Cimarron Corporation

Groundwater Decommissioning Plan

License SNM-928; Docket Number 70-925

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Groundwater Decommissioning Plan

Cimarron Site, Crescent, Oklahoma

Prepared for:
Cimarron Corporation

Prepared by:
ARCADIS U.S., Inc.
630 Plaza Drive
Suite 200
Highlands Ranch
Colorado 80129
Tel 720.344.3500
Fax 720.344.3535

Our Ref.:
GPTRONOX.0004

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Acronyms and Abbreviations

AVS-SEM	acid volatile sulfide and simultaneously-extractable metals
BA#1	Burial Area #1
BA#3	Burial Area #3
cfs	cubic feet per second
cm^2/sec	centimeters squared per second
cm^3	cubic centimeters
CSM	Conceptual Site Model
1-D	one-dimensional
DOE	U.S. Department of Energy
DQOs	data quality objectives
Eh	reduction potential
EXAFS	extended x-ray absorption fine structure
Fe	iron
$FeCO_{3(s)}$	siderite
FeS	iron sulfide
$FeS_{(s)}$	mackinawite
Fe_3O_4	magnetite
Fe_3S_4	greigite
ft/day	feet per day
ft/ft	feet per foot
g	grams
g/cm^3	grams per cubic centimeter
g/kg	grams per kilogram
GER	Groundwater Evaluation Report
GWB	Geochemist's Workbench
H_2S	hydrogen sulfide
HELP	Hydrologic Evaluation of Landfill Performance
ICP-MS	inductively-coupled plasma – mass spectroscopy
IRZ	in-situ reactive zone
M	molar
m/day	meters per day

mg/kg	milligrams per kilogram
mg/L	milligrams per liter
msl	mean sea level
µg/L	micrograms per liter
µ-XRF	micro-x-ray fluorescence
µ-XANES	micro-x-ray absorption near edge structure
NRC	Nuclear Regulatory Commission
O_2	oxygen
ODEQ	Oklahoma Department of Environmental Quality
pCi/L	picocuries per liter
pCi/g	picocuries per gram
pCi/ µg	picocuries per microgram
QAC	Quality Assurance Coordinator
QAPP	Quality Assurance Project Plan
QSM	Quality System Manual
redox	reduction-oxidation
RSO	Radiation Safety Officer
SDP	Site Decommissioning Plan
SEM-EDS	scanning electron microscopy with energy dispersive x-ray spectroscopy
SRB	sulfate reducing bacteria
TDS	total dissolved solids
TOC	total organic carbon
U	uranium
UCL	upper confidence limit
UO_2	uraninite
UO_3	gummite
USEPA	U.S. Environmental Protection Agency
WAA	Western Alluvial Area
WUA	Western Uplands Area
XRD	x-ray diffraction
XRF	x-ray fluorescence

1. Executive Summary

Cimarron Corporation (Cimarron) owns and previously operated under Nuclear Regulatory Commission (NRC) Special Nuclear Material license (SNM-928) a former nuclear fuel production facility near Crescent, Oklahoma. The Cimarron site was closed in 1975 and is currently undergoing decommissioning activities in accordance with an NRC-approved Decommissioning Plan. The license, by amendment, now addresses the decommissioning of the facility, which is complete for all environmental media except groundwater. Cimarron plans to decommission the site for release for unrestricted use under the NRC-stipulated site-specific release criterion of 180 picoCuries per liter (pCi/L) for total uranium in groundwater.

In the NRC-approved Site Decommissioning Plan, Cimarron maintained that natural attenuation may reduce groundwater to concentrations below the stipulated criteria in a reasonable time frame without "active" remediation. The Plan stated that, should continued monitoring of groundwater indicate this is not the case, additional assessment or more aggressive remedial methods would be employed. This document is being submitted to NRC as a license amendment request to fulfill that commitment.

This submittal addresses the active remediation of groundwater in the remaining areas that exceed the groundwater release criteria, including the requirements for groundwater monitoring to confirm the effectiveness of the remediation and the requirements to confirm and justify license termination for the Cimarron facility.

2. Introduction

2.1 Purpose and Objectives

Decommissioning of equipment, structures, and soil at the Cimarron site is complete – all comply with decommissioning criteria for unrestricted release. Groundwater in three areas exceeds site-specific release criteria for groundwater as specified in license condition 27(b). In addition to the activity–based criteria, Cimarron must also meet a risk-based concentration limit of 110 micrograms per liter (µg/L) approved by the Oklahoma Department of Environmental Quality (ODEQ). For the purposes of this document, we will refer to these values as the Criteria. The purpose of this license amendment request, including this Groundwater Decommissioning Plan, is to complete the decommissioning of the site by reducing the concentration of uranium in groundwater to less than the Criteria.

Cimarron seeks NRC's approval to proceed with implementation of the remedial activities detailed in this document by demonstrating that the following objectives will be achieved:

- The concentration of uranium in groundwater will be reduced to less than the Criteria by precipitating the dissolved uranium, converting it from the dissolved to the solid phase.

- Sufficient iron sulfide will be created throughout the impacted zones to prevent the re-mobilization of uranium at concentrations exceeding the Criteria for a minimum of 1,000 years.

Following implementation and upon demonstration that these objectives have been met in the impacted areas, in accordance with the remedy completion demonstration specified in Section 5.3, Cimarron anticipates that NRC will proceed to release the site for unrestricted use and terminate license SNM-928.

2.2 License History / Criteria

The Cimarron facility was operated as a nuclear fuel production facility under License SNM-928 until it was closed in 1975. Facility decommissioning began in 1976 and continues in accordance with a decommissioning plan approved by NRC in August 1999. The licensing history of the site, from issuance through April 1995, is presented in Section 1 of Site Decommissioning Plan (SDP) (Chase Environmental Group, April 1995). The SDP was supplemented by Site Decommissioning Plan – Groundwater

Evaluation Report (GER) (Chase Environmental Group, 1998). NRC approved the SDP and GER on August 23, 1999.

The Radiological Characterization Report for Cimarron Corporation's Former Nuclear Fuel Fabrication Facility (Chase Environmental Group, 1994) divided the Cimarron site into Subareas A through O (Figure 2-1). Subareas A through E were surveyed as un-impacted areas and the final status survey plan for these subareas was approved by the NRC in May 1995. Subareas F through J and Subareas K through O were surveyed as impacted areas and final status survey plans for these subareas were approved in March 1997 and September 1998, respectively.

Cimarron submitted Final Status Survey reports for each subarea from 1996 to 2005. NRC has released all but three subareas in License Conditions 25 and 28 through 30. These three subareas include Subareas F, G, and N. Confirmatory surveys confirm that Subareas G and N comply with all decommissioning criteria and do not have groundwater impacts, but NRC will not release these subareas until groundwater remediation is complete in the areas where groundwater impacts above the Criteria remain.

The SDP and GER presented information indicating that natural attenuation may reduce the concentration of licensed material in groundwater on a timely basis such that active groundwater remediation may not be needed. The GER stated that, should information indicate that natural attenuation may not achieve this, additional assessment and/or remediation may be needed.

Site-Wide Groundwater Assessment Review (Cimarron, 2005) identifies six areas in which groundwater has at some time exceeded license criteria. Groundwater exceeding the Criteria has been delineated, and the hydrogeology and geochemistry of the areas were reported in the Conceptual Site Model, Revision 1 (ENSR, 2006). Three of these areas have now been demonstrated to comply with the criteria. Cimarron submitted a request for NRC concurrence that no further remediation or monitoring is needed for these areas in a submittal dated August 31, 2007. This amendment to the SDP addresses the remediation of groundwater in the three remaining areas.

Three site areas remain in which uranium still exceeds the Criteria in groundwater. These areas are shown on Figure 2-1 and are referred to as:

- Western Upland Area (WUA)
- Western Alluvial Area (WAA)

- Burial Area #1 (BA#1)

These three areas will be referred to using this terminology throughout this Groundwater Decommissioning Plan. This amendment to the SDP addresses the remediation of groundwater in these three areas.

License condition 27(c) stipulates the use of the August 1987 NRC Guidelines for Decontamination of Facilities and Equipment Prior to Release for Unrestricted Use or Termination of Licenses for Byproduct, Source, or Special Nuclear Material for the release of materials. Condition 27(c) also stipulates the use of the October 1981 Disposal or Onsite Storage of Thorium or Uranium Wastes from Past Operations for soils or soil-like material. Condition 27(b) stipulates 180 pCi/L total uranium activity as the release criterion for groundwater.

2.3 Population Setting and Land Use

The Cimarron site is located approximately seven miles south of the town of Crescent, Oklahoma, which has a population of approximately 1,300. It is located approximately ten miles west of the city of Guthrie, which has a population of approximately 11,000. Finally, the site is located approximately 28 miles north of downtown Oklahoma City, which has a population of approximately 540,000 (with a metropolitan area population of approximately 1,200,000).

The immediate area surrounding the Cimarron site is sparsely populated, with approximately four residences within one mile of the site. State Highway 33 runs adjacent to the Cimarron site, and Highway 74 runs approximately north-south through the site.

Surrounding land is predominantly agricultural; used for raising crops (primarily wheat) and cattle. A retail gas station/convenience store is located at the northwest corner of the intersection of Highways 33 and 74. Several hundred acres of the Cimarron site are located within the floodplain of the Cimarron River, and subject to periodic flooding.

The projected future use of the property is to remain agricultural. However, some limited low-impact commercial development may occur, as interest has been expressed in occupying the southwest quarter section of the Cimarron property for industrial storage.

2.4 Organization and Task Management

The Quality System Manual (QSM) for the Cimarron Site presents the management organization for decommissioning activities at the site. The organization chart depicting the personnel responsible for decommissioning activities applies to all activities on site. No changes to the management organization are needed for the groundwater decommissioning.

The roles and responsibilities of the Vice President, Cimarron Corporation, Project Manager, Radiation Safety Officer (RSO), and the Quality Assurance Coordinator (QAC) are the same for groundwater decommissioning as they have been for previous aspects of decommissioning. The RSO and QAC will act in an advisory and control role to monitor and audit the remediation contractor to ensure compliance with the QSM during completion of the decommissioning activities.

The remediation contractor will be responsible for groundwater decommissioning activities as directed by the Project Manager. The remediation contractor will function organizationally as any other contractor performing work on site.

Typical decommissioning activities include:

- Installation of extraction, injection and monitoring wells;
- Installation of remediation system lines and equipment;
- Storage and mixing of treatment reagents with extracted groundwater;
- Reinjection of amended groundwater;
- Collection and analysis of soil and groundwater samples from select locations; and
- Monitoring of groundwater elevations for hydrogeologic assessment.

2.5 Document Contents

The remainder of the Groundwater Decommissioning Plan is organized as follows:

- Section 3 presents a summary of the current understanding of site conditions, including a brief discussion of the site geology and hydrogeology conditions specifically related to the proposed groundwater remediation activities, and the current areas of uranium impacts in groundwater to be addressed by the remediation activities. This section also presents a summary of the hydrology assessment and hydrologic modeling conducted for the site, as well as the

geochemical modeling performed to provide the basis for the proposed remedial activities.

- Section 4 presents a discussion of the uranium immobilization process and provides references documenting the extent of knowledge and experience at other sites as well as laboratory research demonstrating the effectiveness of the bioremediation treatment process for uranium immobilization in groundwater.

- Section 5 includes the proposed groundwater decommissioning activities for implementation of the bioremediation process, including the staged field implementation approach to remediation and the remedy completion demonstration testing to be conducted to confirm the effectiveness and longevity of the groundwater remediation activities.

- Section 6 provides a summary of Cimarron's Quality Assurance Program that ensures the quality of groundwater decommissioning activities.

- Section 7 discusses financial assurance for the groundwater decommissioning activities.

- Section 8 provides a listing of the references cited in the Groundwater Decommissioning Plan.

- Section 9 provides a glossary of key terms used in this Groundwater Decommissioning Plan.

In addition, supporting documentation is provided in the appendices to the Groundwater Decommissioning Plan. These appendices include:

Appendix A:	Groundwater Flow Modeling Report, Cimarron Site (ENSR)
Appendix B:	Hydrology Addendum (ENSR)
Appendix C:	Data Quality Objectives
Appendix D:	Soil Analytical Methods
Appendix E:	Quality Assurance Program Attachments
Appendix F:	Modeling Output Files (CD-ROM)

3. Site Understanding and Modeling

The conceptual site model (CSM) for the Cimarron site prepared by ENSR forms the basis for the understanding of site conditions as needed for successful implementation of the groundwater remedy. A hydrologic assessment was completed to assess the impacts of transient hydrologic conditions on remedy implementation and effectiveness. In addition, hydrogeologic and geochemical modeling were conducted to better understand site conditions and to evaluate the effect of site-specific parameters on the remedy implementation. The following sections provide a discussion of the CSM components that are specifically related to the remediation, and modeling information that was used to develop and support the proposed remedial approach for the site presented in Section 5.

3.1 Conceptual Site Model

A full discussion of the CSM for the Cimarron Site is presented in the Conceptual Site Model, Revision 1 (ENSR, 2006). The following sections present a brief summary of the pertinent geologic and hydrogeologic settings at the site that relate to the planned groundwater decommissioning activities.

3.1.1 Remediation-Specific Site Geology Summary

The localized geology of the Cimarron Site consists predominantly of the Garber Formation. The Garber Formation is exposed along the escarpment that borders the Cimarron River floodplain and consists primarily of sandstone units separated by relatively continuous siltstone and mudstone layers (J.L. Grant and Associates, 1989). The sandstone units frequently have interbedded but discontinuous red-brown shale and mudstone lenses. The identifiable lithologic units at the Site are as follows:

- Sandstone A: Uppermost sandstone unit, generally red-brown to tan in color and up to 35 feet thick. Bottom of this sandstone unit occurs at an approximate elevation of 970 feet above mean sea level (msl).

- Mudstone A: Red-brown to orange-brown, sometimes tan mudstone and claystone that separates Sandstones A and B. Ranges from 6 to 20 feet in thickness.

- Sandstone B: Second sandstone unit, similar in color and sedimentary features to Sandstone A. Found at elevations between 925 and 955 feet above msl and up to 30 feet thick. Found below Mudstone A.

- Mudstone B: Mudstone and claystone separating Sandstone B and Sandstone C. Similar in color to Mudstone A and ranges from 6 to 14 feet in thickness.

- Sandstone C: Lowermost sandstone in the Garber Formation. Similar in color and sedimentary features to overlying sandstones. This unit is at least 55 feet thick in the study area.

Historical movement of the ancestral Cimarron River has carved an escarpment into the Garber Formation. In BA#1 where the escarpment is buried, there is a local transition zone from the sandstones of the Garber Formation to the coarser alluvial materials that is characterized by a clay-rich zone.

3.1.2 Mineralogy

A mineralogical analysis of the sandstones and the mudstones underlying the Site was performed by J.L. Grant and Associates in 1989. An additional analysis of sandstone from the saturated zone was performed by ARCADIS in 2006.

The 1989 analysis consisted of x-ray diffraction to determine the mineral composition of the samples (J.L. Grant and Associates, 1989). According to the Conceptual Site Model, Revision 1 (ENSR, 2006), quartz and feldspar were found to be the main clastic grains with kaolinite and montmorillonite as the clays in the fine-grained fractions. Calcite, iron oxides, and iron hydroxides were identified as the main cementing agents. The clay fraction ranged from 6 to about 20 percent (%) in the sandstones and from about 14 to 50% in the mudstones.

ARCADIS collected saturated soil samples from BA#1 (samples TMW-13 and O2W01), WAA transition zone (sample T-64), and the WAA (sample T-78) and submitted them for analysis by x-ray fluorescence (XRF) and x-ray diffraction (XRD). These results provide a baseline analysis of the soil mineralogy that can be compared with post-remediation results to evaluate mineralogical changes. The results of these analyses are presented below (Tables 3-1, 3-2, and 3-3).

Table 3-1. Summary of X-Ray Fluorescence Results

Sample ID	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	MgO %	CaO %	Na_2O %	K_2O %	TiO_2 %	P_2O_5 %	MnO %	Cr_2O_3 %	V_2O_5 %	LOI %	Sum
T-64	89.5	4.11	0.80	0.25	0.88	0.57	2.14	0.20	0.02	0.03	0.01	<0.01	1.10	99.6
T-78	87.7	4.70	0.48	0.28	1.09	0.65	2.38	0.10	0.02	0.01	<0.01	<0.01	1.46	98.9
TMW-13	89.4	4.10	0.58	0.22	0.84	0.58	2.07	0.14	0.02	0.02	<0.01	<0.01	0.96	99.0
O2W01	75.7	8.46	2.51	1.46	2.13	1.05	2.23	0.53	0.08	0.05	<0.01	0.01	4.98	99.2
DUP: O2W01	75.3	8.43	2.53	1.44	2.12	1.04	2.20	0.54	0.08	0.05	0.01	0.01	4.82	98.6

The XRF results are consistent with the description provided for the 1989 bedrock analysis. The major components are silicates and aluminum oxides. The samples located in the alluvium of BA#1 have major iron phases ranging from 0.5 to 2.5% by weight.

Table 3-2. Summary of Qualitative X-Ray Diffraction Results

Sample	Crystalline Mineral Assemblage (relative proportions based on peak height)			
	Major	**Moderate**	**Minor**	**Trace**
T-64	quartz	potassium-feldspar	plagioclase-feldspar	*mica, *calcite, *dolomite, *pyroxene, *amphibole
T-78	quartz	potassium-feldspar	plagioclase-feldspar	*mica, *calcite, *dolomite, *pyroxene, *amphibole
TMW-13	quartz	potassium-feldspar	plagioclase-feldspar	*mica, *calcite, *pyroxene, *amphibole
O2W01	quartz	potassium-feldspar, plagioclase-feldspar	mica, amphibole, dolomite, nontronite	*calcite, *goethite, *pyroxene

Table 3-3. Summary of Quantitative X-Ray Diffraction Results

Sample ID	T-64 (%)	T-78 (%)	TMW-13 (%)	O2W01 (%)
Quartz	73.3	73.2	80.1	54.6
Microcline	12.6	13.1	11.2	13.8
Albite	9.1	9.6	4.9	11.5
Augite	1.8	1.0	0.9	1.9
Mica	1.2	0.6	0.6	6.3
Actinolite	0.7	0.8	0.6	2.3
Dolomite	0.4	0.7	0.9	2.6
Calcite	0.9	0.9	0.9	1.5
Goethite	–	–	–	1.1
Nontronite	–	–	–	4.4
Total	**100.0**	**99.9**	**100.1**	**100.0**

3.1.3 Remediation-Specific Site Hydrogeology Summary

Generally, groundwater flow at the Cimarron Site is northward from the groundwater high south of the Site toward the Cimarron River. Sandstones of the Garber Formation are interbedded with layers of mudstone, siltstone, or shale of varying thicknesses. Because of this interbedding, groundwater occurs in the individual sandstone layers and may or may not be hydraulically interconnected, at least locally, with adjacent sandstone layers. Within the upper 200 feet at the Cimarron Site, four main water-bearing units have been previously designated as:

- Sandstone A;
- Sandstone B;
- Sandstone C; and
- Cimarron River Alluvium.
- Groundwater in Sandstone A flows from the topographically higher areas to adjacent drainages and reflects local recharge from precipitation events.
- Flow in Sandstones B and C is more regionally controlled and is toward the north to northwest in the direction of the Cimarron River. In the vicinity of BA#1, local groundwater flow in Sandstone B is more to the north and east because Sandstone B is the uppermost water-bearing unit and flow within this unit is influenced by local topography.
- At Cimarron, the river is a gaining stream with flow contribution coming from the alluvium and the underlying bedrock.

Periodic flooding by the Cimarron River temporarily affects bank storage in the alluvium adjacent to the river channel, but this effect is dampened in BA#1 and WAA by their distance from the river. The surface water hydrology and its impact on the variably saturated soils and groundwater are discussed in Appendix B.

Because groundwater flow varies locally across the Cimarron Site, a discussion of groundwater flow for specific areas of interest is presented in the Conceptual Site Model, Revision 1 (ENSR, 2006). The area-specific hydrogeologic considerations as related to the proposed remedial activities are presented in the following sections.

3.1.3.1 Burial Area #1

Groundwater in the vicinity of BA#1 flows across a buried escarpment that acts as an interface between the Sandstone B water-bearing unit and the floodplain alluvium. Groundwater in Sandstone B flows to the north and northeast driven by a relatively steep hydraulic gradient (0.10 feet/foot [ft/ft]) near the boundary between Sandstone B and the floodplain alluvium.

As groundwater enters the transition zone to the floodplain alluvium, the hydraulic gradient decreases to approximately 0.023 ft/ft, and flow is refracted to the northwest. The decrease in hydraulic gradient is due in part to the much higher overall hydraulic conductivity in the floodplain alluvium compared with Sandstone B. The refraction to the northwest may also be due to the coarser-grained material located in the paleochannel near the escarpment prior to the floodplain alluvial sediments. The paleochannel trends northwesterly near the buried escarpment and then north into the floodplain. As groundwater moves through the transitional zone and enters the coarser sands of the alluvium the hydraulic gradient decreases (0.0007 ft/ft).

3.1.3.2 Western Upland Area

In the WUA, the drainage between the former Uranium Pond #1 and the former Sanitary Lagoons acts as a local drain for shallow groundwater from Sandstone A. Groundwater flows toward this drainage from both the east and west, including Burial Area #3 (BA#3) and the former Sanitary Lagoons.

Groundwater gradients steepen along the cliff faces of the drainage. Along the cliff face bordering the Cimarron River Floodplain alluvium just north of the former Uranium Pond #1, groundwater flows north to northwest toward the floodplain in Sandstone A and discharges in small seasonal seeps. Groundwater gradients in Sandstone A near the former Uranium Pond #1 are approximately 0.01 ft/ft toward the drainages to the northeast and northwest and about 0.02 ft/ft toward the north.

Groundwater in Sandstones B and C flows northwest toward the Cimarron River beneath the WUA. In Sandstone B, the groundwater gradient is toward the north-northwest at about 0.023 ft/ft. In Sandstone C, the gradient is also toward the north at about 0.013 ft/ft (J.L. Grant and Associates, 1989).

3.1.3.3 Western Alluvial Area

Groundwater flow in the WAA occurs in the alluvial floodplain of the Cimarron River. Groundwater flow in this area is generally northward toward the Cimarron River. With hydrogeologic characteristics similar to the sandy floodplain alluvium near BA#1, this area exhibits a very low hydraulic gradient. Groundwater flow patterns are not affected significantly by seasonal fluctuations in water levels and periodic flooding as discussed in Appendix B.

3.2 Delineation of Areas of Uranium Impacts Exceeding the Criteria

At the Cimarron Site, groundwater in three distinct areas contains soluble uranium at concentrations in excess of the Criteria. The impacts presented have been documented in prior correspondence with the NRC. The areas of impact delineated in Figures 3-1 and 3-2 are based on data collected in 2004 and 2005, respectively. Sampling results for uranium activity from 2007 are posted on the figures and demonstrate that groundwater impacts have not migrated significantly despite recent record precipitation and multiple transient hydrologic events. Figure 3-1 shows the extent of the uranium area of impact (defined as groundwater activities exceeding 180 pCi/L) in BA#1, while Figure 3-2 displays the area of impacts in the WAA and WUA.

Previous delineation of groundwater impacts and other field investigations have been documented; however, ARCADIS has conducted additional, limited sampling of aquifer conditions in the BA#1, WUA, and WAA areas to better understand the groundwater chemistry. In addition, ARCADIS also conducted analyses of soil chemistry parameters relevant to a bioremediation approach (Section 5.2.1.2).

