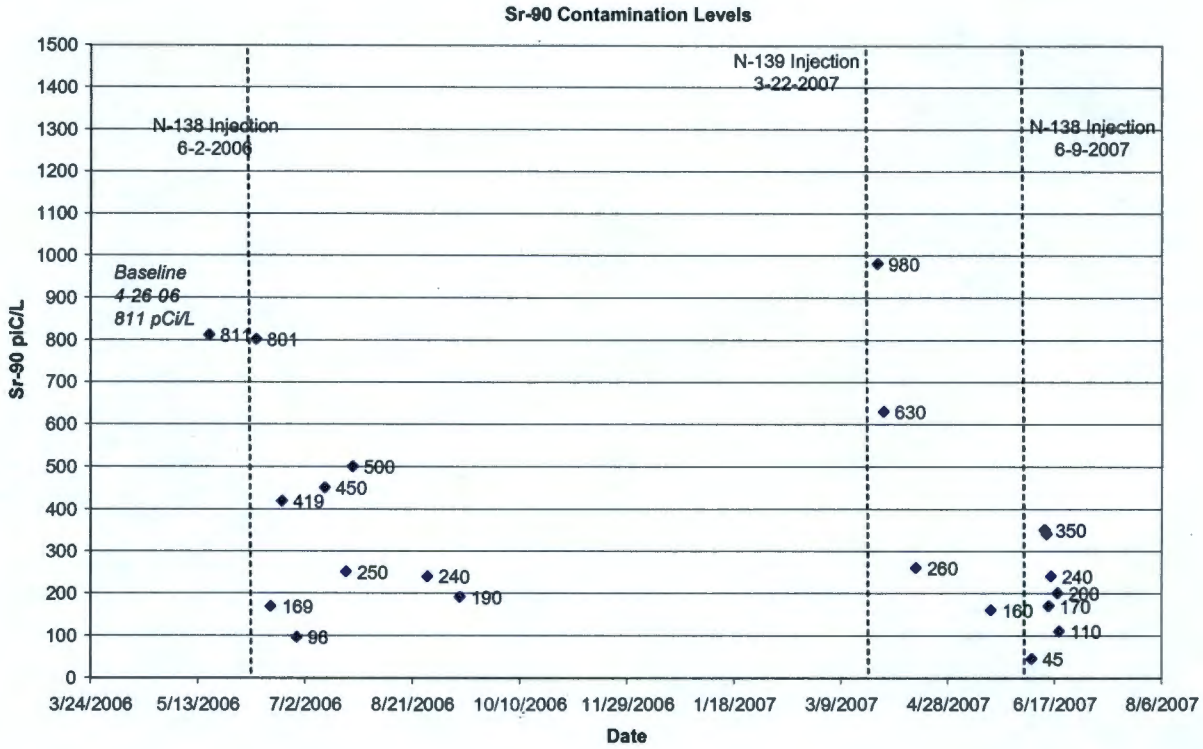
Barrier Performance Preliminary Results

Apatite minerals are very stable and practically insoluble in water and are being used in this test to remove soluble ^{90}Sr from the groundwater. Sequestration of ^{90}Sr is accomplished via substitution of Sr into the structure both during and after the formation of the apatite mineral. Although the rate of metal incorporation into the apatite crystal lattice can be relatively slow, the precipitation reaction is nearly instantaneous on the molecular scale. Initially, the precipitate formed is amorphous apatite, within a short period of time it will transform into a more stable apatite crystal. It was anticipated, based on laboratory bench scale tests that some leaching of the Sr from the soil matrix would occur. However the amount of increase observed after the first pilot test was more that predicted. This was caused by a higher than expected volume of calcium in the soils. Laboratory test were conducted and the chemical formulation was adjusted to minimize calcium and strontium desorption. The graphs below (figure 6) track the strontium levels in the injection wells and four monitoring wells. Injection dates are graphed with dashed lines with the strontium data points in blue. These results are preliminary in nature but indicate predicted trends. There is an increase in strontium levels after each injection which falls off to lower values with time. With each subsequent injection, in and near the selected wells, the desorbed ^{90}Sr is less; with the return to lower values occurring in a shorter amount of time. Baseline samples are highlighted at the beginning of each graph. Latest sample results at all monitoring points are below the original baselines. Again, these values are preliminary and have been influenced by river levels and by the injection of adjacent wells. All injections for 2007 have been completed and we are entering a period of analysis when the wells will not be influenced by injections. This will give the project time to analyze the performance of the barrier and prepare a revised TTP for the high concentration injections in 2008.