3.3 Hydrologic Assessment and Modeling

A hydrologic characterization for areas with groundwater impacts at Cimarron has been prepared (Appendix B) to evaluate the effect of transient hydrologic events on groundwater recharge. The characterization effort considered effects resulting from 1) periods of heavy rainfall; 2) river flood stage events; and 3) ponded water vertically infiltrating to the water table.

Fortuitously, starting in April 2007, the Cimarron Site experienced several months of high precipitation and river flows. These events were closely monitored and both river and groundwater responses to these events have been measured and evaluated. The evaluations included the application of the U.S. Environmental Protection Agency (USEPA) Hydrologic Evaluation of Landfill Performance (HELP) model (Schroeder, et

al, 1994) to estimate recharge volumes through the unsaturated zone to the water table during these periods of extreme precipitation.

3.3.1 Cimarron River Flow

The Cimarron River is a gaining river over its entire course from Freedom to Guthrie, Oklahoma. In the vicinity of the Cimarron Site, the flow is perennial. Because the Cimarron River is fed mainly by base flow from groundwater aquifers, base river flow in the Cimarron River parallels the seasonal fluctuation observed in groundwater levels. Flood statistics for the Cimarron River have been compiled by the United States Geological Survey (USGS, Tortorelli and McCabe, 2001) and indicate that peak flows near the site range from a 2-year flood with a discharge of 26,700 cubic feet per second (cfs) to a 500-year flood with a discharge of 237,000 cfs. These numbers are in general agreement with the numbers calculated by the USGS (2007b) of 27,800 cfs and 233,000 cfs, respectively, and with the values calculated using PKFQWin, described below.

3.3.2 Groundwater/Cimarron River Interaction

Water level information developed for the river and those Site monitoring wells located closest to the river (wells TMW-24 and 02W48) indicate that there is no direct hydraulic influence via the aquifer between river water levels and groundwater elevations at or upgradient of TMW-24 and 02W48 (located approximately 200 feet from the river). Because there is no direct hydraulic influence via the aquifer, there are no anticipated water quality impacts of river water on groundwater at or upgradient of TMW-24 and 02W48. Stiff diagrams created from samples collected from wells 02W48 and TMW-24 are consistent with Sandstone C and Alluvial well waters, respectively - that is, uninfluenced by river water quality. Because groundwater with uranium exceeding the Criteria in the WAA and BA#1 is greater than 200 feet from the river, such rises and falls in the river are not expected to impact groundwater where uranium occurs.

3.3.3 Extreme Rainfall Events

A total of 40.48 inches of rain fell between March 1 and August 21, 2007. This represents an almost 100% increase over typical rainfall during the same time period, and is roughly 5 inches above the normal amount received through the course of an entire year. Maximum river flow occurred on June 30, 2007 and was characterized by a flow rate of 45,000 cfs at the Site. These conditions resulted in flood elevations that caused low-lying drainage features to be inundated and river water to move into the floodplain as far south as the escarpment.

Groundwater elevation changes resulting from these extreme rainfall events are expected to be consistent with what was observed in the wells screened in alluvial soils in the BA#1 area. Differences of 5 to 10 feet were observed in this area in response to these extreme events; however, the overall gradients did not change significantly. Short-term changes in flux are small relative to the total water budget for the Site.

3.3.4 Groundwater Flow Conditions / Responses to Extreme Recharge

Based on groundwater levels measured in the Sandstone B and Transition Zone wells, the transient hydrologic events seen in the spring and summer of 2007 did not result in changes to the groundwater gradients and fluxes that are dramatically different from the changes that might be seen based on seasonally-collected water elevations. This information indicates that groundwater elevations in Sandstone B and Transition Zone soils are fairly stable. Groundwater elevations in alluvial zone soils were far more responsive to transient hydrologic events; however, elevations generally responded uniformly so the groundwater gradients did not change. Fluxes may change, but the largest changes lasted at most eight days; this duration may result in short-term increases of flux, but relative to the total water balance and the scope of the study, these increases are insignificant.

3.3.5 Application of the HELP Model to Simulate Groundwater Recharge Conditions

The HELP model was used with precipitation and soil characteristics to estimate a depth of recharge based on a variety of soil characteristics and depths of rainfall. Factors that control recharge to the water table are the intensity, frequency, and duration of rainfall as well as soil properties.

For an extreme statistical rainfall event, 7-day, 500-year rainfall (total precipitation of 15.5 inches and the resulting ponding based on the precipitation event only), recharge was simulated to be almost 8 inches over 30 days. Over the BA#1 area of impact, this amounts to 48,200 cubic feet or 361,000 gallons over 30 days.

Based on observations made during spring and summer 2007, ponding of 1 to 2 feet from extreme rainfall events lasted approximately 14 days and was estimated to result in a recharge volume over the BA#1 area of 170,000 cubic feet or 1.3 million gallons over 14 days. Additionally, ponding of 1 to 2 feet that persists for 10 days as a result of river bank overtopping at an elevation of 940 feet was estimated to result in a recharge volume over the BA#1 area of impact of 195,500 cubic feet or 1.5 million gallons.

Potential impacts resulting from the recharge of precipitation or ponded water into the groundwater were evaluated in the geochemical modeling performed for the Site as described in the following section.

3.4 Geochemical Modeling and Results

The objective of the modeling analysis was to evaluate the fate and transport of uranium under various geochemical conditions representative of the Site. During in-situ reactive zone (IRZ) treatment, uranium is reductively precipitated as the oxide mineral uraninite (UO_2). The geochemical modeling evaluates the formation and stability of this low solubility mineral phase over time as geochemical conditions return to baseline.

Simulations involving geochemical reaction path modeling were performed with the software package Geochemists' Workbench (Version 6.04, GWB; Rockworks, Golden, Colorado), a geochemical code capable of describing the precipitation, dissolution, and sorption of aqueous compounds including uranium under defined conditions in both batch and transport scenarios. GWB is capable of performing the calculations under either an equilibrium approach or a kinetic approach. With an equilibrium approach, the rate of reaction is not considered; rather, a purely thermodynamic approach is used based on each reaction's equilibrium constant. This approach assumes that all chemical species in the system rapidly reach equilibrium with each other. A kinetic approach assigns a rate to each reaction, rather than assuming that each reaction occurs under equilibrium. This modeling study utilized the equilibrium approach for reaction path modeling because robust reaction rates for the species of interest are not widely available and proven. Thermodynamic equilibrium constants for the system under study are available and verified (NEA, 2007).

3.4.1 Conceptual Basis for Geochemical Model

The proposed treatment technology will involve creation of electrochemically reducing conditions, which will stimulate the biological reduction of soluble uranium to the insoluble uranium oxide uraninite, along with reduced iron sulfide minerals. This process is described in detail in Section 4.2.1. Upon cessation of treatment, oxidizing groundwater will flow into the treated area causing oxidative dissolution of the iron sulfides and the uraninite. The reduced iron sulfides will be oxidized to amorphous iron oxides, and the uraninite will gradually dissolve to form soluble uranyl carbonates. A portion of the aqueous uranyl carbonate will form surface complexes with iron hydroxides, creating a sequestration mechanism for uranium. These chemical reactions were included in the geochemical model. To simulate fate and transport of

uranium, two different models were used: a batch-model that simulates the chemical reactions occurring during reduction and re-oxidation of the aquifer, and a one-dimensional (1-D) transport model that simulates both chemical reactions and the transport of uranium and other elements through the aquifer.

3.4.1.1 Aquifer Geochemistry

The average composition of groundwater input to the geochemical model was based on data from BA#1 collected during August and September 2004 (ENSR, 2006, Table 4-1); parameters used for groundwater composition were confirmed by sampling in the summer of 2007. To use a conservative concentration of oxygen and uranium, the 95% upper confidence limit (UCL) was used for the oxygen concentration, while the highest measured uranium concentration was used as the input to the model (Table 3-4). In the model, groundwater within BA#1 has the same composition as groundwater upgradient from BA#1, except that the upgradient groundwater contains no uranium.

The highest measured uranium concentration during the August/September 2004 sampling event (TMW-09, 4387 pCi/L) was used as the input for the uranium-laden groundwater as a conservative assumption of the uranium concentration in the groundwater. Based on a location-specific conversion factor of 1.6 picoCuries per microgram (pCi/µg), the uranium concentration was calculated to be 2.74 milligrams per liter (mg/L). This site-specific conversion factor was developed as shown in Table 3-5. The composition provided in Table 3-4 is charge balanced to within 3%, demonstrating that the analyses were of high quality. Analytical results are generally considered to be of high quality for samples with analyzed concentrations of cations and anions differing less than 10%, i.e., are charge balanced to within 10% or less.

Table 3-4. Composition of Average Groundwater Samples Collected from BA#1 During August/September 2004; Conservative Values Provided for Uranium and Oxygen.

Species	Concentration [mg/L]	Comment
Ca^{2+}	139.15	Average (ENSR, 2006, Table 4-1)
Cl^-	44.26	Average (ENSR, 2006, Table 4-1)
Fe	1.00×10^{-07}	Not detected, a concentration below analytical detection limit was used
pH	7.11	Average (ENSR, 2006, Table 4-1)
Alkalinity	404.65	Average (ENSR, 2006, Table 4-1)
Mg^{2+}	54.50	Average (ENSR, 2006, Table 4-1)
NO_3^-	0.44	Average (ENSR, 2006, Table 4-1)
Na^+	56.47	Average (ENSR, 2006, Table 4-1)
O_2(aq)	2.92	95% UCL (ENSR, 2006, Table 4-1)
SO_4^{2-}	186.20	Average (ENSR, 2006, Table 4-1)
SiO_2(aq)	6.00	Equilibrium with quartz
U	2.74	Highest measured concentration in BA#1 (ENSR, 2006, Table 4-1)

Note: Conservative values were assumed for uranium (U) and oxygen (O_2).

Table 3-5. Development of Location-Specific Uranium Activity to Mass Conversion Factor

Uranium Isotope	Specific Activity (pCi/g)	Mass Abundance (%)	pCi isotope/µg
^{238}U	3.33×10^5	97.38	0.324
^{234}U	6.19×10^9	0.0197	1.22
^{235}U	2.14×10^6	2.6	0.0556
		Total:	1.6

Note: Specific activity of uranium at Cimarron ranges from 0.6 to 2.7 pCi/g, depending upon location. For example, at BA#1 it ranges from 0.6 to 1.2, while in the WUA it ranges from 0.6 to 1.6, and in the WAA it ranges from 1.3 to 2.7.

The aquifer matrix composition (Table 3-3), together with the aqueous geochemistry presented above (Table 3-4), were used as inputs to the model. The composition was calculated assuming 25% porosity, i.e., for each liter of pore water, the model assumed 3 liters of rock. Assuming a density for the solid material of 2.0 kilograms per liter (kg/L), the ratio of pore water to soil is 1 kg water to 6 kg aquifer matrix. Using a greater density would result in a larger mass of iron hydroxide initially available to maintain reducing conditions at the end of active remediation; thus, it is conservative to assume a lower density. Table 3-6 shows the initial mass of minerals used for the geochemical model. Mineralogical analyses of the sandstones indicate that feldspar and clays (montmorrilonite, kaolinite) also made up a portion of the rock. These less abundant minerals were omitted from the model, as they do not affect its outcome with respect to uranium.

The 95% UCL of the solid-phase uranium content was calculated to be 6.61 milligrams per kilogram (mg/kg) for 168 soil samples (Cimarron Corporation, 2007). Solid-phase uranium was input as the hexavalent uranium oxide gummite (UO_3) (Table 3-6).

Soil samples collected at TMW-9, TMW-13, and TMW-24 were analyzed by ARCADIS for iron content (ARCADIS, 2006). The total iron concentrations ranged from 1,720 to 14,100 mg/kg. Sequential extraction showed that only 3% of the total iron concentration is bioavailable. Therefore, only 3% of 10,000 mg/kg iron was included in the model. To create a mathematically stable model, the iron was input as goethite.

The mineral in which an element is input to the model is irrelevant; the composition of the system is based on the moles of each element input to the system. However, inputting an element (either aqueous or solid-phase) as the thermodynamically most stable phase aids the model to solve the system of mathematical equations that is based on the chemical reactions.

Table 3-6. Mass of Minerals Used in the Geochemical Model.

Mineral	Content of rock (mg/kg or g/kg)	Mass/liter water (g)	Comment
Quartz	98% = 980 g/kg	5,880 g	Clays and feldspars are not considered in the model.
Calcite	1% = 10,000 mg/kg	60 g	Major cementing agent (J.L. Grant and Associates, 1989). Amount assumed.
Goethite	477 mg/kg	2.86 g	Total iron 10,000 mg/kg, 3% reactive iron.
UO_3(s) (gummite)	7.94 mg/kg	47.7 mg	The 95% UCL of the soil survey results for BA#1 is 6.61 mg/kg; this was converted to mass of UO_3 for entry into the geochemical model.

In the 1-D transport model, the mineralogical composition of the aquifer was input as a volume fraction instead of mass, as in the batch model. The mass of minerals was converted to volume such that the composition of the solid aquifer material did not change, and the sum of aqueous- and solid-phase uranium was input as uraninite. The groundwater composition used in the 1-D transport model was the same as in the batch model.

3.4.1.2 Hydrology Inputs to Model

The hydrologic conceptual model used for the 1-D transport model was based on the Conceptual Site Model, Revision 1 (ENSR, 2006, Figure 3). The model domain encompassed a 275-meter (900 feet) transect from the uplands area in the south to the alluvium in the north and was divided into 7 cells, 39 meters (129 ft) each (Table 3-7). Dispersive mixing of water between nearby cells is included in the model by a dispersion coefficient (D), which is calculated from the longitudinal dispersivity (α_L), the

groundwater velocity (v), and the molecular diffusion coefficient (D*), Equation 1 (Fetter, 1994). Appropriate values for diffusion and dispersion coefficients were used as site-specific values have not been determined.

$$D = \alpha_L \cdot v + D^* \qquad (5\text{-}1)$$

Table 3-7. Physical Model Domain for the 1-D Transport Model.

Model domain	Value	Source of data
Model length	275 m (900 ft)	ENSR, 2006
Number of cells	7	Model input
Cell width	1 m (3.3 ft)	Model input
Cell height	1 m (3.3 ft)	Model input
Diffusion coefficient	$1x10^{-8}$ cm^2/s	Model input
Longitudinal dispersivity	$1x10^{-5}$ m	Model input
Linear groundwater velocity	0.18 m/d (0.6 ft/day)	ENSR, 2006

The average linear groundwater velocity in Sandstone B was calculated to 0.6 foot per day in the Conceptual Site Model, Revision 1 (ENSR, 2006). Average linear velocities in the transition zone and the alluvium were slower; 0.03 and 0.3 ft/day, respectively. Thus, using a linear velocity of 0.6 ft/day is the fastest groundwater velocity supported by the site conditions and represents the shortest possible time for the aquifer to re-oxidize after reducing conditions have been established in the IRZ. An average linear velocity of 0.6 ft/day (0.18 m/day) equals a specific discharge of 0.045 m/day, assuming 25% effective porosity. Under these conditions, one pore volume flushes through the system in approximately 4.2 years.

3.4.1.3 Surface Complexation Model

The surface complexation model included in the geochemical model is based on Waite et al. (1994), who investigated uranium sorption onto iron hydroxides, developed a surface complexation model, and derived surface complexation constants based on results from their laboratory experiments. They evaluated surface complexation of hexavalent uranium to two-line ferrihydrite (a poorly-crystalline, amorphous iron oxyhydroxide that is predominant in the environment especially at oxic/anoxic interfaces in an aquifer) under various pH and partial pressures of carbon dioxide and concluded that a two-site model described the data well. The model accounts for complexation of uranyl and ternary uranyl-carbonate surface complexes as well as competitive surface complexation of bicarbonate and carbonate ions. Extended x-ray absorption fine structure (EXAFS) spectroscopy of surface samples indicated that the uranyl and uranyl-carbonate surface complexes were bi-dentate in nature and that a model based on the mixed behavior of mono- and bi-dentate complexation described the surface complexation well. In a mono-dentate complex, one surface site on the iron hydroxide complexes one uranyl ion and in a bi-dentate model, two surface sites form a complex with a single uranyl ion. The model derived by Waite et al. (1994) was modified somewhat and used to model uranium complexation to iron hydroxide surfaces in the aquifer.

Waite et al. (1994) derived the constants for uranyl and uranyl-carbonate surface complexation without considering aqueous calcium-uranyl-carbonate species ($CaUO_2CO_3$ and $Ca_2UO_2[CO_3]_3$) discussed by Ortiz-Bernard et al. (2001). If these aqueous species would have been included in the derived values, the surface complexation constants would have been different. In order not to introduce internal inconsistencies in thermodynamic database, the aqueous calcium-uranyl-carbonate complexes were not included in the database, but only reactions used in the Waite et al. (1994) study were used. This approach was used to model the geochemical behavior of uranium as accurately as possible.

This surface complexation model has been successfully applied to uranium contaminated sediments. In 2004, Davis et al. applied the model to sediments collected from an alluvial aquifer in Naturita, Colorado and concluded that the model simulated the uranium transport accurately, but that it was challenging to determine the amount of reactive surfaces present. After applying the model to soils collected at three Department of Energy (DOE) sites, Barnett et al. (2002) concluded that the model was able to predict the behavior of uranium under various pH and carbon dioxide pressures, even outside of conditions for which the model was originally developed. The model is robust and simulates uranium fate and transport well. The

model should be calibrated to specific sites by adjusting the site-specific concentration of reactive iron.

The model developed by Waite et al. (1994) was included in both the batch model and the 1-D transport model. The model considers protonation reactions of the iron hydroxide surfaces (Equations 1 and 2). Identical acid/base reactions, with identical constants, were assumed for both the strong and weak sites, but only the reactions for the strong site are shown here. All equilibrium constants were derived at 0.1 molar (M) ionic strength (the symbol ">" denotes a mineral surface).

$$>(s)FeOH + H^+ \leftrightarrow >(s)FeOH_2^+ \qquad \text{logK} = 6.51$$

$$>(s)FeOH \leftrightarrow >(s)FeO^- + H^+ \qquad \text{logK} = -9.13$$

Carbonate and bicarbonate surface complexation are described by:

$$>(s)FeOH + H^+ + HCO_3^- \leftrightarrow >(s)FeCO_3H^0 + H_2O \qquad \text{logK} = 3.47$$

$$>(s)FeOH + HCO_3^- \leftrightarrow >(s)FeCO_3^- + H_2O \qquad \text{logK} = 1.28$$

The carbonate surface reactions and the equilibrium constants for the strong and weak sites are identical, but only the reactions between the carbonate species and the strong sites are shown here.

Waite et al. (1994) considered uranyl complexation bi-dentate in the mass balance equations, but modeled the reaction as a mono-dentate complex in the mass action equations. Modeling this mixed mono- and bi-dentate behavior is only possible in the computer program FITEQL; in the Geochemist's Workbench and other software, the coefficient in the mass action equation must be the same as the coefficient in the mass balance equation. In other words, all commonly used geochemical modeling software is only able to model surface complexation as purely mono-dentate or purely bi-dentate. Therefore, to make possible the use of the Waite et al. model, the equations for uranyl surface complexation:

$$>(s)Fe(OH)_2 + UO_2^{2+} \leftrightarrow >(s)Fe(O)_2UO_2 + 2H^+ \qquad \text{logK} = -2.57$$

$$>(w)Fe(OH)_2 + UO_2^{2+} \leftrightarrow >(w)Fe(O)_2UO_2 + 2H^+ \qquad \text{logK} = -6.28$$

were modified by using a coefficient of one in both the mass action and mass balance equations, i.e., the surface complexes were modeled as mono-dentate complexes. This model is a robust platform for simulating uranium complexation to iron hydroxide.

The corresponding equilibrium constants were calculated assuming that pH is 7, which is the pH measured in the field.

$$>(s)FeOH + UO_2^{2+} \leftrightarrow> (s)FeOUO_2^{+} + H^{+} \qquad \text{logK} = 4.43$$

$$>(w)FeOH + UO_2^{2+} \leftrightarrow> (w)FeOUO_2^{+} + H^{+} \qquad \text{logK} = 0.72$$

The charges of the individual surface species differ between the reactions presented in Waite et al. (1994) and the mono-dentate reactions derived for this modeling exercise. In the surface complexation model, however, the activity coefficients for surface species are unity (i.e., the activity of solids is not modified by the aqueous chemical constituents and is 1; Dzombak and Morel, 1990). Thus, the difference in charge representation does not affect the surface complexation constants considerably.

Similar to uranyl surface complexation, tertiary uranyl-carbonate surface complexation is modeled as mono-dentate complexes. The reactions derived by Waite et al. (1994):

$$>(s)Fe(OH)_2 + UO_2^{2+} + CO_3^{2-} \leftrightarrow> (s)Fe(O)_2UO_2CO_3^{2-} + 2H^{+} \quad \text{logK} = 3.67$$

$$>(w)Fe(OH)_2 + UO_2^{2+} + CO_3^{2-} \leftrightarrow> (w)Fe(O)_2UO_2CO_3^{2-} + 2H^{+} \quad \text{logK} = -0.42$$

were simplified to reactions describing mono-dentate complexes and described in terms of basis species in the Geochemist's Workbench:

$$>(s)FeOH + UO_2^{2+} + HCO_3^{-} \leftrightarrow> (s)FeOUO_2CO_3^{-} + 2H^{+} \quad \text{logK} = 0.33$$

$$>(w)FeOH + UO_2^{2+} + HCO_3^{-} \leftrightarrow> (w)FeOUO_2CO_3^{-} + 2H^{+} \qquad \text{logK} = -3.76$$

The two-line ferrihydrite used in the Waite et al. (1994) model was freshly precipitated with large surface area. Aged iron hydroxides are generally more crystalline and have less surface area than freshly precipitated amorphous iron hydroxides. In our model, however, it was assumed that, based on sequential extraction experiments, only the easily dissolved fraction of the total iron hydroxide was available to react with uranium. Thus, only 3% of the total iron was used in the model. The site densities, but not the

surface complexation constants, were adjusted to calibrate the model to the observed aqueous uranium concentration, the solid-phase uranium content, and the bioavailable solid-phase iron.

3.4.2 Modeling Current Conditions

In order to make sure the surface complexation model simulates current conditions accurately, initial conditions were modeled prior to modeling reduction and re-oxidation of the aquifer based on recommendations by Davis et al. (2004). As a result, the surface site densities in the surface complexation model were adjusted such that the model matched observed aqueous concentrations and solid-phase uranium content based on biologically reducible solid-phase iron (Tables 3-4 and 3-6). The site densities were increased slightly compared to Waite et al's (1994) original concentrations assuming 3% reactive iron; the site densities used in the model were 7.3 mole strong sites/mole iron (Fe) and 3.55 mole weak sites/mole Fe. After adjustment, the model successfully modeled conditions at the site: the aqueous uranium concentration in equilibrium with 6.61 mg/kg solid-phase associated uranium was 2.74 mg/L. Thus, the adjusted surface complexation model is applicable to current site conditions.

3.4.3 Modeling Reduction

Reduction of the aquifer during the IRZ was modeled with both a batch model and a 1-D transport model. The batch model is able to describe the geochemical reactions that occur during reduction and assess the amount of mineral precipitation and dissolution occurring within the IRZ. The 1-D transport model does not provide more detail than the batch model but was later used to simulate transport of uranium during re-oxidation of the aquifer. The purpose of using both models during the reduction phase was to compare the results of the 1-D transport model to the less complex batch model to make sure that both models were in agreement and constructed correctly.