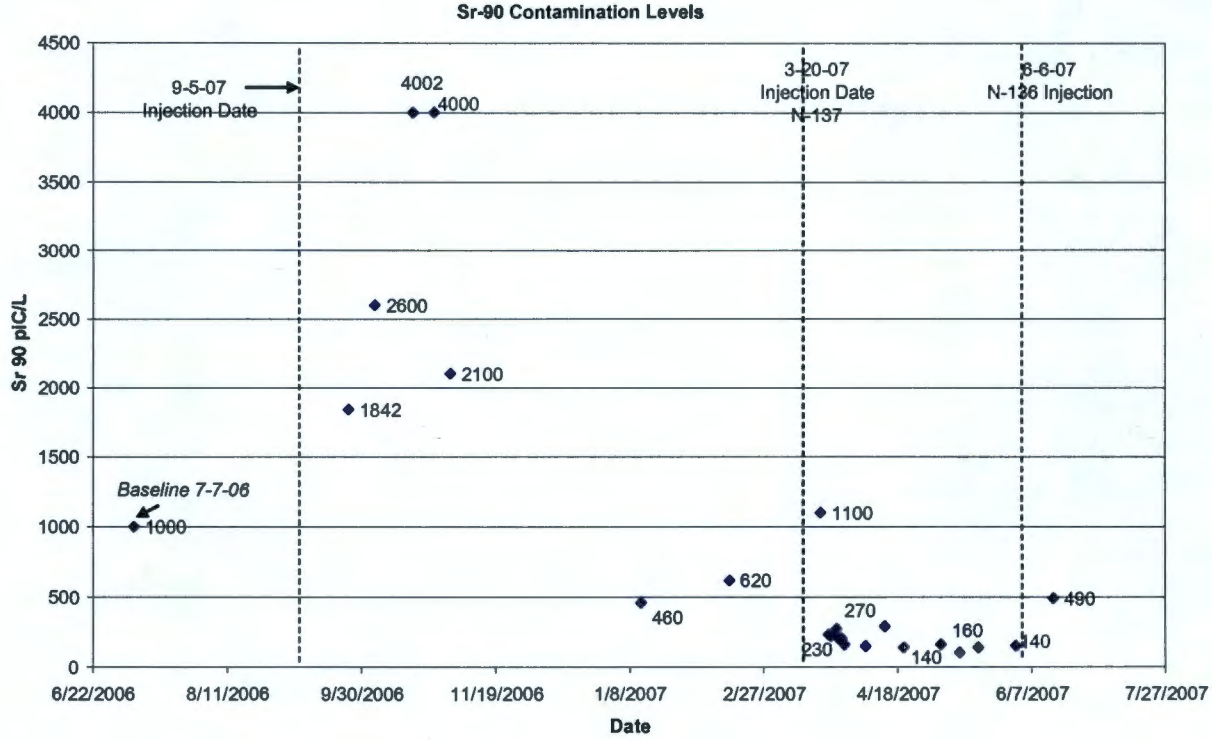
Figure 6. Barrier Performance Graphs

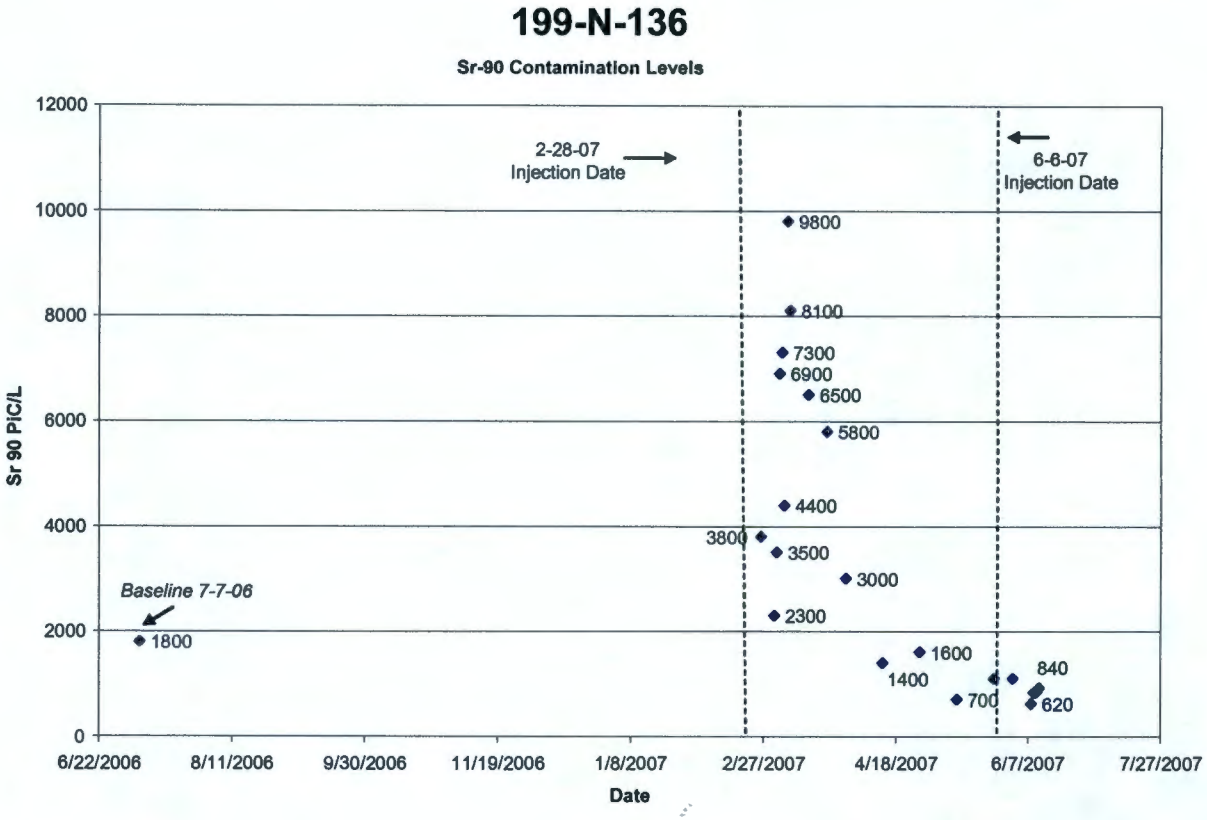


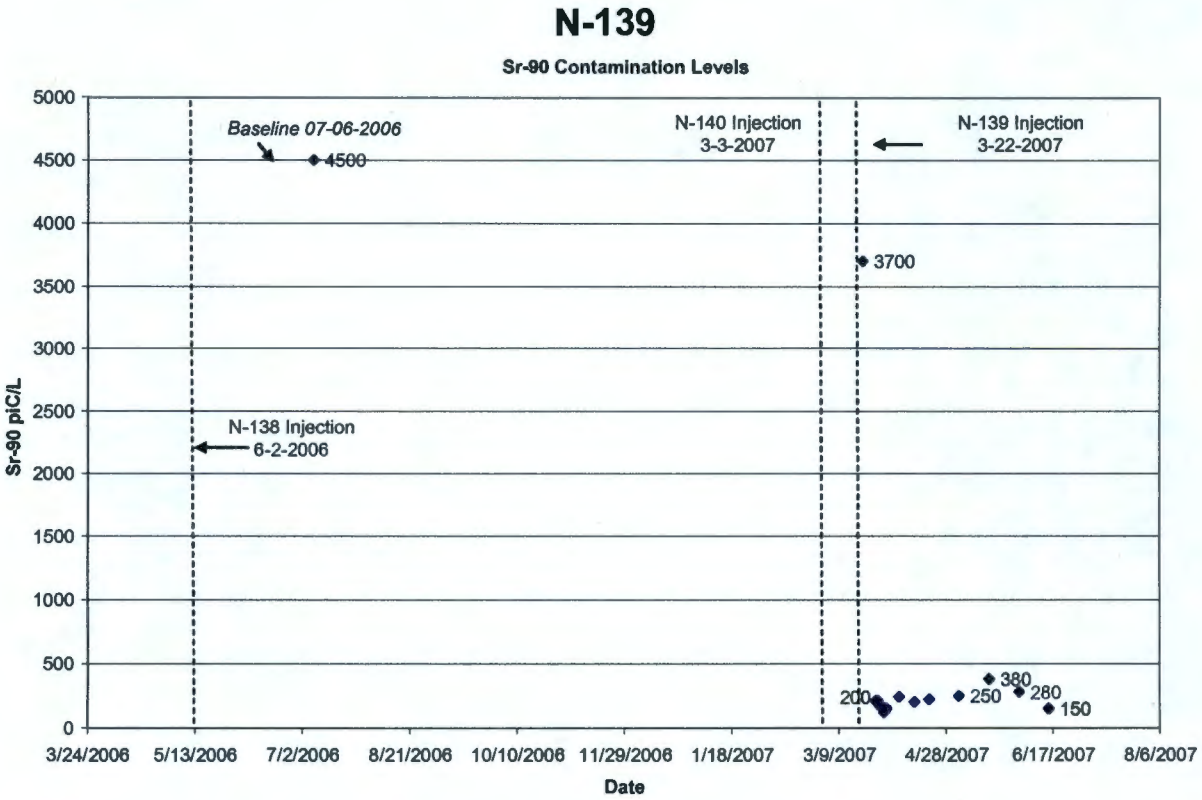
199-N-138