In the batch and the 1-D transport models, reduction of the aquifer was modeled assuming that 4,300 mg/L sodium sulfate (Na_2SO_4) and 8,100 mg/L ferrous sulfate ($FeSO_4$) were added during the remediation injections, while reducing conditions are established. The sulfate and iron will be co-injected with the carbon source during creation of the anaerobic IRZ. In the batch model, this was achieved by titrating sodium sulfate into the aquifer system, at the same time removing oxygen from the system. The oxygen concentration was decreased from 2.92 to 0 mg/L. In the model removal of oxygen is performed in 100 iterations or steps. Biological consumption of organic carbon, which creates sulfate-reducing conditions and lowers or buffers pH, is

not modeled explicitly but is simulated by stepwise decreasing the amount of oxygen (fugacity of oxygen) while keeping the pH constant. This method of stepwise decreasing the amount of oxygen is a commonly used and simplified method of simulating the complex process of oxygen consumption by microorganisms.

In the 1-D transport model, sodium sulfate was added to the initial system at the absence of oxygen (extremely low oxygen fugacity), while an insignificant volume of upgradient water was flushed through the system. Technically, this is performed by adding sodium to the aqueous phase and adding sulfur in the form of mackinawite. The system was only flushed with upgradient oxygenated water for one day to keep the system reduced and to allow comparison between the batch and the 1-D transport models. The purpose of this step is to ensure high quality in the modeling process; the 1-D transport model, if constructed correctly, should yield the same results as the batch model during the very early stage of re-oxidation. The 1-D transport model does not provide information that the batch model cannot provide during the reduction phase. Thus, this step is only performed to check the performance of the more complex 1-D transport model.

3.4.3.1 Batch Model

The current redox poise in the aquifer was reduced by stepwise removing oxygen from system (decreasing the log fugacity of oxygen to -74) while adding 4,300 mg/L sodium sulfate and 8,100 mg/L iron sulfate. Figure 3-3 depicts the predicted reaction path: dissolved and surface complexed uranium precipitates as uraninite [UO_2(s)] when the reduction potential (Eh) decreases below approximately 0.2 volts, and iron hydroxide dissolves reductively and precipitates in mackinawite (FeS[s]) when sulfate reducing conditions set in. The model predicts that uraninite precipitates before geothite dissolves and mackinawite forms (Figure 3-4). The aqueous iron concentration increases and siderite ($FeCO_3$[s]) precipitates when iron hydroxide dissolves. Most iron, however, precipitates as mackinawite under sulfate-reducing conditions in the IRZ phase. Figures 3-4 through 3-16 were all created based on output from the modeling program.

The change in redox poise and change in mineral composition causes the aqueous uranium concentration to decrease significantly (Figure 3-5). During the initially oxidizing conditions, the uranium concentration is 2.74 mg/L and approximately 93% of the uranium is complexed to surfaces. These conditions are based on analyses performed on soil and groundwater samples collected at the Site as discussed above. As iron hydroxide dissolves, the surface complexation sites are depleted and less uranium sorbs to the surfaces (Figure 3-6). As the conditions become reducing, the

model predicts that uranium precipitates as uraninite and the aqueous uranium concentration decreases significantly. Under more reducing conditions, ferric iron is reduced to ferrous iron, causing precipitation of siderite and mackinawite when injected sulfate is reduced to sulfide (Figure 3-4).

3.4.3.2 1-D Transport Model

Input to the 1-D transport model was based on output from the reducing conditions simulated in the batch model (Tables 3-8 and 3-9). The elemental composition was the same as in the batch model, but the starting scenario for the 1-D transport model was the reduced conditions prevailing in the IRZ.

Table 3-8. Mineralogical Composition of the Reduced Aquifer in the 1-D Transport Model.

Mineral	Composition	Mass [g]	Density [g/cm^3]	Volume [cm^3]	Fraction [% volume]
Quartz	SiO_2	7,885	2.648	2978	74.44
Calcite	$CaCO_3$	53.7	2.71	19.8	0.4952
Mackinawite	FeS	2.001	4.17	0.480	0.0120
Siderite	$FeCO_3$	1.006	4.047	0.249	0.00621
Uraninite	UO_2	0.048	10.97	0.00439	1.079×10^{-4}

Table 3-9. Composition of Water in Equilibrium with the Solids in the Reduced Aquifer.

Species	Concentration [mg/L]	Comment
$SiO_2(aq)$	NA	In equilibrium with quartz
HCO_3^-	NA	In equilibrium with calcite.
U	NA	Highest measured concentration (ENSR, 2006, Table 4-1)
Fe	NA	In equilibrium with siderite.
SO_4^{2-}	NA	In equilibrium with mackinawite.
pH	7.11	Average (ENSR, 2006, Table 4-1)
$O_2(aq)$	log $f(O_2)$ = -74	Reducing conditions during IRZ.
Ca^{2+}	2,586.86	Calcite dissolved during reduction.
Cl^-	44.26	Average (ENSR, 2006, Table 4-1)
Mg^{2+}	54.71	Average (ENSR, 2006, Table 4-1)
NO_3^-	0.44	Average (ENSR, 2006, Table 4-1)
Na^+	1,013	Sodium sulfate added during IRZ phase.

The reduced system in the 1-D transport model was flushed with upgradient water for 1 day to avoid changing the composition of the fluid. The results are identical to the results in the batch model. Both models predict that iron is present primarily as mackinawite and that uranium precipitates as uraninite (Figures 3-4 and 3-7). The predicted concentration of iron, sulfur and uranium in the 1-D transport model (Figure 3-8) is the same as during the reducing conditions in the batch model (Figure 3-5). Because iron hydroxide is not present in the system under reducing conditions, there is no surface present for the uranium (data not shown). Both models yield the same

results, and the 1-D transport model simulates the geochemical reactions as accurately as the batch model.

3.4.3.3 Modeling Re-oxidation

After the active remediation phase is terminated, upgradient, uranium-free, oxygenated groundwater will enter the aquifer and begin oxidizing the reduced minerals (uraninite, mackinawite, and siderite). For both the batch and 1-D models, the results from the IRZ simulation were used as the starting point for the re-oxidation simulation.

The batch model was simulated as a "flush-through" model, in which upgradient oxygenated groundwater was added to the system at the same rate as "reacted" groundwater leaves the system. A "flush-through" model tracks the evolution of the solid aquifer material and the groundwater that is in equilibrium with the solids (Bethke, 1996). A total of 2,000 pore volumes of upgradient groundwater were flushed through the system. One pore volume flows through the system in approximately 4.2 years; 2,000 pore volumes represents over 10,000 years of flushing.

As in the batch model, the reduced system in the 1-D transport model was flushed with upgradient groundwater. Groundwater was flushed through the system for a period of 3,000 years, and the aqueous concentration and amount of minerals were tracked in portions of the system.

3.4.3.4 Batch Model

Batch simulations of re-oxidation of the aquifer show that minerals formed during the IRZ phase create considerable redox buffering capacity. The batch model simulates the entire aquifer as one equilibrium system; at a linear groundwater velocity of 0.18 m/day and 25 percent effective porosity, it takes 4.2 years for one pore volume to flow through the 275 m long system. Thus, during 1,000 years approximately 240 pore volumes will flow through the entire system. Figures 3-9 and 3-10 show that throughout flushing of 240 pore volumes, the system will be buffered by mackinawite and the aqueous concentration of uranium will remain very low (0.00001 µg/L). More than 1,650 pore volumes (6,900 years) are needed to provide enough oxygen to oxidize the mackinawite and it takes approximately 1,800 pore volumes (7,600 years) to oxidize the uraninite in the entire system. The model predicts that no oxygen will react with uraninite while mackinawite is present in the system. In reality, however, some uraninite will oxidize before all mackinawite has dissolved; the reactions are not completely step-wise as assumed in an equilibrium model. This is an artifact of assuming equilibrium, which is necessary as reaction rates for these reactions are not

available. Interpreting the results of the model by taking into account this limitation of the equilibrium approach, the aqueous uranium concentration will likely be somewhat greater than 0.00001 µg/L, resulting in controlled leaching of uranium over time.

When uraninite dissolves, the model predicts that the aqueous concentration of uranium increases significantly. Surface complexation to iron hydroxides buffers the concentration slightly, but the rapid dissolution predicted under equilibrium overloads the surface sites (Figure 3-11). This is an artifact of the modeling approach, based on thermodynamic equilibrium and not on rate-limited reactions. Thus, the concentration of uranium is expected to be limited even during this late phase of aquifer oxidation. It should be noted that the same approach, based on thermodynamic equilibrium, is used to understand the role of hydrogen sulfide in limiting uranium mobility after closure of in-situ uranium leach mining projects (Davis and Curtis, 2007).

3.4.3.5 1-D Transport Model

The 1-D transport model yields similar results as the batch model. Oxygen in the incoming groundwater reacts to completion with any available mackinawite before oxidatively dissolving uraninite. The 1-D transport model, as opposed to the batch model, simulates the oxidation front along the flow path. Initially, all incoming oxygen reacts in the most upgradient portion of the model until aerobic equilibrium is reached. The oxidation front then moves downgradient, dissolving mackinawite and precipitating iron as iron hydroxide, followed by dissolution of uraninite (Figure 3-12). During 3,000 years of infiltration of upgradient groundwater, the entire system will not become oxidized. The most downgradient portion of the site will remain reduced as shown in Figure 3-13. Similar to the batch model, equilibrium assumption imposes very sharp changes in the geochemical phases, resulting in unreasonably rapid increase and subsequent decrease in aqueous uranium concentration (Figure 3-14). The second peak in uranium concentration in the most upgradient cell is a result of dispersion from the adjacent cell in the model and is unlikely to occur in reality. Dispersion is more likely to create one broader lower uranium peak.

The time frame for dissolution of uraninite in the 1-D transport model is similar to the time frame predicted by the batch model. Complete oxidation of the system is not predicted to occur within 3,000 years. The model predicts that the oxidation front will slowly move through the system, oxidizing the first 39 m (129 feet) in approximately 1,150 years (Figure 3-12). The very sharp changes in aqueous concentrations predicted in Figure 3-14 are unrealistic and a result of equilibrium assumption. A more realistic scenario is that mackinawite will preferentially oxidize over uraninite and that the two processes will overlap, but at different reaction rates. In a field test of biological

reduction of uranium, Wu et al. (2007) found that the uranium concentration after injection of carbon source ranged between <0.03 and 0.3 mg/L (starting concentrations were 800 mg/kg uranium in the soil and up to 60 mg/L in the groundwater). Re-oxidation tests with up to 10 mg/L dissolved oxygen showed uranium rebounded to no higher than 0.3 mg/L. In their field study, no additional sulfate was injected to create a phase that would buffer redox conditions, and lower uranium concentrations are expected when injecting sulfate. Therefore, uranium is expected to be transported out of the system at a concentration less than 0.1 mg/L, but higher than 0.0001 µg/L predicted by the equilibrium model. Also, the peak concentration predicted under strict equilibrium assumption is unlikely to occur, and a considerably lower maximum uranium concentration is expected.

3.4.4 Modeling Flooding Scenario

When a flooding event occurs, surface water saturated with oxygen will infiltrate into the aquifer. This water may also contain nitrate that can serve as an electron acceptor and potentially increase the rate of mackinawite and uraninite oxidation. In this modeling scenario, it was assumed that surface water reaching the groundwater table contained nitrate at a concentration of 30 mg/L. This high nitrate concentration simulates the effect of agricultural activities and is not representative of current conditions, but is included in the model because of potential future input of nitrate at the Site due to agricultural activities. Vadose zone reactions that would limit the infiltration of these substances were not considered in the model.

ENSR evaluated extreme recharge events that may occur over an extended time period (Appendix B). It was estimated that a 500-year flood would last 30 days, causing ponding on the surface resulting in recharge of approximately 48,000 cubic feet of water to the area of impact. Additionally, river overtopping was identified as a potential extreme recharge event lasting 10 days. It was estimated that 196,000 cubic feet of water would infiltrate to the BA#1 area of impact during each event. The recurrence interval was not reported and, for the purpose of this modeling study, it was assumed to vary between 100 and 500 years. Both scenarios were evaluated. These extreme infiltration events result in an infiltration of 1.4 pore volumes over 1,000 years for the longer recurrence interval and approximately 6.0 pore volumes assuming a recurrence interval of 100 years. These calculations were performed by comparing the volume of water infiltrating from extreme events over a 1,000-year period to the volume of water (pore volume) contained in the area of impact. The area of impact was estimated to be 68,880 square feet; the saturated zone thickness was estimated to be 20 feet, and the porosity to be 25%. In the model, infiltration as a result of accumulated extreme infiltration events was simulated by flushing the system with

oxygenated, nitrate-rich water for 6 years assuming a 500-year recurrence interval, and 25 years assuming a 100-year recurrence interval. The oxygen concentration was conservatively assumed to be 8 mg/L (saturation) and the nitrate concentration 3.4 mg/L.

The flooding scenario was modeled using the 1-D transport model. Prior to flushing the system with upgradient groundwater, the system was flushed for approximately 6 years with infiltrating groundwater to simulate the effect of extreme rainfall events and river flooding. The upgradient groundwater was saturated with oxygen and contained 3.4 mg/L nitrate.

The addition of electron acceptors (oxygen and nitrate) did not significantly increase the rate of mackinawite and uraninite oxidation (Figures 3-15 and 3-16). Thus, over a 1,000-year period, the effect of groundwater from extreme infiltration events is low compared to the effect of oxygen flowing into the system from upgradient portions of the Site.

3.4.5 Conclusions Based on Geochemical Model

Based on the modeling exercise presented in the sections above, the following conclusions can be drawn.

- Geochemical modeling was completed using site-specific geochemical data for BA#1; this area has the highest concentrations of uranium at the Site (4,387 pCi/L at well TMW-09). At the other two evaluated areas, the uranium concentrations are lower (2422 pCi/L at well 1351 in the WUA, and 1058 pCi/L at well MWA-03 in the WAA). BA#1, therefore, challenges the geochemical model and the simulation of the remediation progress to the greatest extent, making the results of the simulation for this area applicable to the other two areas.

- Solid- and aqueous-phase uranium is predicted to precipitate as uraninite under the reducing conditions created in the IRZ. As a result of uraninite formation, the aqueous concentration of uranium will decrease significantly.

- Mackinawite will form as a result of sulfate injection and reducing conditions in the IRZ. After the engineered remediation, inflowing groundwater will preferentially react with mackinawite to form iron hydroxides, which will sorb approximately 90% of the uranium. Strict equilibrium assumption predicts that uraninite dissolution will occur only after all mackinawite is reacted. In reality,

however, it is expected that oxygen will react preferentially with mackinawite over uraninite, but both reactions will overlap at different reaction rates.

- The batch model predicts that it will take 6,900 years to oxidize all the mackinawite in the system and that uraninite will be oxidized after 7,600 years. The 1-D transport model predicts that the oxidation front will move downgradient in the system. After 1,150 years the upgradient 39 m (130 feet) is predicted to be oxidized. The results from the equilibrium model are interpreted such that the aqueous uranium concentration will remain below the regulatory concentration of 0.1 mg/L both during the reduction and oxidation phases.

- Flooding and infiltration of oxygenated groundwater with elevated concentrations of nitrate is not expected to significantly affect the uranium concentration in the groundwater.

4. Uranium Immobilization Process

The IRZ technology proposed for the Cimarron Site is an in-situ biogeochemical process for immobilization of uranium. The following sections describe:

- How uranium is immobilized through reductive precipitation and sorption onto soil particles;
- The expected stability of the immobilized uranium upon completion of treatment; and
- References documenting successful demonstration of uranium immobilization both in the laboratory and at other sites.

4.1 Biogeochemical Processes

Research in the early 1990s clearly demonstrated that the transformation of dissolved uranium to precipitated forms was catalyzed by soil and groundwater microorganisms (Lovely et al., 1991; Francis et al., 1994). The resultant product of this transformation is insoluble uraninite ($UO_{2(s)}$). Recent work has shown that uranium contaminated groundwater can be treated using an engineered system for introduction of organic carbon (ethanol) into the subsurface, even under non-ideal conditions with respect to groundwater geochemistry (e.g., pH as low as 3.4, nitrate in excess of 1 g/L [Wu et al., 2006a, 2006b]). Reliance on achieving slightly reducing conditions using ethanol, acetate, or lactate as electron donors creates a less robust treatment system; carbohydrates such as glucose or complex carbohydrates will support a diverse assemblage of microorganisms that can assimilate a multitude of oxidants (Francis et al., 1991; Madden et al., 2007).

The IRZ technology has been used extensively to degrade chlorinated solvents and to stabilize metals within contaminated aquifers. As of 2006, more than 230 sites have been treated by ARCADIS using the IRZ technology (Lutes *et al.* 2005; Nyer *et al.* 2001; Suthersan 2002; Harrington 2002). Implementation of the IRZ technology consists of the following steps:

1) Determination of background geochemical conditions within the area of impact to be remediated, with special emphasis on the concentrations of dissolved and solid phase electron acceptors present in the area of impact. These electron acceptors typically include dissolved oxygen, nitrate, dissolved and structural mineral-associated iron (III) and manganese (III and IV), dissolved

and adsorbed uranium (VI), and dissolved and structural mineral-associated sulfate.

2) Formation of reducing conditions through the removal of oxygen and nitrates within and around the area of impacted groundwater. Reducing conditions are created by the injection of organic carbon, which is oxidized and degraded by microbial activity (organic carbon oxidation).

3) Creation of reducing conditions results in precipitation of dissolved uranium as a reduced uranium (IV) oxide ($UO_{2[s]}$). The precipitation is catalyzed by microorganisms, where organic carbon is oxidized and uranium is reduced (organic carbon is the electron donor, and uranium is the electron acceptor). Over time, freshly precipitated uranium becomes increasingly crystalline and insoluble (Casas *et al.,* 1998).

4) Other compounds adjacent to and around the uranium are reduced and co-precipitate. These compounds are typically iron sulfides formed as a result of microbial sulfate reduction, where organic carbon is oxidized and sulfate is reduced to sulfide. Reduced Fe(II)-containing hydroxides and oxides including green rusts (Fe(II)Fe(III)-hydroxides) and magnetite (Fe_3O_4) can form (O'Loughlin et al., 2003). Typically, organic carbon injected into groundwater sequentially deoxygenates the aquifer and supports reduction of uranium, followed by reduction of structural iron compounds and dissolved sulfate (Zehnder and Stumm, 1989). All these reactions are microbially-catalyzed reduction-oxidation (redox) reactions. The process can be designed to precipitate iron sulfides at concentrations significantly in excess of the precipitated uranium concentrations.

5) Determination that sufficient reduced minerals have been deposited in the plume to maintain uranium stability. This determination is based upon the use of geochemical modeling to predict the oxidation of reduced compounds within an impacted area by the mass of oxidants entering the system over time. This determination also involves recovery of solid phase material and examination of iron mineralogy and adjustments to the modeling based upon the ratio of reduced uranium to other reduced compounds.

6) Determination that uranium remobilization will not exceed the site cleanup standard. As the natural, slightly oxic redox poise of the aquifer returns after treatment, this must not result in the sufficient release of uranium from the precipitated mass to cause concentrations in groundwater that exceed site

cleanup criteria. This process can be demonstrated numerically through geochemical modeling. Groundwater sampling and post-treatment oxidative aging studies provide empirical data to support the geochemical modeling.

4.1.1 Uranium Removal by Microbial Reduction in Groundwater

Additional information to support the well-documented technical basis for this approach is detailed here, with reference to recent studies that have examined the stability of uranium precipitated and immobilized through bioreduction.

Lovley *et al.* (1991; Lovley and Phillips, 1992) proposed the remediation of uranium in groundwater using an in-situ bioremediation process. Since that proposal, an extensive amount of work has been published documenting the removal of uranium by microbial processes in groundwater or simulated groundwater conditions. This bibliography is summarized in Lloyd and Macaskie (2000). The following papers are particularly relevant to documenting that injection of an organic carbon source into a typical uranium area of impact will result in uranium precipitation as insoluble uranium oxides, and that sulfides can be co-precipitated with the uranium to provide long-term uranium stability.

Senko *et al.* (2002) show that uranium reduction can be rapidly achieved in an aquifer containing excess organic carbon as acetate, lactate, and formate (organic carbon sources) into which soluble uranium is introduced. They also demonstrate the importance of excluding nitrate and denitrification intermediates from the aquifer following uranium reduction to prevent remobilization of the uranium.

Chang *et al.* (2001) showed that sulfate reducing bacteria (SRB) are abundant in groundwater in a zone containing high concentrations of uranium at the Shiprock, New Mexico site, and that these bacteria are capable of uranium reduction, sulfate reduction, and iron sulfide precipitation. Microbially-facilitated uranium reduction resulted in less than 1 pCi/L dissolved uranium activity after bioprecipitation.

Abdelouas *et al.* (2000) performed column studies that showed that excess iron sulfide provides a redox buffer to prevent oxidative dissolution of uranium. They state, "the more iron sulfide present, the higher the stability of uraninite." They documented that a maximum concentration of 29 pCi/L dissolved uranium was formed during re-oxidation of freshly precipitated uranium where excess iron sulfide was precipitated along with the uranium.

Spear *et al.* (2000) showed that uranium reduction proceeds rapidly in the presence of excess organic carbon, and that sulfate reduction will also occur along with uranium reduction if sufficient organic carbon is added and sulfate is available.

Abdelouas *et al.* (1999) also performed column studies where accelerated oxidation experiments documented uranium stabilization for a simulated period of hundreds of years where iron sulfide had been co-deposited with the uranium.

Numerous other recent papers have documented that uranium removal and sulfate reduction follows the injection of sulfate and organic carbon into groundwater containing uranium, as well as the ability of these systems to prevent remobilization of uranium at concentrations of concern (Marsili et al., 2007; Wu et al., 2007; N'Guessan et al., in-press). The recent work by Wu et al., 2007, showed uranium remained immobilized through in-situ bioreduction at the Oak Ridge, TN site after re-oxidation via oxygen injection.

4.2 Enhanced Sorption

4.2.1 Sulfate Reduction and the Role of Iron Sulfides

SRB are ubiquitous in the environment and have been utilized to perform in-situ bioremediation for a wide variety of contaminants, including hydrocarbons, chlorinated solvents, and sequestration of heavy metals. SRB derive energy through the reduction of sulfate to sulfide under anaerobic conditions. Some SRB are capable of utilizing other electron acceptors directly, including uranium (Chang *et al.*, 2001; Spear *et al.*, 2000). SRB use sulfate as an electron acceptor and an organic carbon source as an electron donor. Sulfate is reduced to sulfide which, at low pH, takes the form of hydrogen sulfide (H_2S) and becomes volatile, while at circumneutral to high pH, it takes the form of the bisulfide ion (HS^-). Both forms of sulfide are highly reactive with metal cations such as ferrous iron and quickly precipitate as solid sulfides, specifically iron sulfide.

The sulfate reduction/iron sulfide formation process is the basis for the geochemical modeling performed as discussed in Section 3.4. This process naturally occurs in soils and sediments of lakes, rivers, swamps, and estuaries; it is a nearly universal process wherever oxygen can be excluded or minimized. SRB are often active in clay lenses in otherwise aerobic aquifers and are also abundant in root zones where photosynthetic exudates are produced or plant biomass is degraded (Otero and Macias, 2002).

Precipitation of iron sulfide takes place in a stepwise fashion, where monoferrous sulfides precipitate first and then mature into more stable forms (Rickard, 1975). Amorphous, or disordered, mackinawite (FeS) is the first solid to precipitate under reducing conditions with sufficiently high iron and sulfide concentrations. Amorphous mackinawite is then transformed into ordered mackinawite, which is subsequently converted to the intermediate mineral greigite (Fe_3S_4) that ultimately matures to pyrite, which is considered a stable end product (Wilkins and Barnes, 1996). However, some researchers hypothesize that pyrite, monosulfides and greigite may form simultaneously in sedimentary environments (Morse and Rickard, 2004).