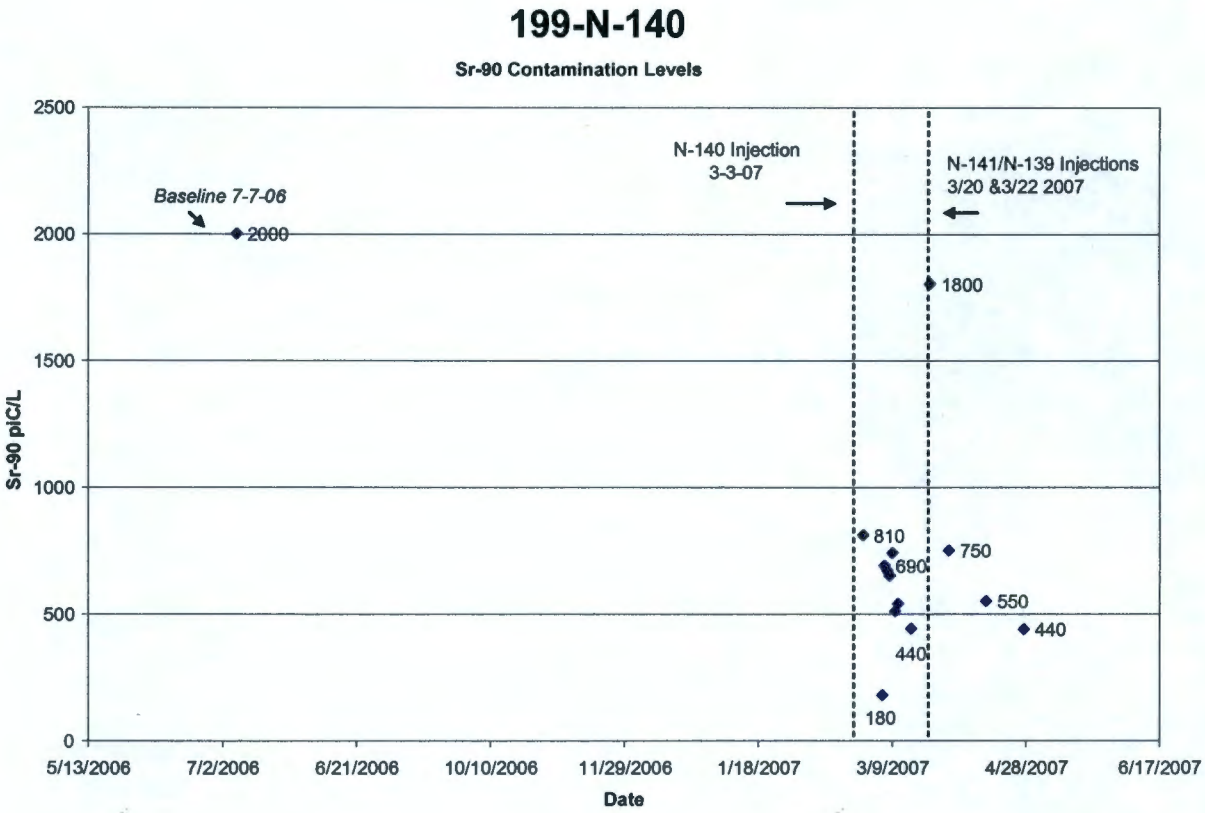


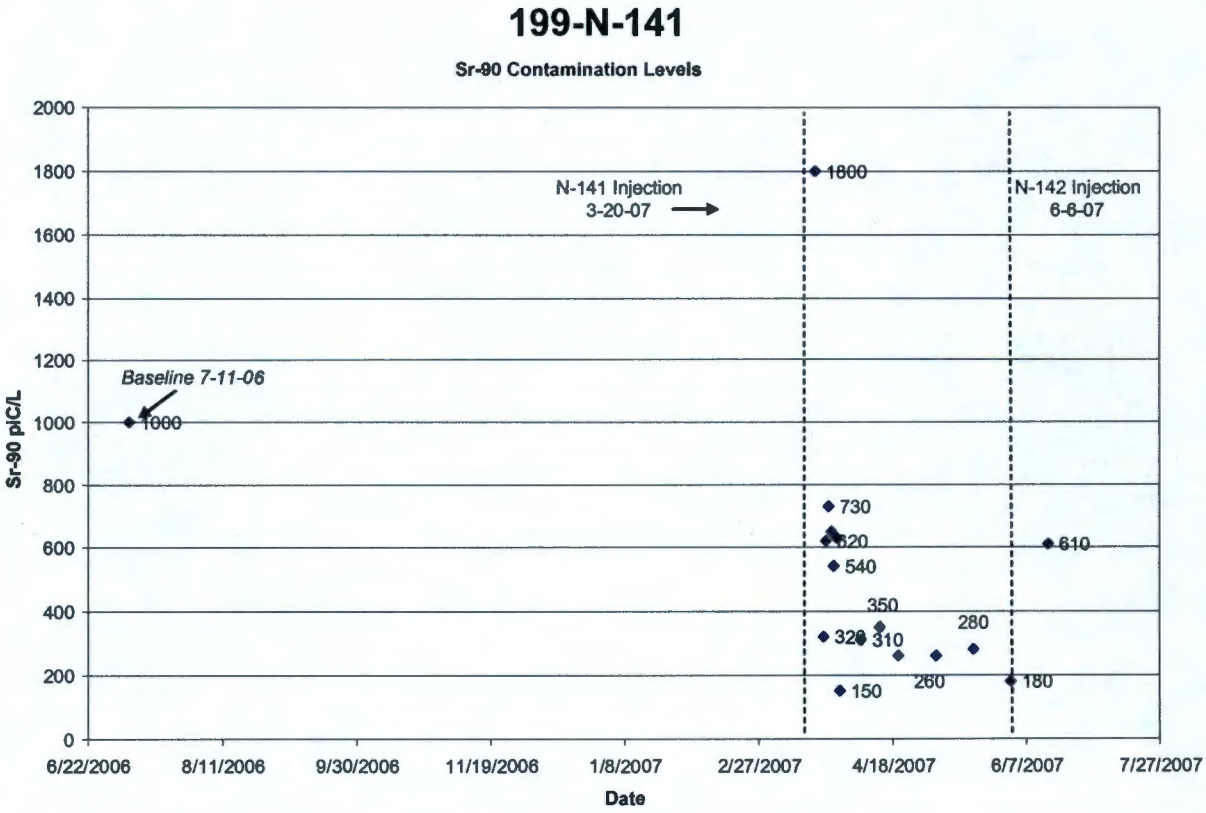
199-N-137

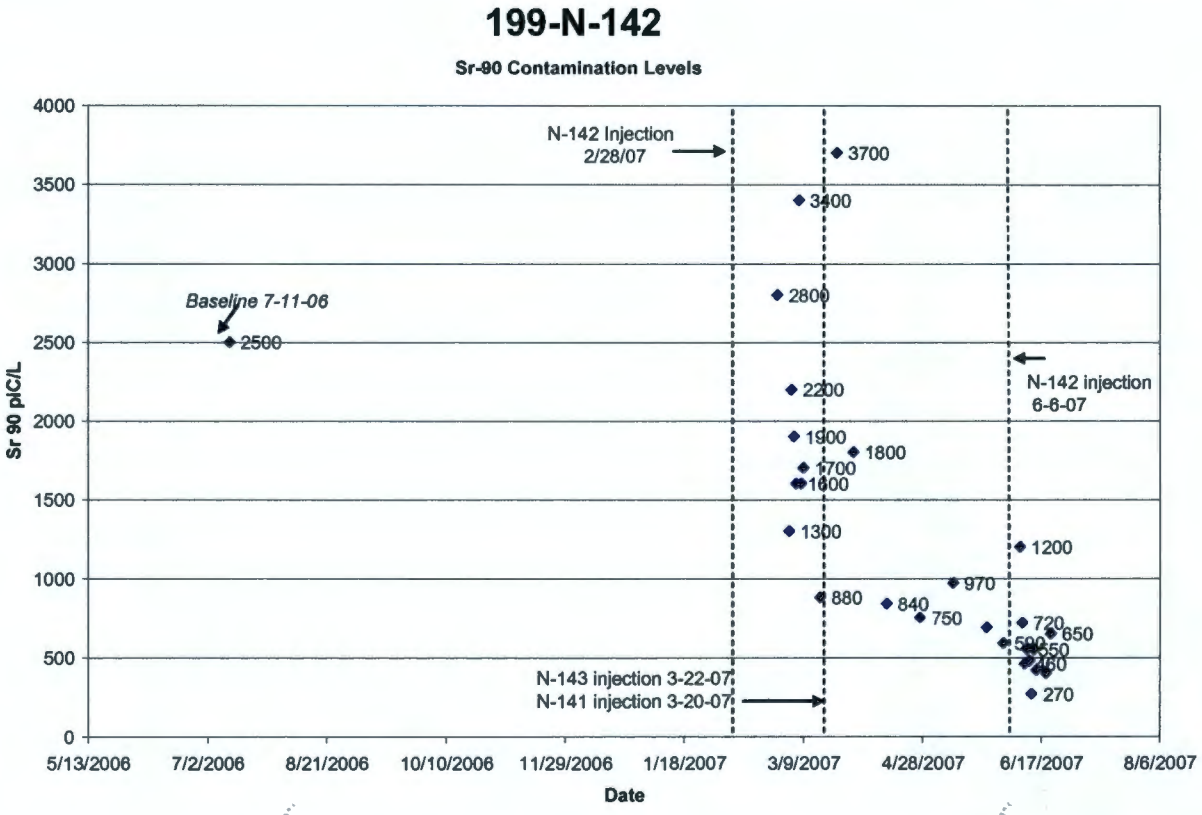


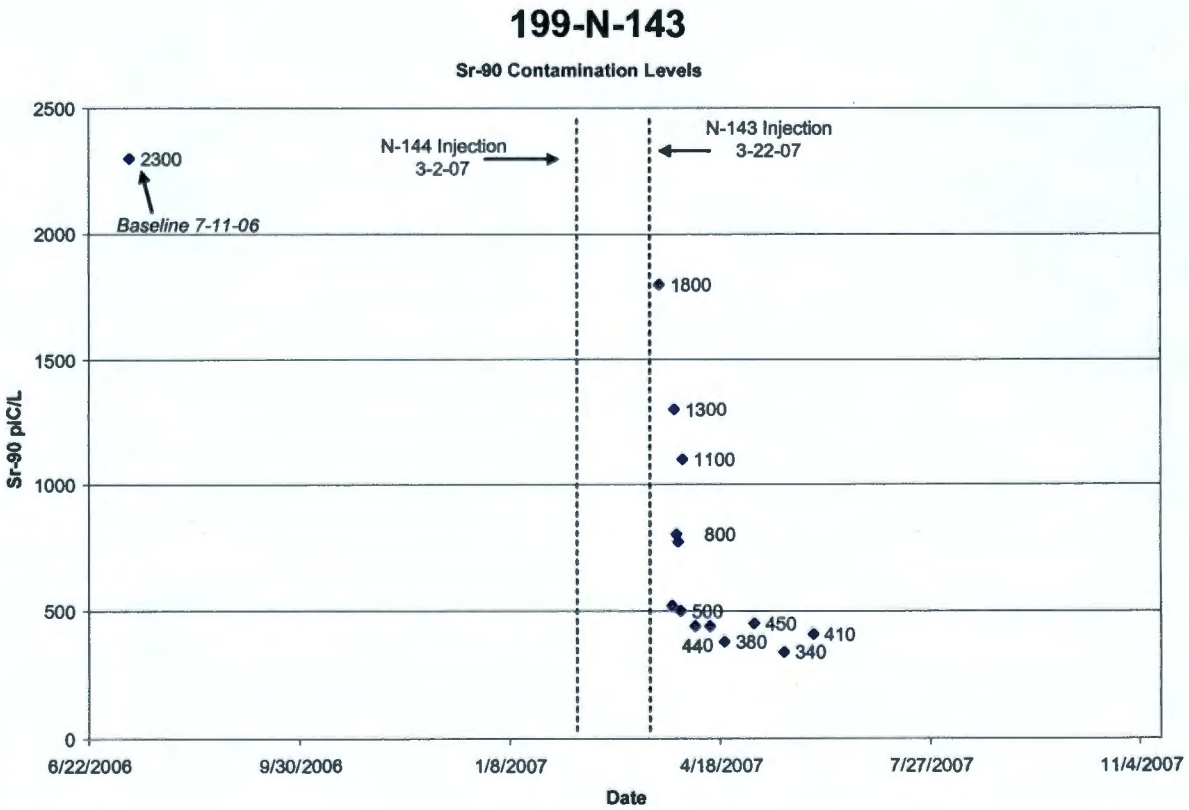

199-N-136
Sr-90 Contamination Levels
Sr 90 PIC/L
Date
2-28-07
Injection Date
6-6-07
Injection Date
Baseline 7-7-06
1800
9800
8100
7300
6900
6500
5800
4400
3800
3500
3000
2300
1600
1400
840
700
620
12000
10000
8000
6000
4000
2000
0
6/22/2006
8/11/2006
9/30/2006
11/19/2006
1/8/2007
2/27/2007
4/18/2007
6/7/2007
7/27/2007

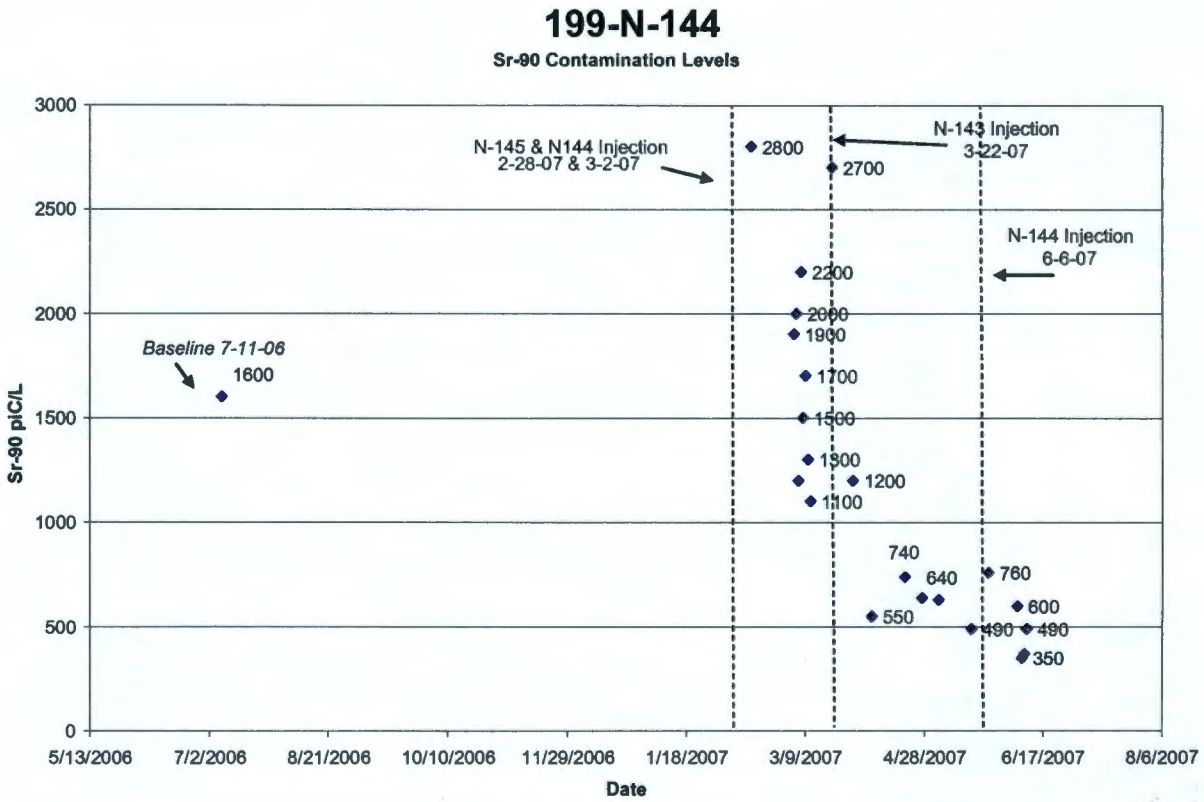

N-139
Sr-90 Contamination Levels
Sr-90 piC/L
Date
Baseline 07-06-2006
4500
N-140 Injection
3-3-2007
N-139 Injection
3-22-2007
3700
N-138 Injection
6-2-2006
200
380
250
280
150
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
3/24/2006
5/13/2006
7/2/2006
8/21/2006
10/10/2006
11/29/2006
1/18/2007
3/9/2007
4/28/2007
6/17/2007
8/6/2007