Because iron sulfide minerals contain iron in the reduced form (ferrous iron) and are unstable under oxidizing conditions, the mineral is subject to re-oxidation to the ferric form. The oxidation of iron sulfide minerals occurs readily, and therefore iron sulfides are one of the first reduced species to undergo oxidation. Due to this property, iron sulfide minerals act as a re-oxidation buffer, delaying oxidation of other reduced compounds in the system. Other reduced minerals, such as uraninite, remain stable until the thermodynamic conditions become more strongly oxidizing. If groundwater containing dissolved oxygen enters the reduced area, iron sulfide minerals will undergo oxidation first, which will remove dissolved oxygen from the water. Therefore, iron sulfide minerals, present in sufficient quantity and deposited based upon oxidant demand, can maintain reducing conditions for a substantial time period after oxidizing conditions return.

When conditions become oxidizing, iron sulfide minerals transform to poorly crystalline ferric oxides, known as ferrihydrite. Ferrihydrite is an amorphous iron hydroxide that forms from the outside in and is stable under oxidizing conditions. Over time, ferrihydrite matures into more crystalline iron oxide minerals such as goethite and hematite. As ferrihydrite forms, it creates an oxidized "rind" around the reduced sulfide and uranium minerals. This coating of ferrihydrite can then provide a physical barrier between the reduced mineral phases and the incoming dissolved oxygen, effectively passivating the surface of the reduced minerals and slowing oxidation. The ferrihydrite provides a highly sorptive surface and can also protect the reduced uranium from re-oxidation.

Iron sulfide has been recognized as being critical to maintaining uranium stability in groundwater during bioremediation (Abdelouas *et al.,* 2000 and 1999) as well as in natural uranium ore deposits. Leventhal and Santos (1981) studied the relative importance of organic carbon and sulfide sulfur for stabilizing and precipitating uranium in a Wyoming roll-type deposit. A very strong correlation was found between uranium and sulfide sulfur, indicating a role for sulfur in depositing the uranium as well as in

maintaining its stability. It is important to note that the sulfide continues to perform a stabilizing function in such deposits, which have been measured as millions of years old. Guilbert and Park (1986) call these deposits "kinetically stable" where the sulfide sulfur acts to control uranium stability. In these geologic conditions, a very small fraction (typically less than 10^{-8} of the uranium in the ore deposit) is made soluble per year (Waste Isolation Systems Panel, 1983). The formation of natural deposits of uranium that are stabilized by sulfide is the basis for roll front and sedimentary deposits that have been stable for geologic time spans. Formation of iron sulfide to stabilize and precipitate dissolved uranium is an approach with strong verification of permanent stability by comparison with these natural systems.

Iron sulfide has also been recognized as an important redox buffer for several situations that are instructive for Cimarron. Pauwels *et al.* (1998) studied the reactivity of naturally occurring pyrite where nitrate was injected. Their data showed that this iron sulfide source, even though aged over geologic time scales, was still reactive toward maintaining in-situ reducing conditions. Nitrate reduction was rapid (half-life of 2 days for nitrate reduction in a sandy aquifer matrix), leading to the oxidation of pyrite to ferric iron and sulfate minerals, which deposited as jarosite and natroalunite. Tesoriero *et al.* (2000) showed that, in aquifers receiving agricultural runoff, oxygen and nitrate in the runoff were reduced by iron sulfide when infiltrated runoff reached the deeper aquifer. Hartog *et al.* (2001) showed that iron sulfide, reduced iron compounds (including siderite) in addition to iron sulfides, and bulk organic matter can all provide redox buffering in aquifers receiving agricultural runoff. ARCADIS cites these examples as relevant for the "resident farmer" scenario, indicating that, even under agricultural runoff scenarios, the uranium can be maintained insoluble by protection of iron sulfide.

An additional factor for maintaining uranium stability, even in conditions where iron sulfide has been exhausted in the aquifer, is the residual iron oxides that form after iron sulfides oxidize. These freshly formed oxides have a higher surface area and are more reactive than those iron oxides that were formed and have been present for thousands of years. Lack *et al.* (2002) showed that ferric iron oxides sorb uranium with strong binding energy (bidentate and tridentate inner-sphere complexes). Ferris *et al.* (2000) showed that these iron oxides could maintain very low dissolved uranium concentrations (less than 30 pCi/L). Martin and Kempton (2000) have shown ferrihydrite to be reactive along a groundwater flow-path and effective at sequestering dissolved metals. Recently Liu et al. (2005) demonstrated that remobilization of uraninite (initially formed by the addition of organic carbon to solutions containing soluble uranyl ion) was mitigated under oxic conditions by the presence of iron hydroxide formed due to oxidation of the bioreduced sediments. Uranium that is

sorbed to freshly precipitated iron hydroxide will become incorporated into the crystal structure as the iron mineral ages to goethite, hematite, and even magnetite. Uranium incorporated into these minerals as they form will be very stable relative to release or remobilization; work by Dodge et al. (2002) showed that uranium incorporated into iron hydroxides and oxides formed inner-sphere complexes with iron, making the incorporated uranium very stable and strongly associated with the solid phase.

4.2.2 Uranium Stability Summary

The papers referenced above provide the information needed to identify the necessary characteristics of a stable, fully-reduced treatment zone. To remain stable over long periods of time, a reduced zone must contain a variety of reduced compounds after treatment, including some combination of the following:

- Iron sulfides (ranging from amorphous FeS to pyrite). To ensure very low soluble uranium concentrations over long periods of time, the concentration of iron sulfides must be present in excess relative to the concentration of uranium in the reducing zone;
- Residual reduced organic carbon, either incorporated in cellular biomass or stored by microorganisms; and
- Reduced uranium (UO_2).

In the IRZ treatment zone, the re-oxidation and remobilization of uranium is limited by the oxygen that is available to react with the precipitated uranium. The available oxygen can be controlled by the presence of stored, reduced compounds emplaced in the aquifer by the treatment process.

In relative terms, expressed in molar ratios of uranium to other reduced compounds stored in the aquifer, the potential oxidation of uranium will be very low compared with the potential oxidation of iron, sulfur, and other reduced species. As the aquifer materials are exposed to oxygen, FeS oxidizes at least as rapidly as precipitated UO_2 and consumes the available oxygen. When the ratio of iron sulfide to uranium is very large, a very limited amount of oxygen will be available to react with uranium. In addition, because UO_2 is precipitated first during treatment, the FeS precipitate is typically emplaced over the UO_2 as an FeS layer; "banks" of FeS are established in the aquifer surrounding the UO_2. FeS is therefore exposed to the oxygen in the groundwater before the uranium-containing precipitates. A small amount of the uranium in the aquifer will mobilize very slowly as the FeS is depleted and, because

there is so much more FeS in the aquifer material, uranium can only mobilize at very low levels, typically less than 50 pCi/L. As noted above, this mobilization of very low levels of uranium in time reduces the total mass of residual uranium in the aquifer; eventually, no significant uranium mass remains in the aquifer. The details of this approach can be confirmed by geochemical modeling.

4.3 Application to the Cimarron Site

The creation of significant quantities of iron sulfide minerals within the treatment zone is central to the ARCADIS remediation approach for this Site. The ARCADIS process primarily relies on SRB to utilize the added carbon source to transform soluble sulfate (both naturally occurring and amended) and iron naturally present (or amended) to sulfide and ferrous iron. Sulfide then chemically reacts with ferrous iron to form iron sulfide. Because uranium is reduced prior to the formation of iron sulfide, the iron sulfide will coat and embed the uraninite, providing a physical and chemical barrier against re-oxidation. In uranium ore geology terms, ARCADIS will be creating a "regionally reduced" host aquifer at the Cimarron Site. The time period iron sulfides buffer the aquifer is calculated using the geochemical model and exceeds 1,000 years.

To initially activate the sulfate reduction process at the Cimarron Site, ARCADIS will add only organic carbon. As the microbial population proliferates and consumes the organic carbon, higher energy electron acceptors such as oxygen, nitrate, and iron will be depleted and sulfate will become the dominant electron acceptor. Additional iron and sulfate may be added as remediation progresses. Geochemical modeling was used to calculate the mass of iron sulfide needed to provide protection against re-oxidation in excess of 1,000 years, thus protecting the uraninite from re-oxidation once active maintenance of anaerobic conditions ceases. This calculation was based on groundwater flow conditions that are more extreme than currently measured at the Site and that include the highest observed dissolved oxygen concentration. Based on these conditions, 1.8 grams of iron sulfide per liter of aquifer material (solid and liquid) is needed in the treatment area. This is equivalent to 0.03% by weight (based upon a density of the aquifer solids at 2 g/cm^3, porosity of 25%, and 1 liter of groundwater (with a total volume of 4 liters solid and solution). The proposed remediation plan anticipates the introduction of oxygen via natural pathways and provides for sufficient reduced compounds to exhaust these sources of oxygen. For the Cimarron areas of impact, the iron oxides that will form as oxygen enters the areas of impact (transported by diffusion in rainwater and in groundwater) will ensure that any uranium that is remobilized will be at levels well below the Criteria.

Based on analysis of soil samples from the Site, the mass of iron naturally occurring in the aquifer matrix (ferric minerals) is estimated to be sufficient to form the target concentration of iron sulfide minerals needed to maintain stability of the uraninite. However, existing concentrations of sulfate in the treatment areas are not adequate to form the requisite mass of iron sulfide. Therefore, sulfate, likely in the form of ferrous sulfate, will be added to the aquifer during the organic carbon injections as needed to form the appropriate mass of iron sulfide minerals.

Changes in the mineralogical composition of the aquifer occurring during biochemical reduction of the aquifer could potentially affect the porosity and therefore the hydraulic conductivity of the aquifer. Using the geochemical model described in Section 3.4, the porosity is predicted to increase minimally (0.1 percent). This increase in porosity is expected to increase the hydraulic conductivity less than 0.4%. This small change in hydraulic conductivity will not affect the groundwater flow during or after active remediation. The effect of microbiological activity and iron mineral transformation, and resulting change in porosity and its effect on hydraulic conductivity, was calculated using the Kozeny-Carman equation; this equation relates porous medium properties to permeability (Baer, 1972).

5. Bioremediation Work Plan

5.1 Overview of Approach and Objectives

Cimarron will remediate groundwater in all three areas of uranium impacts exceeding the Criteria by immobilizing dissolved uranium through biological reduction, with the creation of geochemical conditions that will prevent re-mobilization of uranium at concentrations above the license criterion. The objectives of the groundwater remediation activities are to ensure that:

1) Uranium in groundwater in all areas undergoing treatment is below the Criteria

2) Iron sulfide mass is accumulated to the target for maintaining treatment longevity (mass ratio of 1 part uranium to 80 parts iron).

This section provides an overview of the approach for groundwater remediation.

The groundwater remediation activities at the Cimarron Site will follow the 6-step biogeochemical treatment process outlined in Section 4.1. The first step consists of conducting baseline sampling in all three areas of uranium impacts to generate "time-zero" hydrogeologic, chemical and geochemical data sets.

In Step 2, ARCADIS will initiate establishment of reducing conditions through the implementation of initial treatment areas at select locations within BA#1, the WAA and the WUA. The IRZ development will be accomplished through delivery of the treatment reagent to the affected groundwater and capillary fringe area using a recirculation system consisting of injection and extraction wells arranged in transects. Groundwater will be extracted from the periphery of the areas of impact, amended with organic carbon and reinjected into the interior portion of the area of impact. This recirculation will continue until reagent distribution achieves specified criteria.

Batch-type injections alone, without recirculation, can result in unpredictable and non-uniform treatment; remediation of the uranium area of impact requires control over reagent distribution and deposition of iron sulfide across heterogeneous geological units. Therefore, the proposed approach consists of combined extraction and re-injection of amended groundwater for delivery of reagents to the subsurface to allow the manipulation of large volumes of groundwater in all three dimensions throughout the zones of treatment. Recirculation provides engineered delivery of injected fluids with sufficient head control to provide hydraulic capture and avoid displacement of existing uranium impacts. The hydraulic control also facilitates the engineering of

dynamic flow patterns, prevents stagnation zones, and improves reagent distribution throughout semi-confined aquifer units.

Initial treatment areas will be developed at six select locations within the areas of impact as described in Section 5.2.2 below. ARCADIS will determine the frequency of delivery and the concentration of reagents required to develop the geochemical conditions essential to immobilize dissolved uranium, as well as the appropriate spacing of injection and extraction wells to ensure complete coverage of the impacted groundwater areas based on results from the initial treatment areas. Based on information gained from monitoring in the initial treatment areas, ARCADIS will expand the treatment system to full-scale systems as required to inject reagents throughout all three areas of groundwater currently exceeding the Criteria to create the necessary geochemical conditions.

Step three includes continued operation of the full-scale remediation system as required to precipitate uranium as a reduced uranium oxide (UO_2). The reducing conditions developed will force the precipitation of dissolved uranium. Groundwater and soil sampling and analysis will enable ARCADIS to verify that uranium has been converted from the dissolved to the solid phase. This sampling and analysis will also enable ARCADIS to identify other co-precipitated minerals, which are needed to ensure that remobilization of uranium is permanently controlled, as described in Step 4 in Section 4.1. If needed, iron and/or sulfate will be added to the reinjected groundwater to ensure that adequate mineralogy is formed throughout the treatment areas.

Recovery of soil samples and analysis of the samples to assess the iron mineralogy emplaced will be conducted as per Step 5 of the process. Achievement of the adequate mineralogy will trigger cessation of active treatment. Remedy completion demonstration testing will then be conducted to ensure that groundwater concentrations are below the Criteria and that the rate of uranium remobilization will not exceed the Criteria over the project 1,000-year compliance period (Step 6). Remedy completion demonstration testing includes soil and groundwater sampling and analysis, as well as oxidative aging studies as described in Section 5.3.2 to confirm the remediation longevity and to provide empirical data to support the geochemical modeling.

5.2 Remediation Approach

Figure 5-1 presents a flow chart depiction of the bioremediation process. As discussed above, a staged field implementation approach has been developed to ensure the

success of the bioremediation activities. Stage 1 of the remediation consists of development of a conceptual remedial design, as presented in this Groundwater Decommissioning Plan. Stage 2 of the process will begin upon NRC approval of the Groundwater Decommissioning Plan and consists of baseline data collection and implementation of the initial treatment areas. Stage 3 includes expansion of the treatment system to full-scale and continued treatment until the remediation objectives are achieved. Stage 4 consists of remedy completion demonstration testing and license termination. The following sections provide detailed descriptions of Stages 2, 3 and 4 of the bioremediation process.

5.2.1 Stage 2 - Baseline Data Collection and Initial Treatment Areas

5.2.1.1 Baseline Data Collection

Baseline hydrogeological and geochemical data will be generated to establish conditions at "time zero". This data set will include groundwater elevation measurements and collection of both groundwater and soil samples for baseline analyses as described in the following sections.

Hydrogeologic Measurements

Prior to collection of samples, depth to groundwater will be recorded for existing wells in all three areas of uranium impacts above the Criteria as depicted on Figures 3-1 and 3-2. This will enable ARCADIS to determine the potentiometric surface and evaluate groundwater flow directions and gradients prior to beginning groundwater extraction and re-injection.

Groundwater Sampling and Analysis

To establish baseline geochemical conditions (i.e., groundwater conditions prior to the start of injections), an initial round of groundwater quality samples will be collected. The collection and analysis of groundwater samples will provide pertinent information regarding relative concentrations of dissolved uranium, electron acceptors, reduced electron acceptors, field parameters, and other indicator parameters. Baseline samples will be collected from 32 wells in the monitoring network. The preliminary selection of 29 wells to be included in the monitoring program is shown on Figure 5-2; wells have been selected to provide complete coverage of the different hydrogeologic and geochemical conditions in each of the three areas at the Site. The remaining three monitoring well locations will be selected in the field, as appropriate, based on additional information obtained during the baseline data collection activities. Sampling

will be performed in accordance with the site-specific Sampling and Analysis Plan. Each sample will be analyzed for the list of biogeochemical analyses summarized in Table 5-1, which is included as the third page of Figure 5-1. Analytical methods and data quality objectives (DQOs) for these analyses are provided in Appendix C; uranium will be analyzed by both inductively-coupled plasma mass spectrometry (ICP-MS) as well as by radiochemical methods to provide both mass and activity measurements.

Soil and Mineralogical Analysis

The purpose of this study is to establish baseline mineralogy so that changes in iron species during remediation can be quantified. To establish baseline geochemistry and mineralogy, soil cores for analysis will be collected from the saturated zone within the impacted groundwater areas and correlated with the screened interval of the injection/monitor well screens during well installation. Samples will be collected at locations representing three different geologic zones (sandstone, transition, and alluvial sand) with high uranium concentrations, in accordance with the site-specific Sampling and Analysis Plan. Soil cores will be collected, sealed immediately upon collection, wrapped in black plastic bags, and stored in an ice chest packed with dry ice to exclude light and oxygen, thus preserving the geochemical integrity of the sample. Analytical methods and DQOs for soil sampling and analysis are summarized in Appendix C.

Analytical methods that may be utilized for soil cores are listed in Table 5-1; details of the soil analytical methods to be employed are provided in Appendix D. Briefly, selective chemical extraction of the soil will provide information about changes in the crystallinity of the iron, the quantity of iron sulfide phases, and about the creation of sorbed ferrous iron. Measurement of acid volatile sulfide and simultaneously-extractable metals (AVS-SEM) will quantify the amount of reactive iron sulfide that is created. X-ray diffraction (XRD) will identify the major mineral phases, and microprobe methods (scanning electron microscopy with energy dispersive x-ray spectroscopy [SEM-EDS] and x-ray absorption spectroscopy) will provide detailed information on minor mineral phases, iron transformations, and uranium in the soil. The total uranium content will be quantified through total activity measurements, alpha-spectroscopy (isotopic analysis), and by ICP-MS following strong acid digestion.

5.2.1.2 Initial Treatment Areas

Stage 2 of the bioremediation process continues with installation and operation of initial treatment areas at six locations within the groundwater areas of impact. The initial treatment areas will be located in the three hydrogeologic units (alluvium, transitional

alluvium and sandstone bedrock) present in each area of impact (BA#1, WAA and WUA) as shown on Figure 5-2. The initial treatment areas at the Cimarron Site will include:

1) The downgradient portion of the area of impact in the sandy alluvium in BA#1.

2) The transitional alluvium in BA#1 in the middle of the uranium area of impact near the bedrock escarpment.

3) The upland sandstone bedrock of BA#1, near the former burial trenches.

4) The downgradient portion of the area of impact in the sandy alluvium in the WAA.

5) The transitional alluvium in WAA in the middle of the uranium area of impact near the bedrock escarpment.

6) The upland sandstone bedrock of the WUA.

Each initial treatment area will consist of a recirculation unit, with one extraction well and one or two injection wells, placed based on the preliminary design estimates of appropriate spacing for each hydrogeologic unit. The recirculation units for the initial treatment areas may not encompass full transects, as some areas could require more than two wells per transect for the full-scale design. This approach is intended to minimize the number of wells installed until the appropriate spacing is estimated from the hydraulic and transport parameters obtained during operation of the initial treatment areas. The injection and extraction wells will be installed in accordance with the site-specific Sampling and Analysis Plan, and will be screened across the entire saturated interval.

The full-scale system will be constructed and operated based on the data obtained during operation of the initially-installed recirculation units. This data will provide information for the optimization of the following:

- Injection well spacing for full-scale design;
- Injection volumes, pressures, frequency and expected rates of delivery; and
- Required reagent concentrations to achieve effective distribution.

Information from the Conceptual Site Model, Revision 1 (ENSR, 2006) has been used to develop a conceptual (Stage 1) design for the application of reagents in each of the three areas targeted for groundwater treatment as presented in this Groundwater Decommissioning Plan. Figure 5-3 shows the simulated total organic carbon (TOC) distribution in each of the three treatment areas after a continuous 7-day injection based on the initial well spacing developed in the conceptual design effort.

The objective of the simulations was to identify a preliminary well layout and the necessary extraction/injection rates that will provide adequate distribution of organic carbon substrate. To reach this objective, TOC transport was simulated under various scenarios by coupling the transport model MT3DMS (Zheng and Wang, 1999) with the Modflow groundwater model developed by ENSR (Appendix A). Initial simulations were conducted at TOC injection concentrations of 100 mg/L. A 20-day half-life was used for TOC biodegradation in the simulations presented herein. Only key results of representative simulations that illustrate the significant conclusions of the modeling effort are presented. Simulations after 7 days of continuous TOC injection were completed, and contour maps of resulting TOC concentration are presented in Figure 5-3. These contours show that 7 days of continuous TOC injection provides enough lateral coverage between wells. The output from the numerical TOC transport modeling is included in Appendix F on CD-ROM.

The relatively rapid distribution of TOC indicated by the TOC transport modeling in this aquifer suggests that successful treatment can integrate both active and passive approaches to IRZ remediation. Recirculation of extracted, amended and reinjected groundwater will only have to take place for a discrete period of time. This period of time will be determined by the time it takes to achieve an appropriate area of influence that provides coverage between wells. The recirculation system will then be turned off to allow further distribution of TOC in the downgradient direction under ambient (natural flow) conditions. Therefore, the objective of the TOC distribution is to achieve complete coverage in the lateral direction (i.e., between injection and extraction wells). The TOC coverage areas shown in Figure 5-3 only demonstrate the lateral coverage anticipated through the recirculation of amended groundwater; dispersion and advective transport of TOC are not shown, but will result in complete coverage of the areas of impact as a result of multiple recirculation periods.

The TOC transport model provides a way to evaluate a preliminary well layout and target flow rates; however, initial treatment areas will be established prior to full-scale system installation. Hydraulic and tracer testing will be conducted during the establishment of the initial treatment areas to provide the flow and transport parameter information needed to develop the full-scale design as discussed above. The well

layout presented in Figure 5-3 is therefore preliminary. The well layout configuration will be revised once the key transport parameters are quantified through field testing. The hydraulic and tracer testing approach and data collection during the initial treatment area operation are detailed in the following sections.

Hydraulic and Tracer Testing Approach

The first part of the hydraulic and tracer testing will focus on evaluation of sustainable injection and extraction yields. This testing will be conducted by observing the temporal response in water levels in nearby monitoring wells within the initial treatment areas, as shown on Figure 5-2, for several injection rates that will be increased in a step-wise manner during the testing. The extraction and monitoring wells used during the testing will be equipped with pressure transducers that will log the water levels to monitor the mounding generated during the injection, establish the sustainable flow rates for full-scale operation, and evaluate fluid accommodation by the aquifer during re-injection.

Once the injection yield is determined, the water levels will be allowed to recover and an injection/tracer test will then be conducted by injecting a fluorescein (non-toxic, non-degradable) dye tracer into each injection well at a continuous flow rate. The injection testing will be conducted for at least seven days, or until the response in the selected monitoring well network indicates that the appropriate coverage has been achieved. The extraction well will provide the make-up water that will be amended for re-injection in the injection wells. The duration of the tracer injection will be determined based on the tracer arrival and achievement of steady state concentrations at the extraction well. At this point, tracer injection will be discontinued but monitoring of the tracer will continue in the cross-gradient and downgradient monitoring wells. Fluorescein dye concentration data, as detected at the extraction and downgradient monitoring wells, will be used to estimate mobile porosity, groundwater velocity, and the spatial coverage that can be achieved by liquid injection of treatment reagents. Analytical methods and DQOs for the hydraulic and tracer testing are provided in Appendix C.