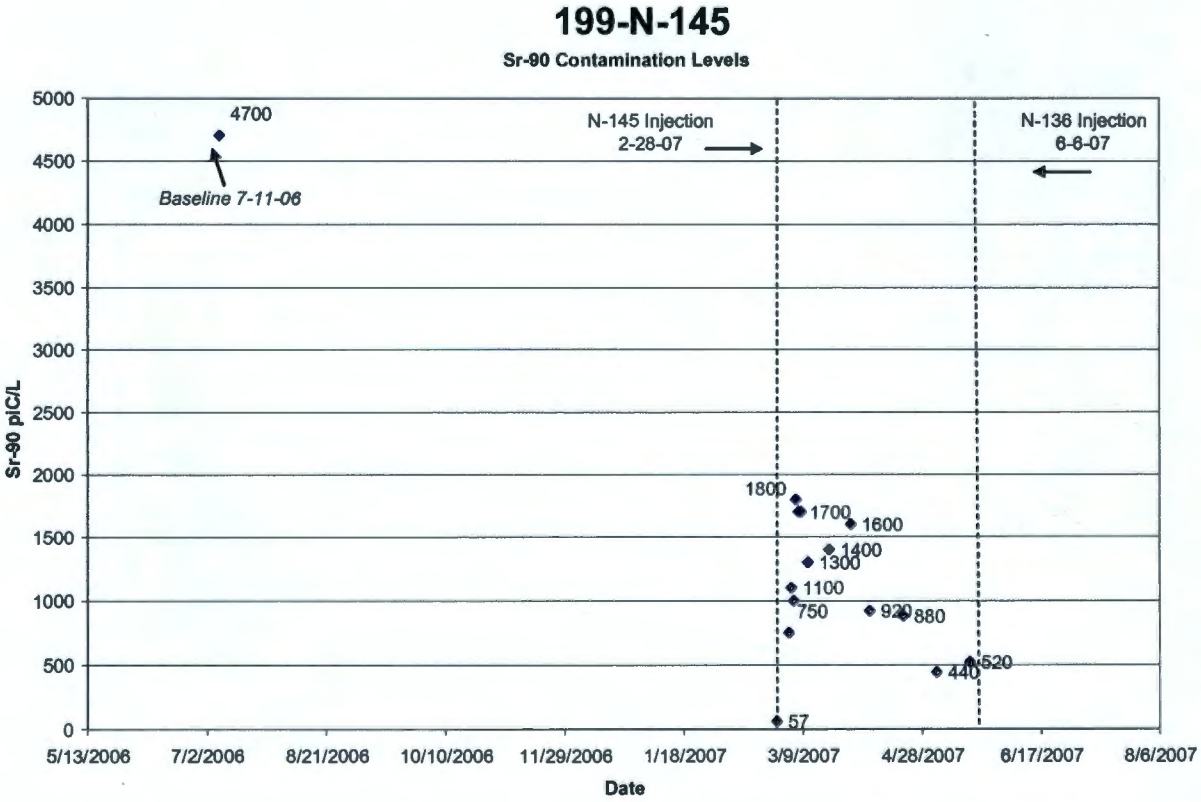

199-N-140
Sr-90 Contamination Levels
Sr-90 piC/L
Date
Baseline 7-7-06
N-140 Injection
3-3-07
N-141/N-139 Injections
3/20 &3/22 2007
2000
1800
810
690
750
550
440
440
180
2500
2000
1500
1000
500
0
5/13/2006
7/2/2006
6/21/2006
10/10/2006
11/29/2006
1/18/2007
3/9/2007
4/28/2007
6/17/2007


199-N-141
Sr-90 Contamination Levels
Sr-90 piC/L
Date
Baseline 7-11-06
N-141 Injection
3-20-07
N-142 Injection
6-6-07
1000
1800
730
620
540
610
350
320
310
280
260
150
180
2000
1800
1600
1400
1200
1000
800
600
400
200
0
6/22/2006
8/11/2006
9/30/2006
11/19/2006
1/8/2007
2/27/2007
4/18/2007
6/7/2007
7/27/2007

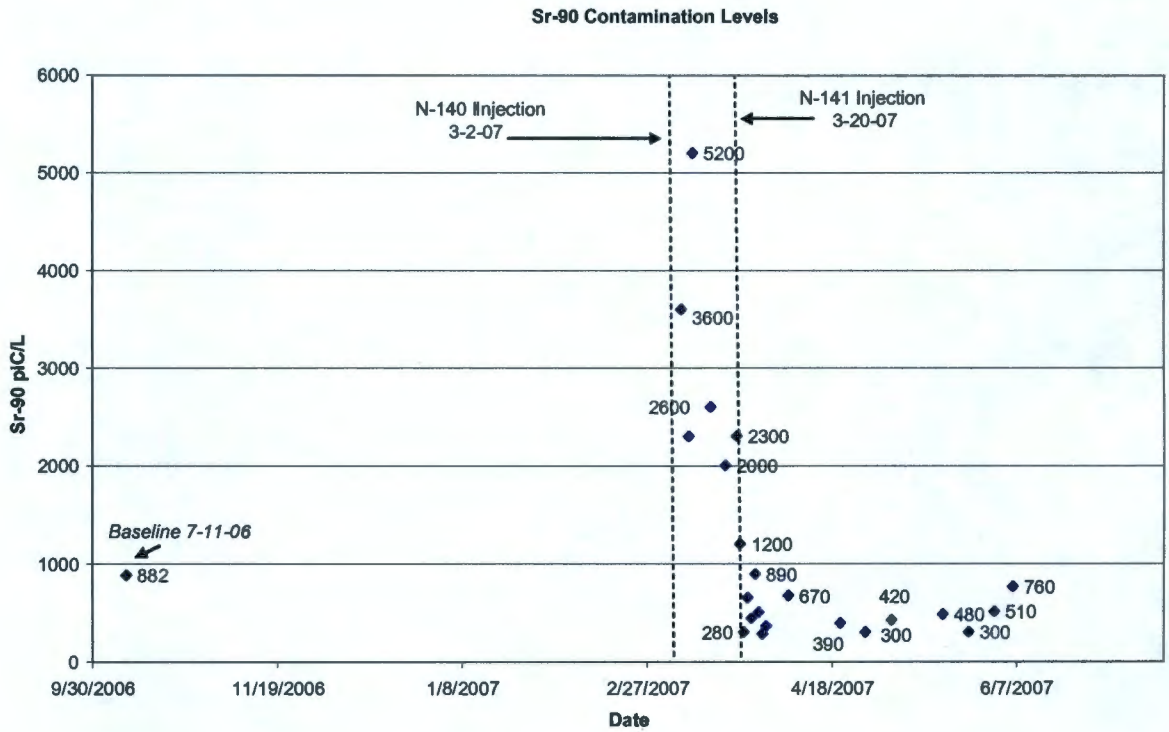

199-N-142
Sr-90 Contamination Levels
Sr 90 piC/L
Date
N-142 Injection
2/28/07
N-142 injection
6-6-07
N-143 injection 3-22-07
N-141 injection 3-20-07
Baseline 7-11-06
2500
3700
3400
2800
2200
1900
1800
1700
1600
1300
1200
970
880
840
750
720
650
270
4000
3500
3000
2500
2000
1500
1000
500
0
5/13/2006
7/2/2006
8/21/2006
10/10/2006
11/29/2006
1/18/2007
3/9/2007
4/28/2007
6/17/2007
8/6/2007