Data Collection and Results

After hydraulic and tracer testing in the each of the initial treatment areas, amendment delivery will be conducted to confirm effective delivery and distribution of the amendment. Monitoring of groundwater chemistry during delivery of the amendment in the initial treatment areas will enable ARCADIS to refine its calculations of the injected concentrations of TOC, iron, and sulfate needed to ensure both impacted groundwater remediation and long-term uranium stability. The organic carbon substrate used to

amend the extracted groundwater will consist of a dilute organic carbon solution to facilitate optimum reducing conditions and establishment of multiple groups of reductive microorganisms capable of uranium immobilization.

As noted above, the extracted water will be amended with an organic carbon solution (e.g., molasses) before it is reinjected into the aquifer. While the reinjection process may result in the introduction of minimal amounts of oxygen into the extracted water, the addition of carbon donor at concentrations on the order of hundreds of milligrams per liter is designed to overwhelm the demand of all competing electron acceptors present in the groundwater, including any residual dissolved oxygen that might be introduced into the water during the recirculation process. Any oxygen that is injected along with the organic carbon will be rapidly reduced due to the high concentrations of excess organic carbon present in the injection area, and no negative effects on the IRZ implementation will be observed.

The injection, extraction and monitoring wells located within the initial treatment areas will be monitored closely throughout the active recirculation period and throughout a follow-up period of stabilization. Data to be collected from each well will include:

- Depth to water measurements (to evaluate flow direction and mounding during injections);
- Field parameters: pH, temperature, dissolved oxygen; and
- Groundwater chemistry parameters: TOC, total dissolved solids (TDS), sulfate, sulfide, total dissolved iron and ferrous iron (Fe^{2+}), alkalinity, and uranium (both mass and activity).

Data collection frequency for water level and field parameters will be daily until field conditions stabilize or until conditions dictate a less frequent interval. Groundwater samples for laboratory analysis will be collected at the completion of the initial treatment area operation period. Analytical methods and DQOs for the initial treatment area operation are included in Appendix C.

5.2.2 Stage 3 - Full-Scale Implementation

Stage 3 of the bioremediation process will consist of expanding the treatment system to provide coverage across the entire areas of impact with uranium activity exceeding the Criteria. The flow and transport parameters (hydraulic conductivity, injection and extraction well yields, mobile porosity and dual-domain mass transfer coefficient)

obtained during the Stage 2 initial treatment area installation and operation will be input in the TOC transport model and a series of simulations will be conducted to complete the full-scale (Stage 3) design. The numerical model simulation results will be used to determine the appropriate injection and extraction well spacing, recirculation period, frequency of recirculation periods, and appropriate injection/extraction flow rates for the full-scale design.

Following development of the full-scale design, Stage 3 activities will include amendment selection, full-scale system installation, full-scale injection program, and performance monitoring as described in the following sections.

5.2.2.1 Amendment Selection and Loading

The addition of electron donor in the form of organic carbon is central to the creation of a reducing treatment zone. All easily degradable organic carbon sources will promote the sequential reduction of available electron acceptors as discussed in Section 4.0. Both a carbohydrate-based donor and the use of alcohol as an organic carbon source have been considered. The differences between these organic carbon sources are as follows:

- The use of complex carbohydrates, such as dilute molasses, is advantageous because of cost and ease of handling, and because the concentration of micro- and macronutrients in molasses and other carbohydrates promotes microbial cell reproduction and growth, thus increasing the microbial biomass in the aquifer.

- The use of alternative carbon sources, such as alcohols, will achieve the same reducing conditions, yield more reducing equivalents, and offer better control over the size of the IRZ. However, the acclimation period required to build up the biomass in the aquifer may be slightly longer due to nutrient limitations.

It is anticipated that a dilute molasses solution will be used for the initial treatment area activities. Final decisions on specific carbon donors to be used for the full-scale system will be made once the baseline and initial treatment area analytical data are available.

As noted above, the extracted water will be amended with an organic carbon solution (e.g., molasses) before it is reinjected into the aquifer. While the reinjection process may result in the introduction of minimal amounts of oxygen into the extracted water, the addition of carbon donor at concentrations on the order of hundreds of milligrams

per liter is designed to overwhelm the demand of all competing electron acceptors present in the groundwater, including any residual dissolved oxygen that might be introduced into the water during the recirculation process. Any oxygen that is injected along with the organic carbon will be rapidly reduced due to the high concentrations of excess organic carbon present in the injection area, and no negative effects on the IRZ implementation will be observed.

Substrate loading will be designed to provide sufficient organic carbon residence time to sustain the activity of sulfate-reducing microorganisms. The substrate concentration will also be controlled to maintain this activity within the targeted zone of the aquifer to manage the overall footprint of the IRZ. This will ensure that the iron sulfide minerals are deposited within the areas of uranium impact. Substrate loading will be adjusted in the field as warranted based on the data collected.

The injection fluid may also be amended with ferrous sulfate and or ferrous chloride to augment the ferrous iron and, if needed, the sulfate concentrations in the aquifer. Iron loading will initially be based on creating an aquifer material weight percent of 0.03 as iron sulfide and will be adjusted based on the dissolved iron concentration and other monitoring data. Baseline geochemical analyses discussed in Section 5.2.1 will provide an indication of the amount of bioavailable iron in the treatment area that may contribute to the remedial process.

5.2.2.2 Full-Scale System Installation

IRZ development across the areas of impact include addressing the sandy, more prolific zone of the alluvial aquifer within BA#1 and the WAA; the transitional alluvial zone containing a higher percentage of silts and clays present within BA#1 and the WAA; and the sandstone units associated with BA#1 and the WUA. Within each zone, the spacing of individual injection wells and groundwater extraction wells to ensure appropriate treatment coverage will depend on the variability of specific hydrogeologic characteristics such as hydraulic conductivities, stratigraphy, hydraulic gradients, saturated thicknesses, depth to water and effective porosities, as discussed above, and will be based on the results of the initial treatment area monitoring. The injection and extraction wells for the full-scale system will be installed in accordance with the site-specific Sampling and Analysis Plan, and will be screened across the entire saturated interval.

In general, the delivery of treatment reagents and IRZ development within the affected groundwater will be accomplished through continuous injection via recirculation until appropriate amendment coverage is achieved. This approach will ensure treatment

coverage throughout the areas of impact and will promote rapid substrate distribution. The objective is to create treatment zones within the hydraulic influence area of each injection well that will overlap with the treatment zones created by adjacent injection wells. The conceptual design of the delivery systems to establish the IRZ in each of the targeted areas is discussed in the following sections.

Burial Area #1

Based on the distribution of the impacted groundwater within BA#1, IRZ development will be implemented within three zones of varying hydrogeologic conditions. These include the upland zone in the former source area, which consists predominantly of sandstone; the transitional alluvial zone located adjacent to the escarpment consisting of sand with silts and clays; and the sandy alluvial zone consisting primarily of sands with high hydraulic conductivities.

Based on the understanding of hydrogeologic conditions presented in the CSM and the TOC transport modeling described in Section 5.2.2, the conceptual design contemplates an injection well spacing of 100 feet or less within the treatment grid encompassing the sandy alluvium. Injection well spacing will be further evaluated during the initial treatment area installation and operation, as discussed in the previous section. Other hydraulic parameters (i.e., flow rates, frequency of injection, etc.) will be evaluated and adjusted on an ongoing basis based on routine performance monitoring.

IRZ development within impacted groundwater in the transitional zone and upland sandstone in BA#1 will be accomplished in similar manner, with the well spacing adjusted to ensure appropriate coverage. Based on the CSM and the TOC transport modeling described in Section 5.2.2, it is estimated that a 60-foot spacing will be required to provide adequate coverage in the transitional zone, and a 30-foot spacing will be required to adequately treat the and adjusted appropriately in the initial treatment implementation stage.

Western Upland Area

The extent of groundwater impacts within the WUA appears to be more limited in size, and uranium impacts have occurred sporadically. The approach for treatment within the WUA is similar to the approach for the upland zone of the BA#1 with an estimated 30-foot spacing between injection and extraction wells to provide adequate coverage of the potentially impacted groundwater zones. Injection well spacing for the WUA will be further evaluated during the initial treatment area installation and operation.

Western Alluvial Area

The delivery of treatment reagent and IRZ development within the affected groundwater of the WAA will be accomplished using the same design basis as the sandy alluvial zone of BA#1, with a well spacing of 100 feet or less within the treatment grid. A series of injection and extraction wells will be located throughout the area of impact. Injection well spacing for the WAA will be further evaluated during the initial treatment area installation and operation.

5.2.2.3 Injection Program

The injection program will consist of a continuous delivery of organic carbon and other amendments to the aquifer during a specific time period. The duration of the injection period and its frequency will be established after quantitative analysis of the data collected during the initial treatment area operation (Stage 2). The length of the injection phase will be determined based on the time required to achieve adequate lateral coverage between wells, but is expected to range from several days to several weeks. The frequency of the injection period will be optimized to maintain an anaerobic geochemical environment (i.e., sulfate-reducing conditions), which will depend primarily on groundwater velocity and carbon utilization (expected range: every two weeks to every month). The frequency and duration of the recirculation period may be adjusted during the operation of the IRZ, as performance data are collected as part of the adaptive design. A less frequent injection schedule may be used after the IRZ is established and the geochemistry has stabilized.

Figure 5-4 presents a schematic of the proposed recirculation flow process. The reagent solution will be mixed with recovered groundwater from the extraction wells and redistributed to the injection wells. In Configuration A, as shown on Figure 5-4, the injection and extraction lines will be permanently installed to the treatment equipment enclosure. For areas of the site where flooding may occur, temporary lines and a mobile injection trailer will be employed, as shown in Configuration B. The solution will be injected using a mobile manifold injection system. The mobile manifold system will be capable of injecting into all the injection wells in one transect at the same time. Injection pressures and groundwater levels for all injection wells will be monitored to ensure that injection well seal failure or short-circuiting does not occur.

5.2.2.4 Performance Monitoring of the IRZ

Monitoring during operation will provide data with which to make judgments related to TOC concentration and frequency of injections, as well as whether additional

amendments (iron and/or sulfate) are required. The objectives of the monitoring program are to: 1) ensure that the systems are operating successfully in terms of organic carbon utilization, sulfate reduction, and uranium precipitation; and 2) determine the progress of the treatment toward completion of the groundwater remediation.

Groundwater and soil samples collected for the performance monitoring program will be analyzed for the following parameters:

- Groundwater: pH, temperature, dissolved oxygen, TOC, TDS, sulfate, sulfide, total dissolved iron and ferrous iron (Fe^{2+}), alkalinity, and uranium (both mass and activity).

- Soil: Bulk iron mineralogy, including selective chemical extraction and XRD. Quantification of iron sulfide content. Changes in iron mineralogy induced by the metabolism of organic carbon; these will be determined by microprobe methods that include SEM, micro-x-ray fluorescence analysis (μ-XRF), and micro-x-ray absorption near edge structure (μ-XANES).

The frequency of sampling for groundwater and soil performance monitoring are presented in Table 5-1 (included as page 3 of Figure 5-1). Analytical methods and DQOs for the soil and groundwater analyses to be conducted as part of the performance monitoring program are included in Appendix C.

Groundwater performance monitoring will determine the progress of uranium removal from the groundwater, TOC utilization, and sulfate reduction. The goal of the iron mineralogy testing during the performance monitoring period will be to demonstrate that the changes to the iron mineralogy, required for the long-term efficacy of the groundwater treatment, have been established and are occurring as predicted by the conceptual remediation model and the geochemical modeling. The following ratio of iron to uranium is expected: 80 parts iron by weight to 1 part uranium by weight, or 340 parts iron (moles) to 1 part uranium (moles).

The active remediation phase (Stage 3) will be complete when the performance monitoring establishes that the following goals have been met:

- Uranium in groundwater in all areas undergoing treatment (32 wells) is below the Criteria.

- Iron sulfide mass has accumulated to the target mass ratio of 1 part uranium to 80 parts iron as required for maintaining treatment longevity.

When these goals are met, the remediation program will transition from active remediation to remedy completion demonstration testing (Stage 4). The remedy completion demonstration testing to be conducted is described in the following section.

5.2.3 Stage 4 - Remedy Completion Demonstration Testing

Stage 4 of the bioremediation process includes the remedy completion demonstration testing and license termination. An extensive numerical modeling analysis was performed to evaluate the stability and longevity of solid phase uranium in groundwater under various geochemical conditions representative of the Cimarron Site. The model approach simulated the reductive precipitation of soluble uranium to the mineral uraninite and then evaluated the stability of this insoluble mineral phase over time as geochemical conditions return to baseline oxidizing conditions. The fate and transport of the oxidatively dissolved uranium was evaluated in the context of sorption and other attenuation mechanisms.

Model simulations were run using Geochemists' Workbench as described in Section 3.4. The study first modeled the electrochemical reduction of soluble uranium currently existing at the Site by the addition of organic carbon to the groundwater system. This results in the precipitation of the uranium mineral uraninite and the precipitation of the iron mineral mackinawite, which are stable under reducing conditions. Upon cessation of the organic carbon addition, the Site groundwater will return to background oxidizing conditions. Therefore, the stability of the uraninite and mackinawite were evaluated using GWB to determine the period during which the uraninite was stable and then the concentration of soluble uranium expected to leach into groundwater over time. Finally, modeling simulations were run using the same tools to evaluate the effect of sorption to attenuate the newly dissolved uranium.

Geochemical data used in the model were obtained from analysis of groundwater at the Site. Because the amount of iron in the system that is available to react is important to the permanence of the uraninite, model runs were performed based upon only 3% of the total iron being "reactive" or capable of conversion to iron sulfide. Remediation will proceed until uranium concentrations in groundwater are below the release criterion and iron sulfide has accumulated to a concentration predicted by the modeling to assure longevity of the immobilized uranium. As remediation progresses and performance monitoring data is obtained, the geochemical model will be updated with data from the field in order to re-evaluate and update the model predictions. This

iterative process of sampling and modeling will be used to define the optimum remediation targets, in terms of aquifer mineralogy, to achieve compliance.

5.2.3.1 Remedy Completion Demonstration Testing: Groundwater

Groundwater monitoring will continue in 16 select wells across all three areas (BA#1, WAA, and WUA). Wells will be selected to encompass a range of hydrogeologic conditions within the treated areas (leading edge, middle, and upgradient within the areas of impact). The selection of wells for sampling will therefore be biased and will not be random; the bias will be toward identifying locations representative of the broad range of hydrogeologic conditions (within the various groundwater-bearing units) and contaminant chemistry (within locations where uranium concentrations were once highest and lowest). The compliance monitoring will take place over a period of eight quarters. Table 5-1 summarizes the groundwater remedy completion demonstration testing. Analytical methods and DQOs for the remedy completion demonstration testing of groundwater are included in Appendix C.

Analyzing the Trends

Uranium activities in the monitored wells must be below the Criteria for 8 quarters. Trend analysis will be conducted to assure that there are no increasing trends in the data as described below.

In the environment, the concentration of a given parameter can rise or fall with time independent of a release or rebound. The purpose of the trend analysis is to distinguish between natural fluctuations and a true rebound event. The U.S. Environmental Protection Agency (USEPA) has recommended the use of Sen's Slope Estimator or the analogous Mann Kendall Test to determine if there is a slope present in a data set and whether the slope indicates a statistically significant trend. It is proposed that the uranium activity values be entered for each of the selected 16 monitoring wells for eight consecutive quarters. The tests will be run at 5% significance. The tests will estimate the slope and determine whether the slope is statistically significant. If no rebound is taking place and the uranium values are fluctuating randomly, it is expected that the tests will show that about half of the wells will have a positive slope and about half will have a negative slope. The slopes should be statistically insignificant. If none of the tests indicate a statistically significant increasing slope, then remediation has been demonstrated. There is a chance the test could identify a statistically significant falling trend; this would not be a compliance concern.

Minimizing the Chance of False Negative Readings

False negative readings are not impossible in a detection monitoring setting. However, the number of wells and quarters involved makes it impossible for uranium to rise above the Criteria without this situation being eventually detected in one of the wells.

In the same way, it is highly improbable that a statistically significant trend would be missed. The USEPA advocates that statistical tests be conducted in groups of at least eight to provide sufficient power to prevent a false negative from being undetected. Experience has shown that ten tests is conservative and assures that the statistical power will suffice to detect a significant trend. We are proposing to collect data from sixteen wells for use in testing for trends. Thus, if any well is damaged or destroyed and can no longer be monitored, or if there are other problems, then the number of wells will still be sufficient to provide guarantees against false negative readings.

Minimizing the Chance of False Positive Readings

If any monitoring well is shown to have a uranium activity greater than the Criteria, the well will be resampled. If the exceedance is confirmed, then there is evidence of a rebound. This situation should be investigated to determine if supplemental remediation is needed to rectify the rebound.

If any well shows a statistically significantly increasing slope, monitoring of that well will be extended for four extra quarters. After 12 quarters, analysis with Sen's Slope Estimator will be repeated at that well. If the analysis does not indicate a significant upward trend, then remediation has been demonstrated. If the trend is still positive and significant, then there is evidence of a rebound. Additional monitoring or remediation will be performed.

It should be noted that the definition of the significance of the Sen's Slope Estimator (α) is probability that the test will falsely identify a trend. That these proposed tests have $\alpha = 0.05$ means that there is a 5% chance that a false positive error will be committed with every well. Further, the probability that there will be at least one false positive in a set of twelve tests is 56%. The site-wide false positive rate, A, can be computed from the test-wise false positive rate, α, and the number of tests, n, using the following relation:

$$A = 1 - (1 - \alpha)^n$$

Given that n = 16 and α = 0.05, it can be readily seen that A = 0.56, or 56%. The greater the number of wells, the greater the value of A will be. For example, if we monitored eight wells, A would be 33.7%. In effect, there is a trade-off between controlling false negatives and false positives. However, a re-testing provision decreases the chance of a false positive. If k is the sum of tests and retests (that is, k = 2), then:

$$A = 1 - \left(1 - \alpha^k\right)^n$$

When n = 16, A = 4.0%. In summary, the provision to extend tests that fail the trend criterion drops the false positive rate dramatically. Only the well (or wells) with the significant trend would be resampled for four extra quarters.

In conclusion, we propose to demonstrate that rebound is not taking place by showing that uranium is below the Criteria in each well for eight quarters and by showing that there are no statistically significant increasing trends in sixteen monitoring wells. The trends will be checked using a USEPA-approved method, Sen's Slope Estimator. The number of wells and quarters is designed to protect the testing process from false negative results. Retesting provisions will protect the integrity of the test from the second form of error, false positives.

5.2.3.2 Remedy Completion Demonstration Testing: Soil

Establishing that the required iron mineralogy has been achieved is a trigger for the remedy completion demonstration testing phase for soil. Soil samples for iron mineralogy testing will be collected when the groundwater concentrations have been reduced below 180 pCi/L as shown on Figure 5-1. Figure 5-5 depicts the conceptual basis for the iron mineralogy determination.

Oxidative aging testing will occur during the beginning of Stage 2 (during the initial period of active remediation) in order to characterize the redox buffering capacity of the aquifer, and again after adequate iron mineralogy has been established based upon the performance monitoring results for soil. Table 5-1 summarizes the remedy completion demonstration testing for soils. Soil samples will be taken at two depth intervals within the treatment zone and at three locations across the areas of impact within each of the different geologic types present (alluvium, transition alluvium and upland bedrock).

Soil will be obtained under anoxic conditions (by collecting intact cores and sealing in an inert-gas filled gloved bag in the field) and subjected to oxidative aging column testing, conceptually diagrammed in Figure 5-6. In the laboratory, the columns will be placed in an anaerobic (nitrogen) gloved bag and instrumented with inlet and outlet stainless-steel tubing and in-line dissolved oxygen and pH sensors. Advective flow of ambient upgradient groundwater will be initiated, and influent and effluent dissolved oxygen, and pH will be monitored for a pre-determined period (20 to 40 days). Periodically, influent and effluent samples will be collected for analysis of nitrate, sulfate, and iron. At the end of the experiment, the soil cores will be opened in the anaerobic glove box, and sections of the core will be sampled (upstream, mid-column, downstream relative to oxidant introduction). These samples will be analyzed using the same protocol as that described for iron mineralogy testing:

- Bulk iron mineralogy including selective chemical extraction and XRD.
- Quantification of iron sulfide content.
- Changes in iron mineralogy induced by the introduction of oxidants; these will be determined by microprobe methods that include SEM, μ-XRF, and μ-XANES.

The goal of the oxidative aging testing will be to show oxygen consumption by the reduced minerals in the soil column and to demonstrate the conversion of iron sulfide to iron (hydr)oxide mineral phases. This analysis supports the remedy completion demonstration based upon the following:

- Demonstration that upgradient oxidants will be consumed by the aquifer soil validates the geochemical modeling and mechanisms upon which uranium immobilization, and maintenance of the immobilization is based.
- Demonstration that upgradient oxidants catalyze the conversion of iron sulfide to iron (hydr)oxides validates the mechanism of immobilization of uranium through sorption described by the geochemical modeling.

Similar testing was recently described by Thornton et al. (2007) to determine the lifetime of an iron-sulfide based barrier deposited in the vadose zone by hydrogen sulfide. Although the deposition method (hydrogen sulfide gas) proposed in this publication is much less robust than the creation of iron sulfide through microbial reductive dissolution of aquifer iron, subsequent iron sulfide precipitation, and

introduction of additional iron proposed herein, the method of laboratory testing is relevant to this work.

5.3 Compliance with Requirements for License Termination

Treatment completion is based upon a robust set of direct measurements including the following:

Stage 3:

- Attainment of the Criteria for uranium in groundwater (<180 pCi/L or 110 µg/L) with concentrations consistently below the criteria in performance monitoring wells across the treatment area.

- Iron mineralogy testing demonstrating that predicted changes have occurred and reactive iron sulfides have formed in the aquifer as a result of treatment.

Stage 4:

- Oxidative aging testing showing that the reactive iron species will consume oxygen and transform to sorptive iron minerals upon oxidation.

- Remedy completion demonstration monitoring of groundwater showing the absence of a statistically significant upward trend in groundwater concentrations in compliance wells across the treatment areas selected as key observation locations. Statistical analyses will be applied using USEPA-approved statistical methods.

In addition, geochemical modeling simulations will be adjusted based upon the testing described so that the empirical data is incorporated into the model runs and the output used to demonstrate expectations in terms of longevity of treatment.

The information obtained from field and laboratory testing will be used to support a license termination request submitted in Stage 4 of the bioremediation process. The request will include submission of a treatment completion report.

The completion report will present the groundwater and soil monitoring data collected in accordance with the performance and remedy completion demonstration testing program as described above. The data presentation will include an assessment of the compliance and remedy demonstration monitoring results with respect to the DQOs

established for this data. In addition, the completion report will include a comparison of the remedy completion demonstration testing results with the geochemical model parameters and estimates, including a discussion of how the data demonstrates that the remedy has achieved the requirements for longevity. Analytical laboratory reports documenting the analytical results can be provided upon request.

5.4 Schedule

Upon NRC and ODEQ approval of the Groundwater Decommissioning Plan (concluding Stage 1), Cimarron will contract with ARCADIS to initiate groundwater remediation. ARCADIS will mobilize within six months of NRC and ODEQ approval. As shown in Figure 5-1, Stage 2 remediation activities will begin with completion of baseline monitoring to establish "time-zero conditions". Initial treatment area systems will then be installed and operated as discussed in Section 5.2.2. It is anticipated that the baseline data collection and initial treatment area installation and operation will require approximately one year for completion.

The information collected during the initial treatment area operation, including the recirculation testing to establish hydraulic parameters and the amendment delivery demonstration results, will be used to complete the design for the full-scale remediation system. In addition, the data collected will be used to refine both the CSM and the geochemical modeling. Data collected during Stage 2 and any updates to the Site models will be shared with the NRC and ODEQ at the completion of this stage.

It is anticipated that Stage 3, construction of full-scale remediation systems, will be implemented during year two. Treatment will be expanded to address all impacted groundwater areas during the full-scale remediation implementation. Performance monitoring will be conducted during the full-scale implementation phase as described in Section 5.2.4, and the results used to optimize the treatment system as needed. The information obtained from the performance monitoring phase will also be used as appropriate to update the Site models to assess the effectiveness of the treatment activities, and this information will be shared with the NRC and ODEQ at the end of the first full year of full-scale remediation.

Initial estimates of the time frame required for active remediation with the full-scale treatment system (Stage 3) are one to three years. Ongoing performance monitoring results will indicate the progress towards achievement of the Criteria in groundwater. In addition, depending on the progress of the remediation, it is anticipated that soil samples will be collected at the beginning of year three, as discussed in Section 5.2.4, to assess the development of the required mineralogy in the subsurface.

At the point that the groundwater concentrations in the impacted groundwater areas are all reduced to below the release criterion, the Radiation Protection Program currently in place for the Site may be terminated. At this point, assuming that the first round of soil samples indicate that the remediation process is proceeding as expected, the active remediation phase will be terminated and a second round of soil samples will be collected for mineralogic and oxidative aging analyses. If the soil samples indicate that the required mineralogy has been emplaced, the remedy completion demonstration testing phase (Stage 4) will be initiated. If the soil samples indicate that adequate iron mineralogy is not in place, additional active remediation will be conducted, and a third round of soil samples will be collected following additional treatment.

Stage 4 includes the remedy demonstration completion testing phase as described in detail in Section 5.3. This phase will consist of 8 quarters of groundwater monitoring of 16 wells across the three treatment areas to confirm that no rebound of uranium concentrations is occurring following cessation of active treatment. At the end of the anticipated two-year remedy completion demonstration testing phase, Cimarron will submit a license termination request based on the results of the remedy completion demonstration testing. It is anticipated that the license termination request will be submitted at the beginning of the seventh year following approval of the work plan, or early if the active treatment phase is less than the maximum expected duration of three years.

6. Quality Assurance Program

All of the documents described in this section are living documents. That is, a document is to be reviewed as the project proceeds and revised as necessary to reflect additional knowledge learned and any additional requirements needed as a consequence.

6.1 Quality System

The Cimarron Site Quality System was originally designed around the applicable requirements of 10 CFR 50 Appendix B and NQA-1 (Quality Assurance Requirements for Nuclear Facility Applications) when the Cimarron Site was operating as a nuclear fuel processing facility.

As decommissioning of the site has proceeded, the above referenced quality systems were found to not fully address decommissioning quality requirements.

Therefore, the Cimarron Site Quality System has been revised to address applicable requirements of Regulatory Guide 4.15, Interim Revision 2 (March 2007), "Quality Assurance for Radiological Monitoring Programs (Inception Through Normal Operations to License Termination)—Effluent Streams and the Environment".

Cimarron's Quality System describes a systematic approach to quality assurance. Quality Assurance Project Plans (QAPPs), Activity Planning, and a combination of the two are included as elements.

The Quality System has been designed to provide for control of decommissioning critical activities. This includes:

- Adequate documentation of the planning, implementation, and monitoring phases of the project such that an ongoing "history" of the project is available for reference by those involved in the decommissioning activity and for use by outside reviewers.

- Provision for instructions that are adequate to describe how specific tasks are performed.

- Provision for adequate training of workers implementing the instructions to ensure that the work is performed properly.

- Provision for appropriate QC activities to ensure the "goodness" of data obtained.

A Quality Assurance Coordinator (QAC) has been retained by Cimarron Corporation. In the event of multiple contractors participating in the remediation project, the QAC will coordinate quality activities among the contractors.

Appendix E includes additional information provided to demonstrate the scope of the Cimarron Quality System:

- Appendix E-1: Cimarron Quality System Table of Contents
- Appendix E-2: QA Cross Reference Table
- Appendix E-3: Cimarron Quality System chart which serves to illustrate the decommissioning critical activities controlled by the Quality System

6.2 Data Quality Objectives (DQOs)

DQOs are qualitative and quantitative statements that clarify technical and quality goals. DQOs serve to 1) define the appropriate type of data (numerical and non-numerical); and 2) specify tolerable levels of potential decision errors needed to support decisions.

The NRC release criterion for groundwater is 180 pCi/L total uranium. The ODEQ criterion for groundwater is 110 µg/L total uranium. Both criteria are addressed in the DQOs.

A summary list of DQOs is provided in Appendix C. In addition to this summary list, DQOs are addressed in the following sections of this document:

- Section 5.2.1: Baseline Geochemical Data Collection
- Section 5.2.2: Initial Treatment Areas
- Section 5.2.4: Performance Monitoring of the IRZ
- Section 5.3: Remedy Completion Demonstration Testing

These DQOs are preliminary and are subject to change as additional knowledge is obtained.

7. Financial Assurance

7.1 Cost Estimate

ARCADIS has proposed to perform groundwater remediation in all three areas for a fixed price offer, and ARCADIS will obtain insurance to ensure that the geochemical conditions stipulated as demonstration of compliance are met within the time frame provided by the schedule presented in Section 5.5. ARCADIS' offer and the total fixed price offer amount are contingent upon NRC approval of this Site Decommissioning Plan – Groundwater Decommissioning Amendment.

Should NRC require modification of this Site Decommissioning Plan – Groundwater Decommissioning Amendment in ways that change the substance of the plan, both the cost and schedule may be impacted. A more detailed cost estimate and financial assurance can prepared once NRC and ODEQ have approved this license amendment.

7.2 Financial Mechanism

Cimarron will modify the existing standby trust agreement and surety bond in accordance with the detailed cost estimate prepared upon NRC and ODEQ approval of this license amendment.

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9. Glossary of Terms

Amendment: Solutions added to the aquifer via injection to supplement the natural chemistry of the aquifer in order to promote the desired geochemical transformations; amendments for the bioremediation process included in this Groundwater Decommissioning Plan include organic carbon sources such as molasses as well as other chemicals such as iron and/or sulfate.

Amorphous substance: Amorphous substances differ from minerals in that they do not have a fixed structure. Commonly, amorphous substances form more rapidly than minerals.

Anaerobic conditions: Reducing conditions that are brought about through the metabolic activity of microorganisms.

Anoxic: A condition in the aquifer in which oxygen has been consumed and is absent.

Area of Impact: Extent of Uranium subsurface contamination that exceeds the License Criterion of 180 pCi/L.

Batch-model: A geochemical model in which the system is composed of a fixed volume. Geochemical reactions are simulated within the system and constituents can enter and leave, but transport processes are not considered.

Bi-dentate: Describes a chemical complex in which two chemical binding sites of a ligand molecule or surface chemical species participates in the formation of the complex with a metal or radionuclide.

Bioavailable: The availability of a chemical present in the aquifer or added as an amendment to participate in biological reactions, such as serving as an acceptor of electrons for metabolism of organic carbon.

Bioreduction: Transformation of oxidized uranium (uranyl [U(VI)]) to reduced uranium (uranous [U(IV)]) by a microbial metabolic process.

Bioremediation: Treatment of a chemical or radiological contaminant in groundwater or soil through a microbial process.

Capillary fringe: Subsurface layer above the water table where pores are filled with capillary water so that the saturation approaches 100%.

Criteria: Pre-determined concentration or activity standards that serve as a target for remediation. For this Groundwater Decommissioning Plan, the site-specific release criterion for groundwater as specified in license condition 27(b) is 180 pCi/L. In addition to the activity–based criteria, Cimarron must also meet a risk-based concentration limit of 110 µg/L approved by the Oklahoma Department of Environmental Quality (ODEQ).

Dissolution: The transformation of a chemical in the aquifer from the solid phase to the dissolved phase, usually catalyzed by microbial processes.

Dissolved: The concentration of a chemical in solution determined by filtering the analytical sample to remove any particulate matter prior to mass analysis of the sample.

Dual-domain mass transfer coefficient: First-order rate coefficient of mass transfer that characterizes the exchange between mobile and immobile domains.

Electron acceptor: A sink for electrons released through microbially-catalyzed electron-transfer reactions in the aquifer, specifically oxygen, nitrate, uranyl, ferric iron, or sulfate. Oxidized forms of elements act as electron acceptors.

Electron donor: Source of electrons for microbially-catalyzed electron-transfer reactions in the aquifer, specifically organic carbon present in carbohydrates, organic acids, or alcohols. In addition, reduced forms of elements act as electron donors.

Equilibrium constant: A number that relates the relative concentration of the product(s) of a chemical reaction to the reactants; the constant describes whether the reaction has a propensity to proceed to the right (or to completion).

Equilibrium model: A geochemical model assuming that all chemical reactions in the system reach equilibrium. This is the same as assuming that all reactions occur rapidly.

Extraction: Solvents and/or reagents, such as water and acids, are used to dissolve parts of solid samples.

Full-scale: Scale of treatment necessary to target the entire area of impact.

IRZ: *In situ* reactive zone where migrating contaminants are intercepted and permanently inmobilized or degraded into harmless end-products through the creation of strongly reducing conditions throughout the reactive zone.

Kinetic model: A geochemical model where reaction rates are assigned to chemical reactions.

Mobile porosity: The portion of total porosity that contributes to advective flow and transport in aquifers.

Mono-dentate: Describes a chemical complex in which one chemical binding site of a ligand molecule or surface chemical species participates in the formation of the complex with a metal or radionuclide.

Natural recharge: Hydrologic process where a percentage of rainfall water moves downward to the groundwater. When the front of infiltrating water reaches the capillary fringe, it displaces air in the pore spaces and causes the water table to rise. The time of movement of the infiltrating water is a function of the thickness of unsaturated zone and the vertical hydraulic conductivity.

One-dimensional transport model: A geochemical model in which geochemical reactions and transport processes are considered simultaneously. Transport processes include advection and dispersion and are affected by the geochemical reactions.

Oxic: A condition in the aquifer in which oxygen is present and available to serve as an electron acceptor.

Protonation reaction: Reaction involving a base (hydroxyl ion) or an acid (hydrogen ion).

Reagent: Solutions added to the aquifer via injection to promote the transformation of soluble uranium to insoluble, precipitated forms of uranium and to create iron sulfide mineral phases. Substrate and amendment chemicals are reagents.

Recirculation: Extraction of water from the aquifer, followed by amendment with substrate and reinjection back into the saturated subsurface. Recirculation facilitates the delivery of substrate and fluid manipulation to allow the creation of large areas of delivery of reagents as required for full-scale treatment.

Reducing conditions: A condition in the aquifer in which the concentrations of the predominant electron acceptors (oxygen and nitrate) are deficient so that oxidized chemicals (e.g., iron, uranium, sulfate) are transformed to a lower valence state (accept electrons).

Remobilization: The introduction of formerly immobilized uranium (either precipitated, reduced, or sorbed) to the aqueous phase.

Re-oxidation: The transformation of immobilized uranium (from the reduced U[IV] form) to the soluble, oxidized form of uranium (U[VI]).

Saturated zone: Saturated soils below the seasonal low water level

Seasonally saturated zone: The zone between the seasonal high and low water level where water levels fluctuate resulting in soils that are saturated or unsaturated depending on the time of year.

Sorption: The partitioning of a dissolved-phase chemical species to the aquifer solid-phase (mineral surface or soil particle) through specific chemical reactions at the surface; these reactions may be based on the electrostatic charge or surface potential, direct chemical complexation (chemical bond formation), or precipitation of the dissolved species at a surface.

Substrate: Carbon source added to the aquifer via injection in order to stimulate the metabolic activity of indigenous microorganisms.

Sulfate reducing bacteria: A specific group of microorganisms capable of utilizing oxidized sulfur (sulfate) as an electron acceptor for growth, resulting in the creation of reduced sulfur (sulfide).

Surface complexation model: A geochemical model in which the mineral surface is considered, specifically its role in regulating the concentration of dissolved chemicals. The surface is described by discrete chemical reactions (e.g., protonation and deprotonation), similar to those that occur in the dissolved phase.

Total: The concentration of a chemical in an unfiltered sample for mass analysis which includes both the dissolved and particulate fraction. When used in connection with an activity determination for a radionuclide, total refers to the sum of the isotopes present in the analytical sample.

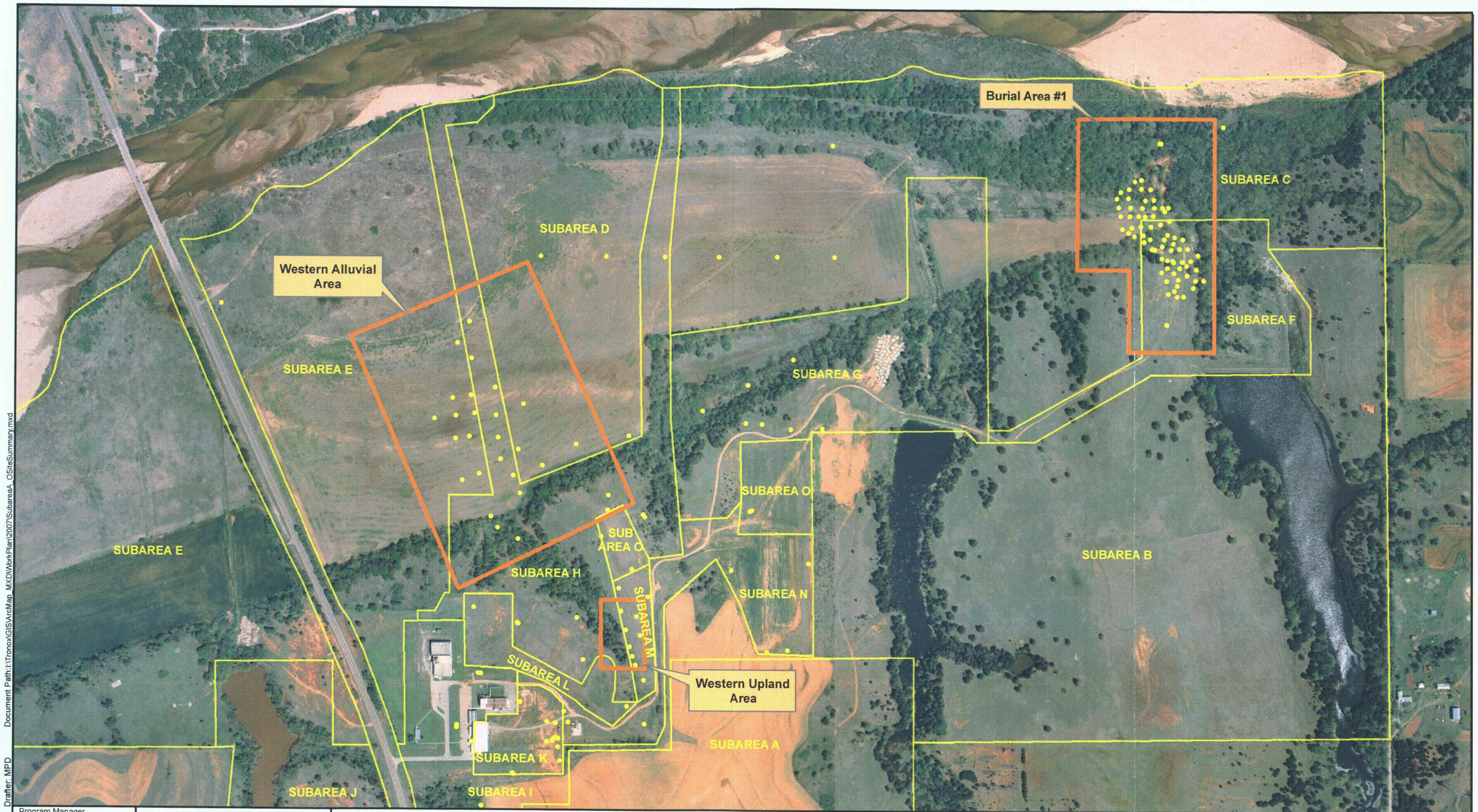
Tracer: A non-degradable and non-toxic constituent that is intentionally introduced into the subsurface to track and measure the flow, distribution, and transport behavior of fluids and solutes in the aquifer.

U(IV): Uranium present in the +4 oxidation state (the reduced, insoluble form of uranium).

U(VI): Uranium present in the +6 oxidation state (the oxidized, soluble form of uranium).

Uranyl: Hexavalent uranium in the UO_2^{2+} form. Uranyl can be aqueous or can be a constituent of solids.

Vadose zone: Unsaturated soils above the seasonal high water level.



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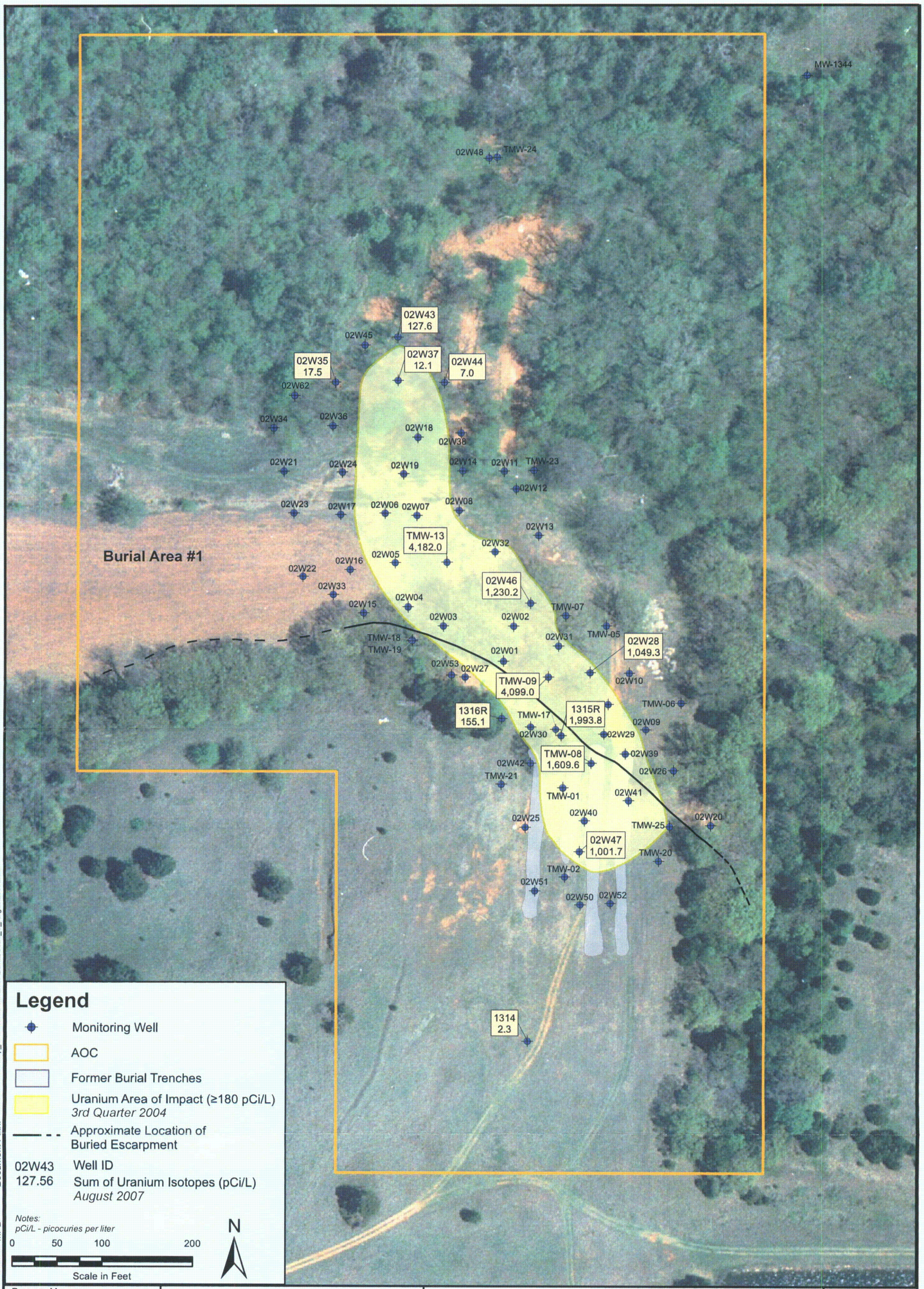
Drafter: MPD

Program Manager Erhardt Werth Project Manager Sara Handy Task Manager Janis Lutrick Technical Review Jeff Gillow	ARCADIS 630 Plaza Drive, Suite 100 Highlands Ranch, Colorado 80129 Tel: 720-344-3500 Fax: 720-344-3535 www.arcadis-us.com	Legend Site Subareas Areas of Concern Monitoring Well N 0 250 500 Scale in Feet	Cimarron Site Subareas Cimarron Corporation Crescent, Oklahoma	Date: 04/18/2008 FIGURE 2-1



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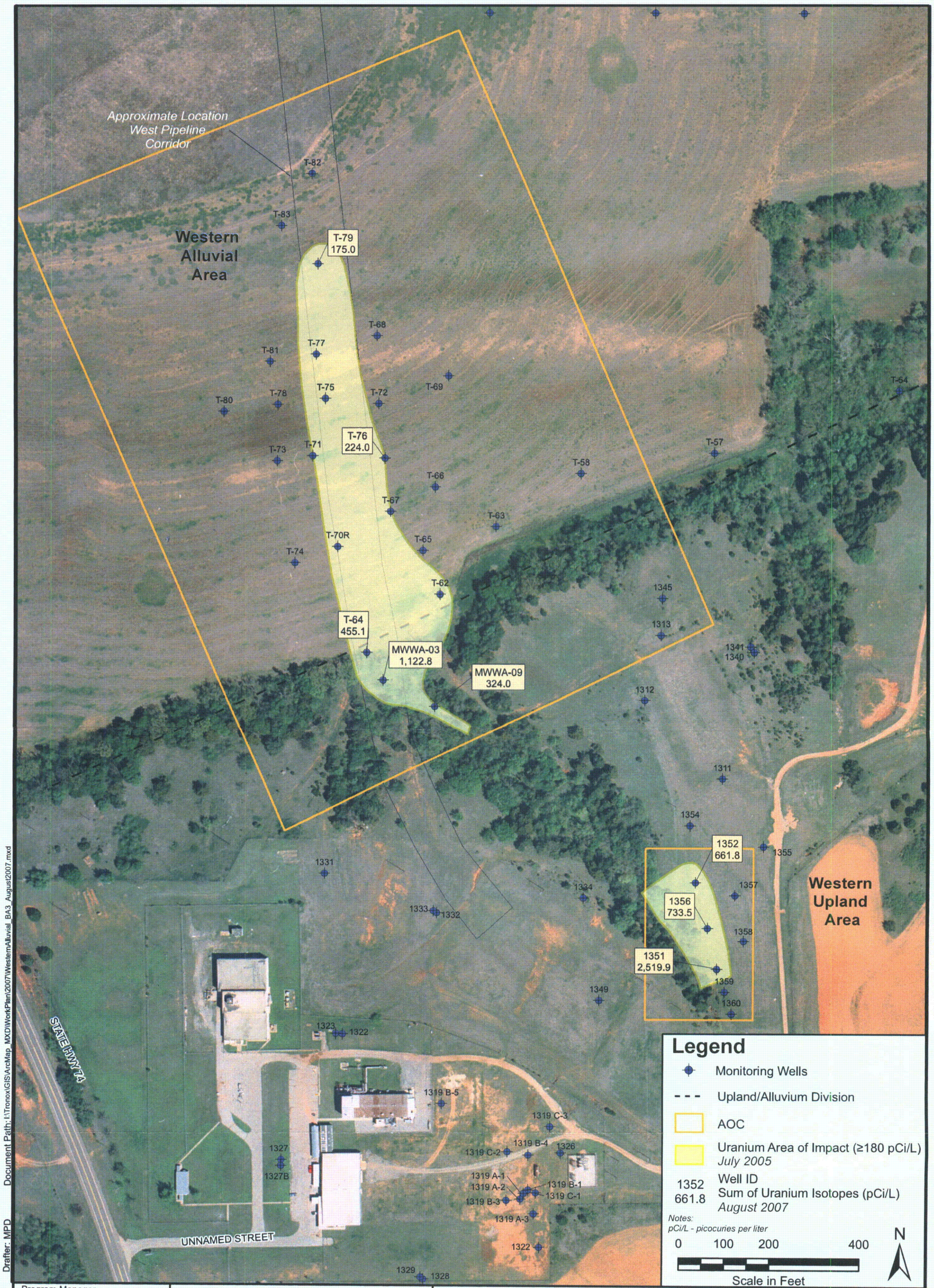
Program Manager Erhardt Werth	ARCADIS 630 Plaza Drive, Suite 100 Highlands Ranch, Colorado 80129 Tel: 720-344-3500 Fax: 720-344-3535 www.arcadis-us.com	Burial Area #1 Area of Impact Cimarron Corporation Crescent, Oklahoma	Date: 04/18/2008
Project Manager Sara Handy			FIGURE
Task Manager Janis Lutrick			3-1
Technical Review Jeff Gillow			