199-N-143
Sr-90 Contamination Levels
Sr-90 piC/L
Date
N-144 Injection
3-2-07
N-143 Injection
3-22-07
Baseline 7-11-06
2300
1800
1300
1100
800
500
450
440
380
410
340
2500
2000
1500
1000
500
0
6/22/2006
9/30/2006
1/8/2007
4/18/2007
7/27/2007
11/4/2007

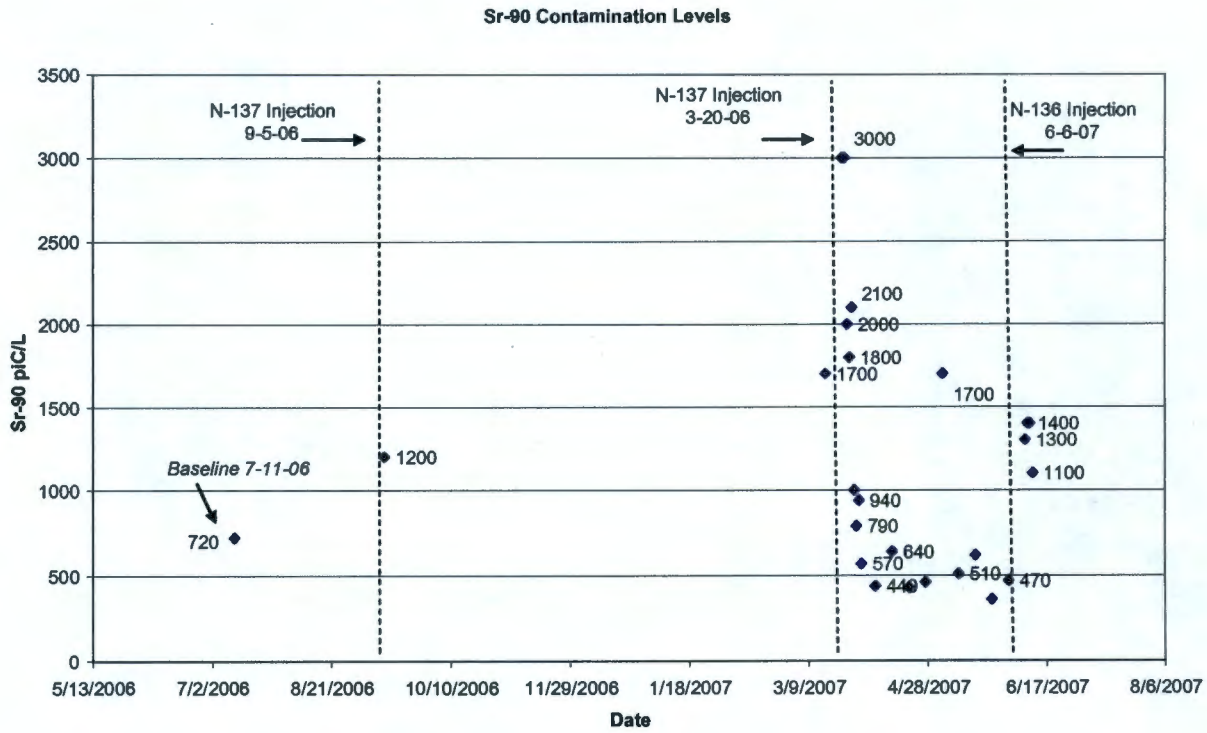

199-N-144
Sr-90 Contamination Levels
Sr-90 piC/L
Date
N-145 & N144 Injection
2-28-07 & 3-2-07
N-143 Injection
3-22-07
N-144 Injection
6-6-07
Baseline 7-11-06
1600
2800
2700
2200
2000
1900
1700
1500
1300
1200
1100
740
640
760
600
550
490
490
350
0
500
1000
1500
2000
2500
3000
5/13/2006
7/2/2006
8/21/2006
10/10/2006
11/29/2006
1/18/2007
3/9/2007
4/28/2007
6/17/2007
8/6/2007


199-N-145
Sr-90 Contamination Levels
Sr-90 piC/L
Date
4700
Baseline 7-11-06
N-145 Injection
2-28-07
N-136 Injection
6-6-07
1800
1700
1600
1400
1300
1100
750
920
880
520
440
57
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5/13/2006
7/2/2006
8/21/2006
10/10/2006
11/29/2006
1/18/2007
3/9/2007
4/28/2007
6/17/2007
8/6/2007

199-N-146



199-N-147



2007 - 2008 Calendar Year Scheduled Activities

Fluor Hanford with the assistance of PNNL will begin modifying the Treatability Test Plan to allow for a high concentration of apatite forming chemical with a completion date of January 2008. A single well pilot injection is planned for June 2008. Based on the results of the pilot injection the remainder of the wells will be injected in June-July of 2008. The injections will be scheduled to take advantage of high river stages. This will allow for a single injection in each well which will treat both the Ringold and the Hanford formations. The high concentration injection should provide for a robust barrier with a life expectancy of 300 years.

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