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Drafter: MPD

Program Manager Erhardt Werth	ARCADIS 630 Plaza Drive, Suite 100 Highlands Ranch, Colorado 80129 Tel: 720-344-3500 Fax: 720-344-3535 www.arcadis-us.com	Western Alluvial and Western Upland Areas of Impact Cimarron Corporation Crescent, Oklahoma	Date: 04/18/2008
Project Manager Sara Handy			FIGURE
Task Manager Janis Lutrick			3-2
Technical Review Jeff Gillow			

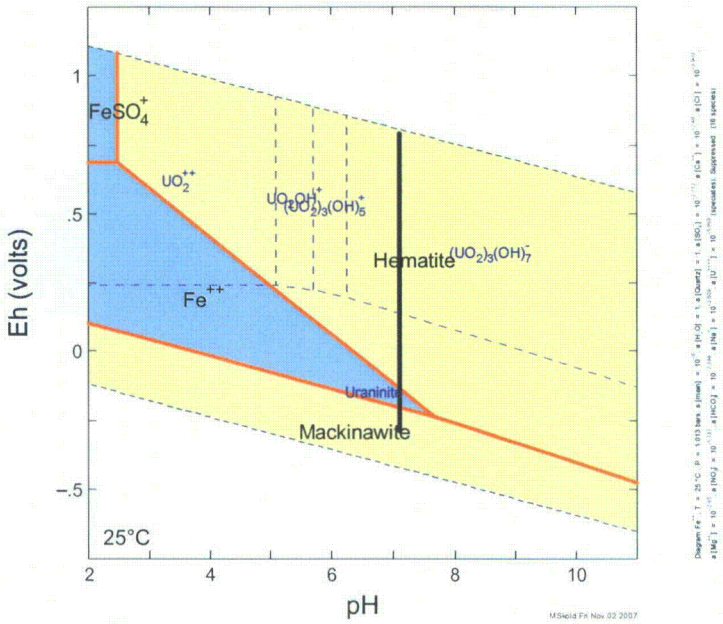

Figure 3-3. Eh-pH Diagram Showing Iron Minerals and Uranium Speciation. Reaction path from the batch model (from high to low Eh) shows reactions occurring during the IRZ phase. The figure was created in the Geochemist's Workbench.

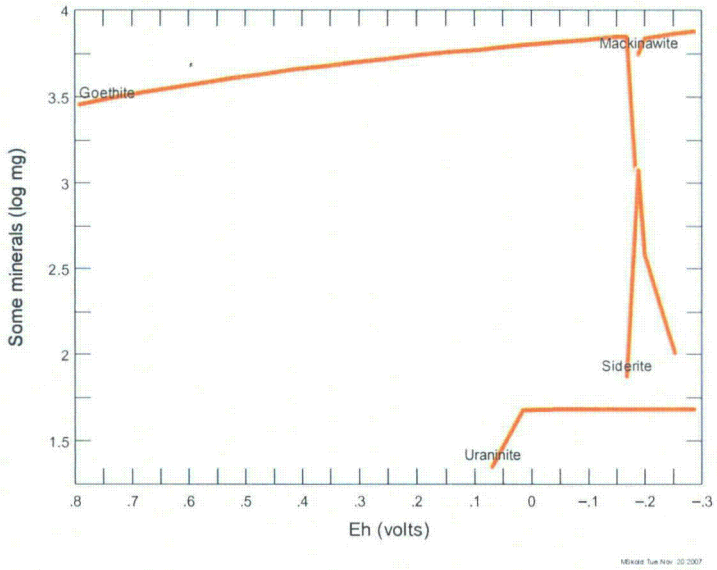

Figure 3-4. Predicted Change in Minerals Composition During Development of Reducing Conditions Using the Batch Model (from high to low Eh). The figure was created in the Geochemist's Workbench.

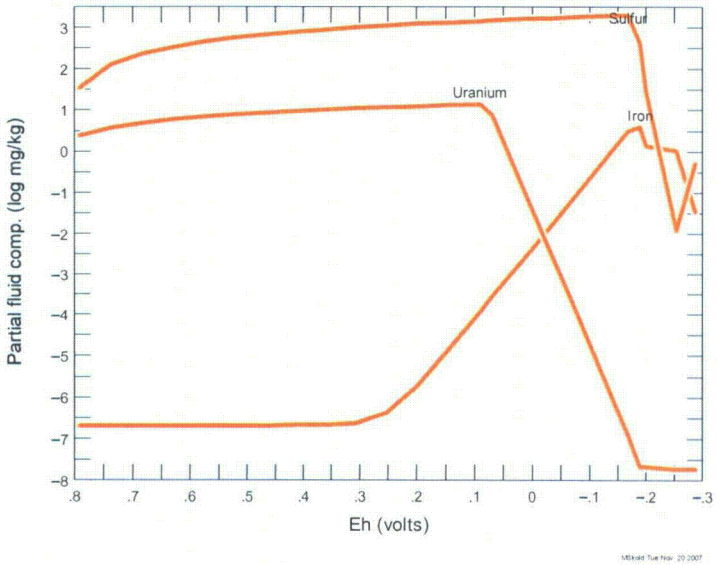

Figure 3-5. Predicted Aqueous Concentrations of Uranium, Iron and Sulfate During Development of Reducing Conditions Using the Batch Model (from high to low Eh). The figure was created in the Geochemist's Workbench.

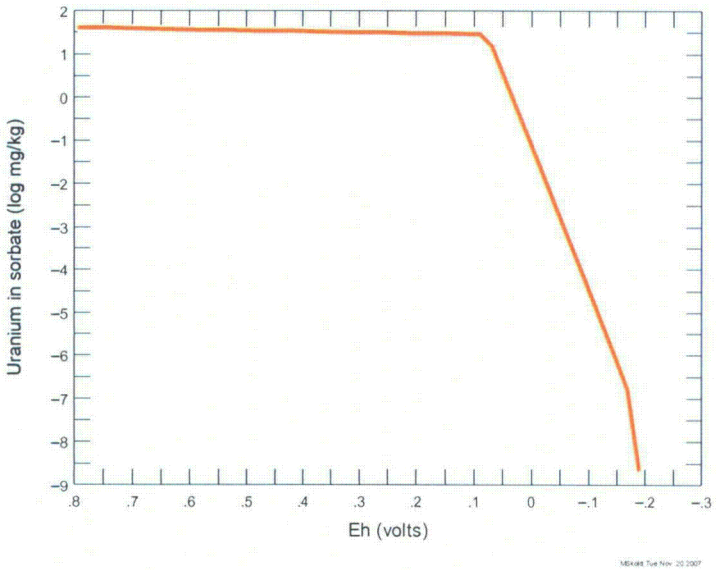

Figure 3-6. Predicted Uranium Sorbed to Iron Hydroxides During Development of Reducing Conditions Using the Batch Model (from high to low Eh). The figure was created in the Geochemist's Workbench.

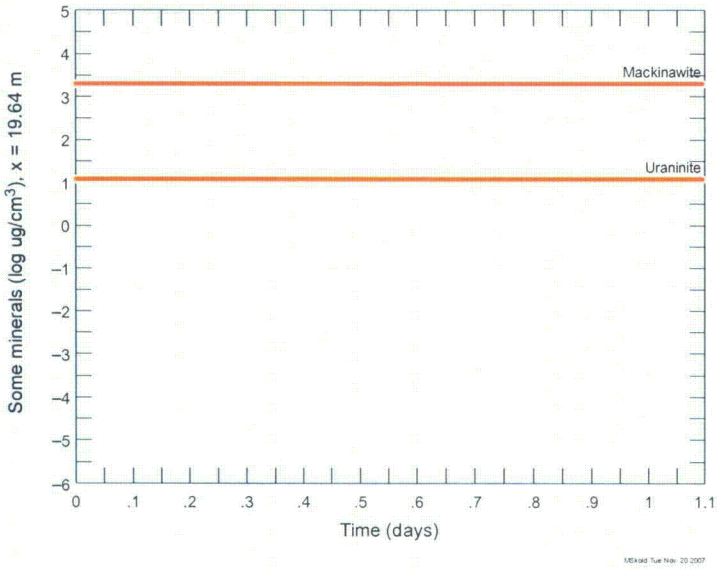

Figure 3-7. Predicted Mineralogical Composition of the Reduced Aquifer in the Most Upgradient Cell in the 1-D Transport Model. The figure was created in the Geochemist's Workbench.

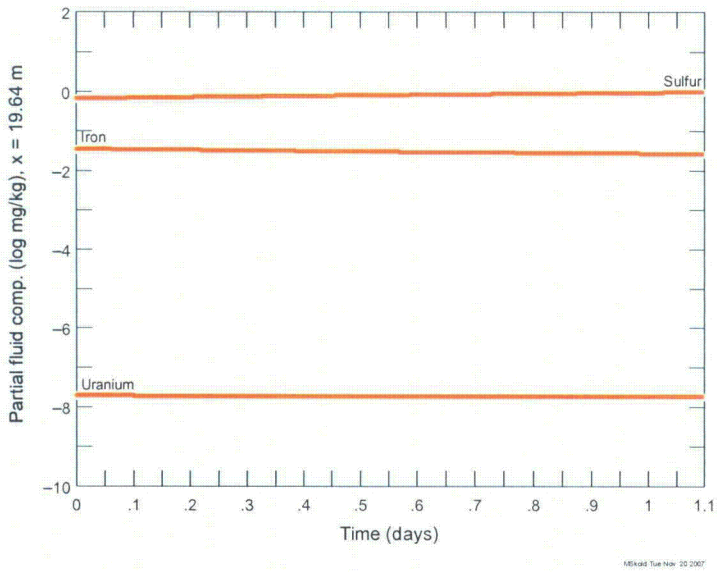

Figure 3-8. Predicted Aqueous Composition of the Reduced Aquifer in the Most Upgradient Cell in the 1-D Transport Model. The figure was created in the Geochemist's Workbench.

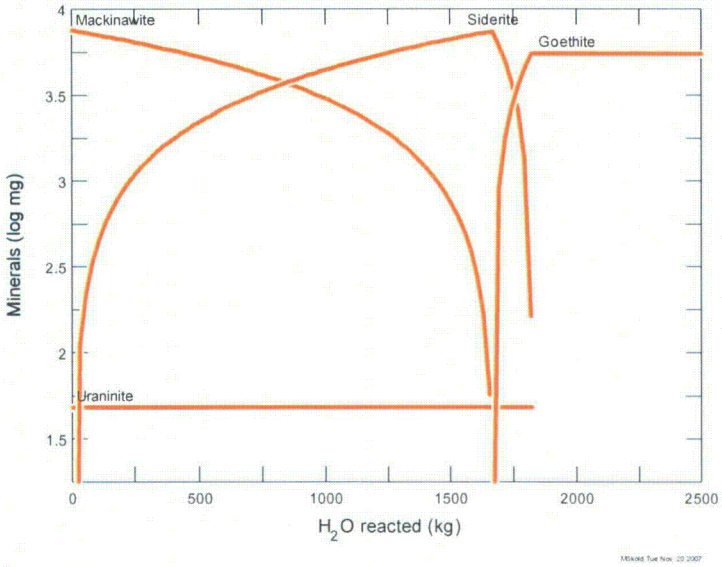

Figure 3-9. Predicted Changes in Mineral Composition During Re-oxidation of the Aquifer Using the Batch Model. One kg of reacted water represents flushing the system with one pore volume. The figure was created in the Geochemist's Workbench.

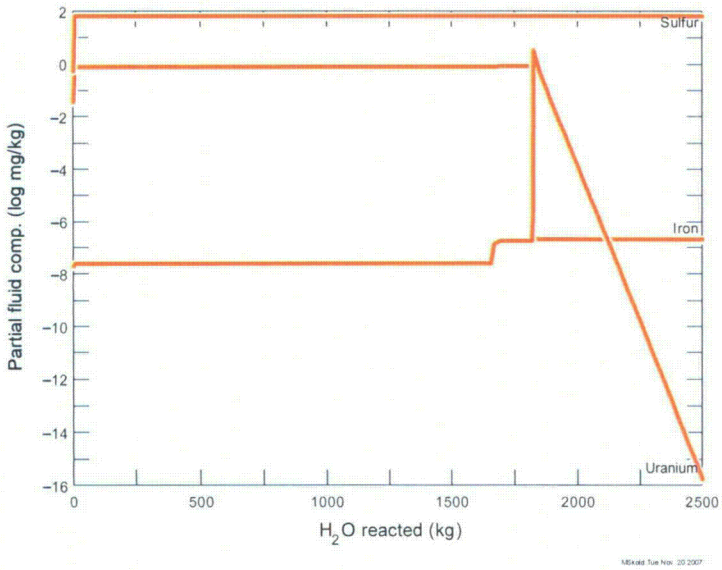

Figure 3-10. Predicted Aqueous Concentration of Uranium, Iron and Sulfate During Re-oxidation of the Aquifer Using the Batch Model. One kg of reacted water represents flushing the system with one pore volume. The figure was created in the Geochemist's Workbench.

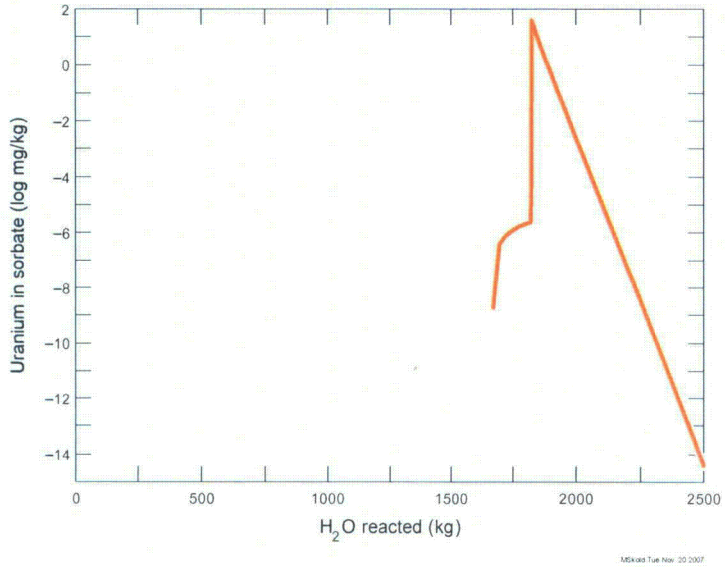

Figure 3-11. Predicted Uranium Sorbed to Iron Hydroxides During Re-oxidation of the Aquifer Using the Batch Model. One kg of reacted water represents flushing the system with one pore volume. The figure was created in the Geochemist's Workbench.

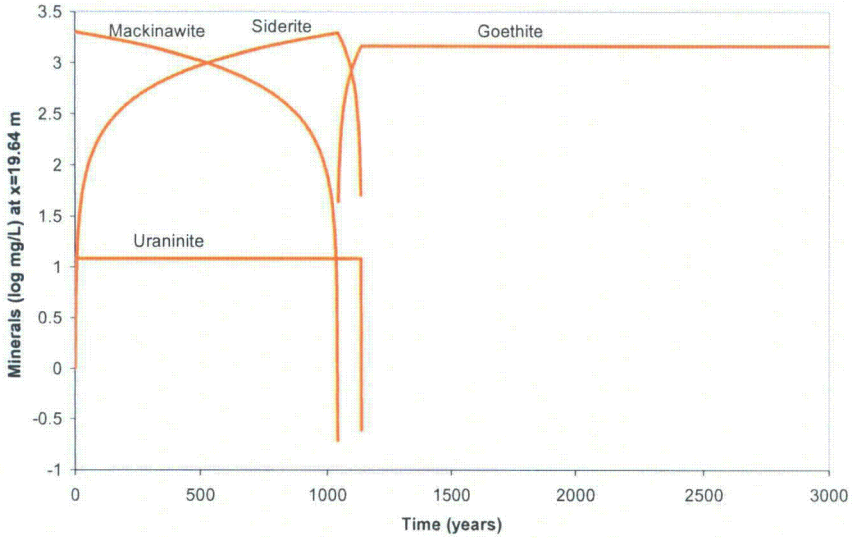

Figure 3-12. Predicted Changes in Mineral Composition in the Most Upgradient Cell in the 1-D Transport Model During Re-oxidation of the Aquifer. This simulation includes inflowing upgradient water, but does not simulate extreme infiltration events. The figure was created in the Geochemist's Workbench.

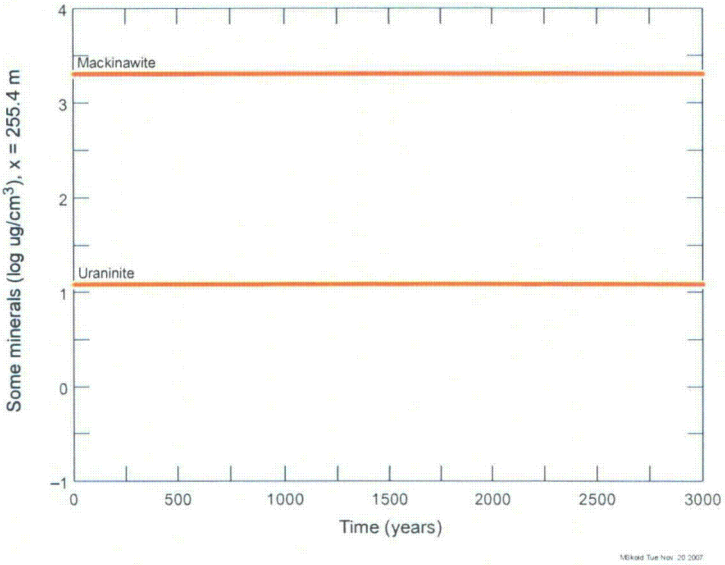

Figure 3-13. Predicted Mineral Precipitation in the Most Downgradient Cell in the 1-D Transport Model During Re-oxidation of the Aquifer. This simulation includes inflowing upgradient water, but does not simulate extreme infiltration events. The figure was created in the Geochemist's Workbench.

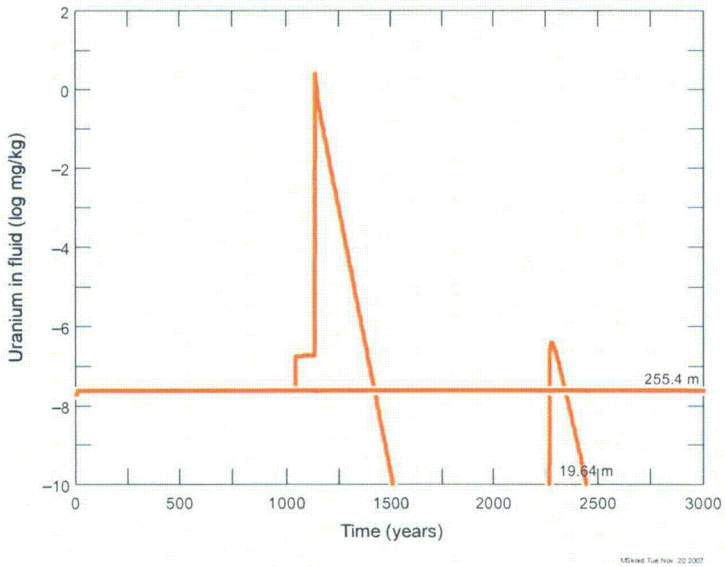

Figure 3-14. Predicted Uranium Concentration in the Most Upgradient and Most Downgradient Cells in the 1-D Transport Model During Re-oxidation of the Aquifer. This simulation includes inflowing upgradient water, but does not simulate extreme infiltration events. The horizontal line represents the low, constant uranium concentration in the most downgradient cell (center at 255.4 m), while the line with the two peaks represent the uranium concentration in the most upgradient cell (center at 19.64 m). During the first 1,100 years, the uranium concentration is uniform in the entire system, making the two lines fall on top of each other. The

second peak in the most upgradient cell is a result of dispersion of uranium from the adjacent cell. The figure was created in the Geochemist's Workbench.

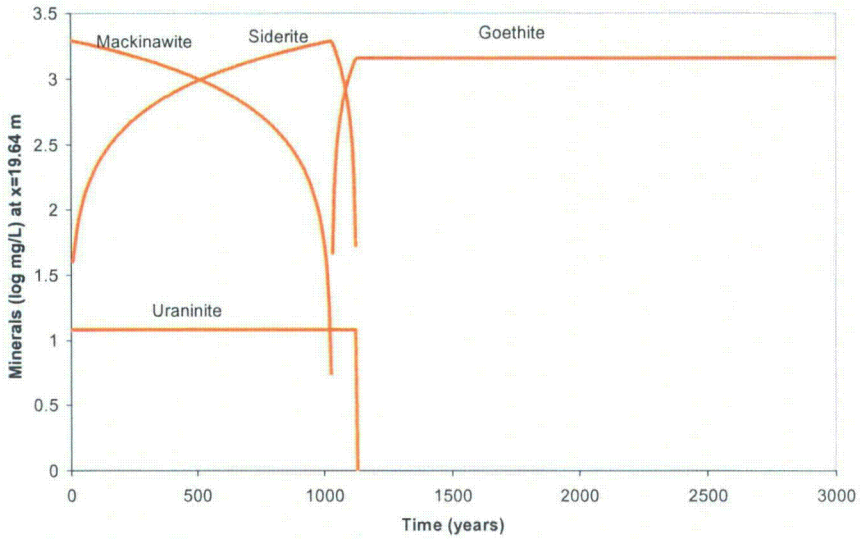

Figure 3-15. Predicted Changes in Mineral Composition During Re-oxidation of the Aquifer in the Most Upgradient Cell in the 1-D Transport Model. The scenario includes infiltration of oxygenated flooding water with elevated nitrate concentrations. The recurrence interval of river over-topping was 100 years in this figure. Assuming a 500-year recurrence interval does not affect the re-oxidation rate. The figure was created in the Geochemist's Workbench.

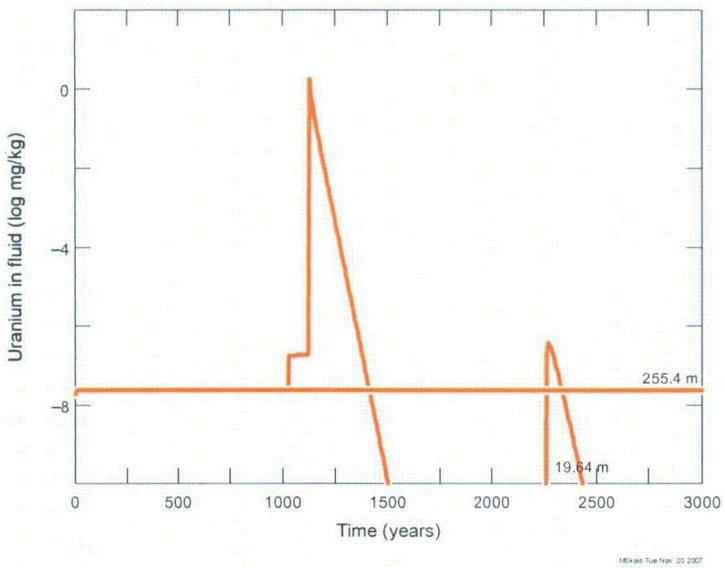

Figure 3-16. Predicted Aqueous Uranium Concentration in the Most Upgradient and Most Downgradient Cells in the 1-D Transport Model During Re-oxidation of the Aquifer. The scenario includes infiltration of oxygenated flooding water with elevated nitrate concentrations. The recurrence interval of river over-topping was 100 years in this figure. Assuming a 500-year

recurrence interval does not affect the re-oxidation rate. The horizontal line represents the low, constant uranium concentration in the most downgradient cell (center at 255.4 m), while the line with the two peaks represent the uranium concentration in the most upgradient cell (center at 19.64 m). During the first 1,100 years, the uranium concentration is uniform in the entire system making the two lines fall on top of each other. The second peak in the most upgradient cell (center at 19.64 m) is a result of dispersion of uranium from the adjacent cell. The figure was created in the Geochemist's Workbench.

Stage 1 – Development of Groundwater Decommissioning Plan/Conceptual Design

Groundwater Decommissioning Plan Approval (by the NRC and ODEQ)

Stage 2 – Baseline Sampling and Initial Treatment System Installation

- Additional field characterization as needed in each of the three areas to advance the conceptual design to the initial treatment system design; establish soils mineralogy baseline (Table 5-1)
- Adjust site models and utilize outputs in initial treatment system design considerations
- Complete initial treatment system design for all 3 remediation systems
- Share new information with the NRC and ODEQ (estimated at 6 months from GDP approval)

Install and operate initial treatment system components in the forward, middle and rear portions of the groundwater areas of impact

Utilize initial system installation efforts to collect:

- Groundwater - water quality and flow information
- Soils - iron mineralogy information

Update/adjust site models as appropriate and share new information with the NRC and ODEQ

Complete full-scale design

Year 1

Stage 3 – Full-scale Systems Operation/Active Treatment

- Expand treatment systems to complete functionality
- Initiate full-scale treatment throughout all areas of uranium impacts

Continue to collect system operations and impacts data

Monthly Groundwater Data Collection (Table 5-1)

- water quality sampling (full suite)
- flow information

Update/adjust site models as appropriate and share new information with the NRC and ODEQ

Make basic remediation system adjustments

Year 2

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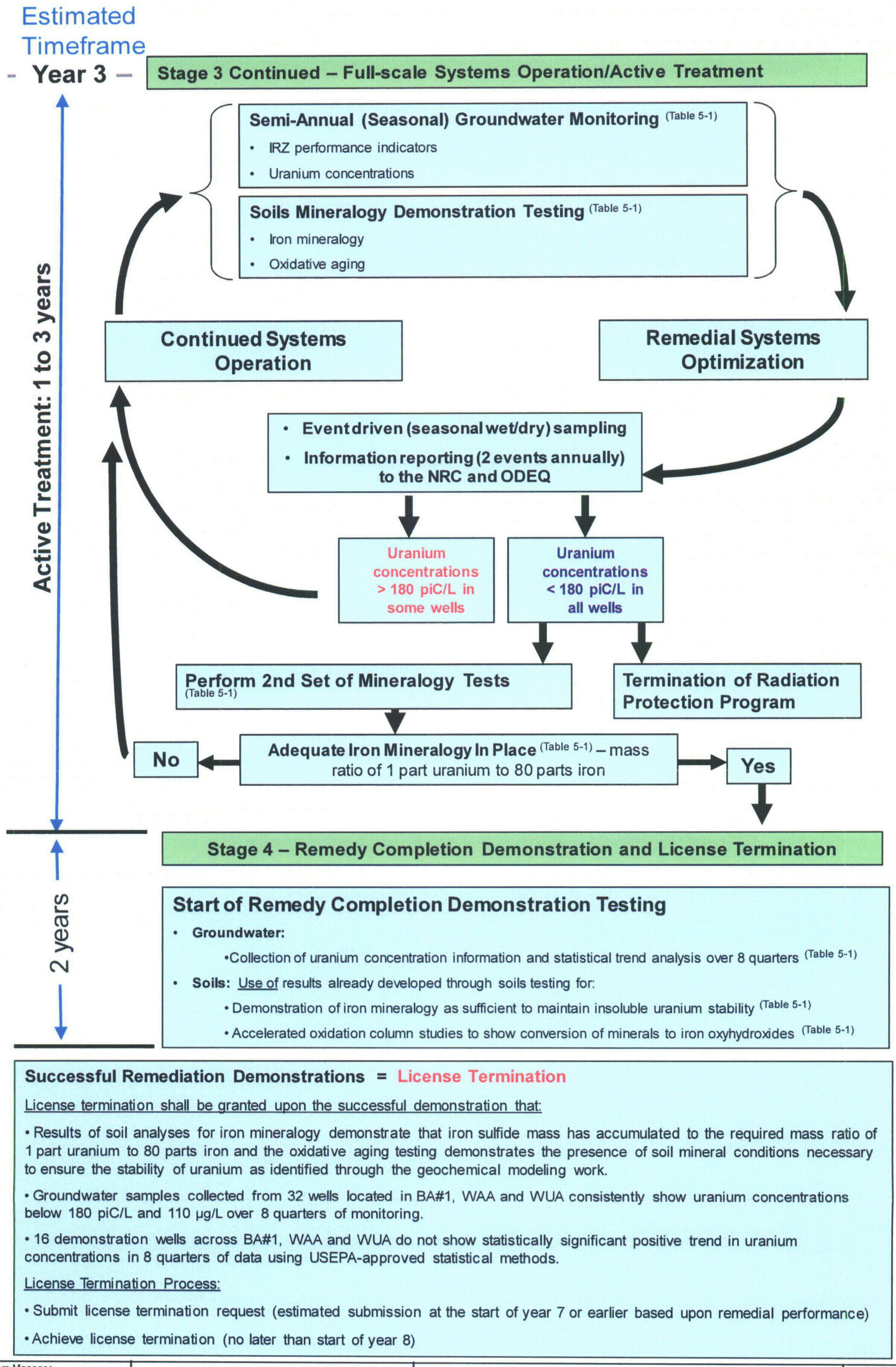
Program Manager Erhardt Werth	ARCADIS 630 Plaza Drive, Suite 100 Highlands Ranch, Colorado 80129 Tel: 720-344-3500 Fax: 720-344-3535 www.arcadis-us.com	Bioremediation Implementation Process Cimarron Corporation Crescent, Oklahoma	Date: 04/18/2008
Project Manager Sara Handy			FIGURE
Task Manager Janis Lutrick			5-1
Technical Review Jeff Gillow			Page 1 of 3



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Program Manager Erhardt Werth	ARCADIS 630 Plaza Drive, Suite 100 Highlands Ranch, Colorado 80129 Tel: 720-344-3500 Fax: 720-344-3535 www.arcadis-us.com	Bioremediation Implementation Process Cimarron Corporation Crescent, Oklahoma	Date: 04/18/2008
Project Manager Sara Handy			FIGURE
Task Manager Janis Lutrick			5-1
Technical Review Jeff Gillow			Page 2 of 3

Table 5-1. Summary of Baseline, Performance and Remedy Completion Demonstration Monitoring

# of Sampling Locations	Sampling Frequency	Analyses to be Conducted
Stage 2: Baseline Monitoring		
Groundwater Monitoring:		
32 wells across all 3 areas: BA#1, WAA , WUA	One-time sampling event	• pH • Temperature • Dissolved oxygen • Total organic carbon • Total dissolved solids • Alkalinity • Sulfate/sulfide • Nitrate • Dissolved/ferrous iron • Uranium – total activity, isotopic, mass concentration
Existing wells across all 3 areas: BA#1, WAA, WUA	One-time sampling event	• Water levels
Soil Monitoring:		
3 borings installed within each area of impact with 2 soil samples from different depth intervals in each boring (total of 6 samples from each area of impact)[a]	One-time sampling event	• Bulk iron mineralogy including: ○ selective chemical extraction ○ x-ray diffraction • Iron sulfide content quantification • Uranium – total activity, isotopic, mass concentration • Induced mineralogy changes including microprobe methods to examine soil mineralogy changes induced by TOC addition and anaerobic microbial processes using: ○ SEM with EDS ○ μ-XRF ○ μ-XANES
Stage 3: Performance Monitoring:		
Groundwater Monitoring:		
32 wells across all three areas: BA#1, WAA , WUA	Monthly for the first 6 months of IRZ operation Semi-annually starting 12 months after start of IRZ operation and continuing until the start of remedy completion demonstration testing for groundwater	• pH • Temperature • Dissolved oxygen • Total organic carbon • Total dissolved solids • Alkalinity • Sulfate/sulfide • Nitrate • Dissolved/ferrous iron • Uranium – total activity, isotopic, mass concentration
Soil Monitoring:		
3 borings installed within each area of impact with 2 soil samples from different depth intervals in each boring (total of 6 samples from each area of impact)[a]	Minimum of two sampling events based on observed results	• Bulk iron mineralogy including: ○ selective chemical extraction ○ x-ray diffraction • Iron sulfide content quantification • Uranium – total activity, isotopic, mass concentration • Induced mineralogy changes including microprobe methods to examine soil mineralogy changes induced by TOC addition and anaerobic microbial processes using: ○ SEM with EDS ○ μ-XRF ○ μ-XANES
Stage 4: Remedy Completion Demonstration Monitoring:		
Groundwater Monitoring:		
16 wells across all 3 areas: BA#1, WAA, WUA	Quarterly for 8 quarters	• Uranium – total activity, isotopic, mass concentration
Soil Oxidative Aging Testing:		
3 borings installed within each area of impact with 2 soil samples from different depth intervals in each boring (total of 6 samples from each area of impact)[a]	• Initial Testing – near beginning of Stage 3 • Second Testing – upon determination of adequate mineralogy	Column testing to assess: • Oxygen consumption • Iron oxidation Oxidative aging testing to be conducted using a PNNL methodology (Thornton et al 2007)

[a] - Locations for sampling will be selected so that soil is retrieved from 1) within the areas of the highest concentration of uranium in groundwater at the start of remediation, 2) within the leading edge of the area of uranium impacts, and 3) within the area of uranium impacts upgradient from the highest concentration location. The selection of locations for sampling will be refined as the groundwater remediation progresses.

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Program Manager
Erhardt Werth
Project Manager
Sara Handy
Task Manager
Janis Lutrick
Technical Review
Jeff Gillow

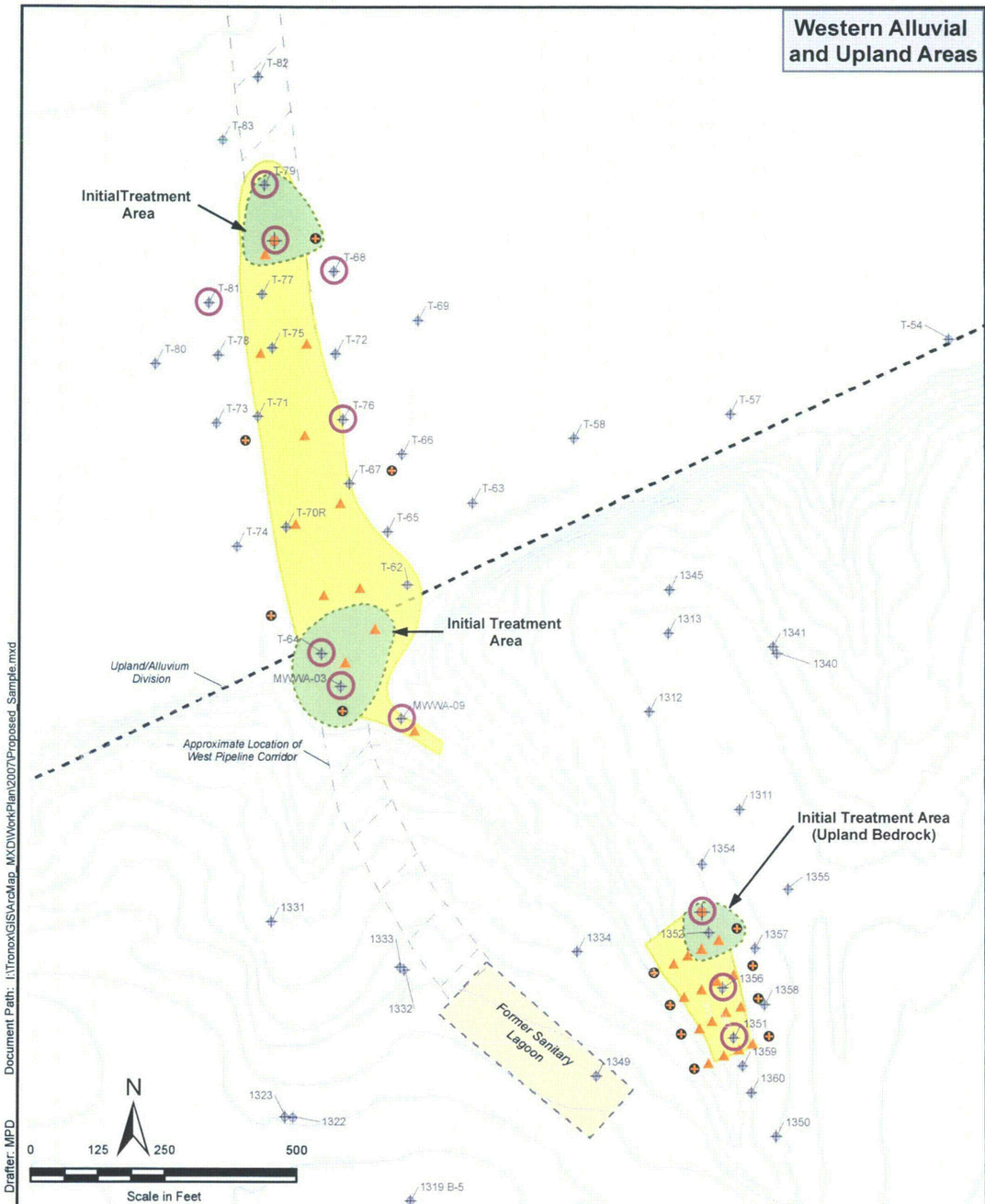
ARCADIS
630 Plaza Drive, Suite 100
Highlands Ranch, Colorado 80129
Tel: 720-344-3500
Fax: 720-344-3535
www.arcadis-us.com

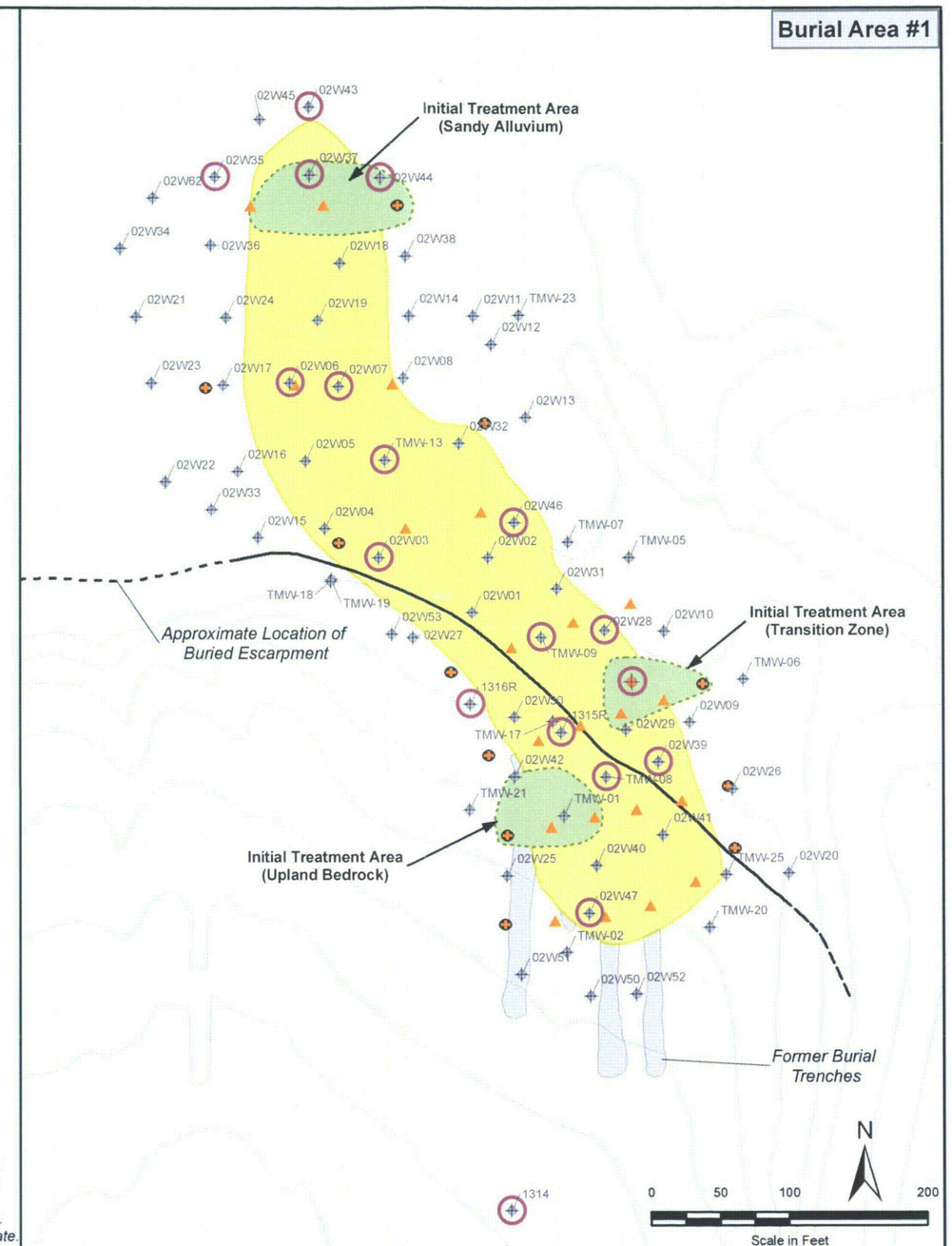
Bioremediation Implementation Process

Cimarron Corporation
Crescent, Oklahoma

Date: 04/18/2008

FIGURE
5-1





Note:
- *Western Alluvial area of impact: July 2005*
- *Burial Area #1 area of impact: 3rd Q 2004*
- *Monitoring well locations may change dependent on final injection well locations. More locations may be added at a later date.*

Drafter: MPD Document Path: I:\Tronox\GIS\ArcMap_MXD\WorkPlan\2007\Proposed_Sample.mxd

Program Manager	Erhardt Werth
Project Manager	Sara Handy
Task Manager	Janis Lutrick
Technical Review	Jeff Gillow

ARCADIS
630 Plaza Drive, Suite 100
Highlands Ranch, Colorado 80129
Tel: 720-344-3500
Fax: 720-344-3535
www.arcadis-us.com

Legend

- Extraction Well
- Injection Well
- Monitoring Well
- Proposed New Monitoring Well
- Proposed Monitoring Well Locations
- Contours (5 foot interval)
- Uranium Area of Impact (≥180 pCi/L)
- Areas of Testing
- Former Sanitary Lagoon

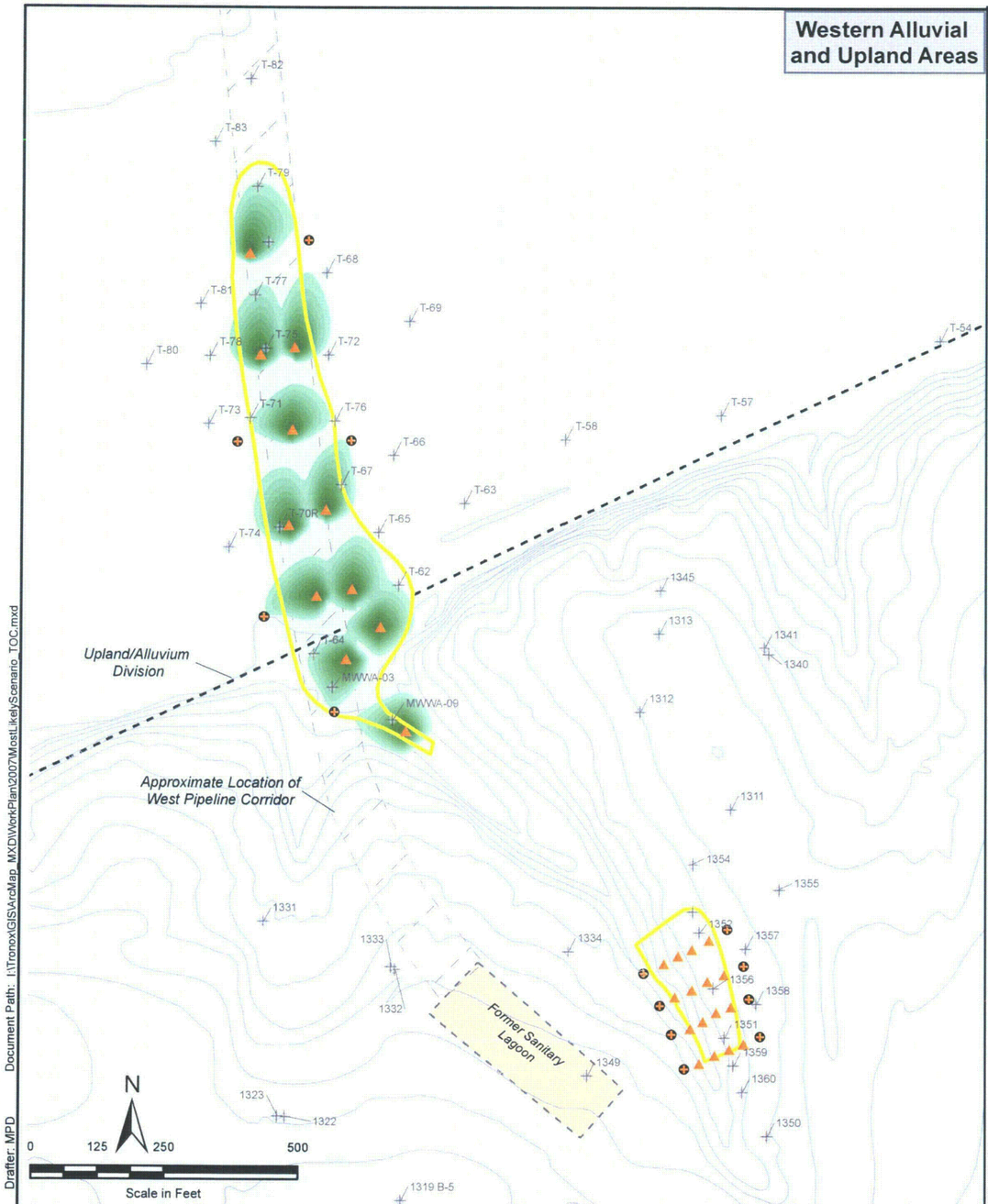
Proposed Monitoring Well Locations and Initial Treatment Areas

Cimarron Corporation
Crescent, Oklahoma

Date: 04/18/2008

FIGURE

5-2



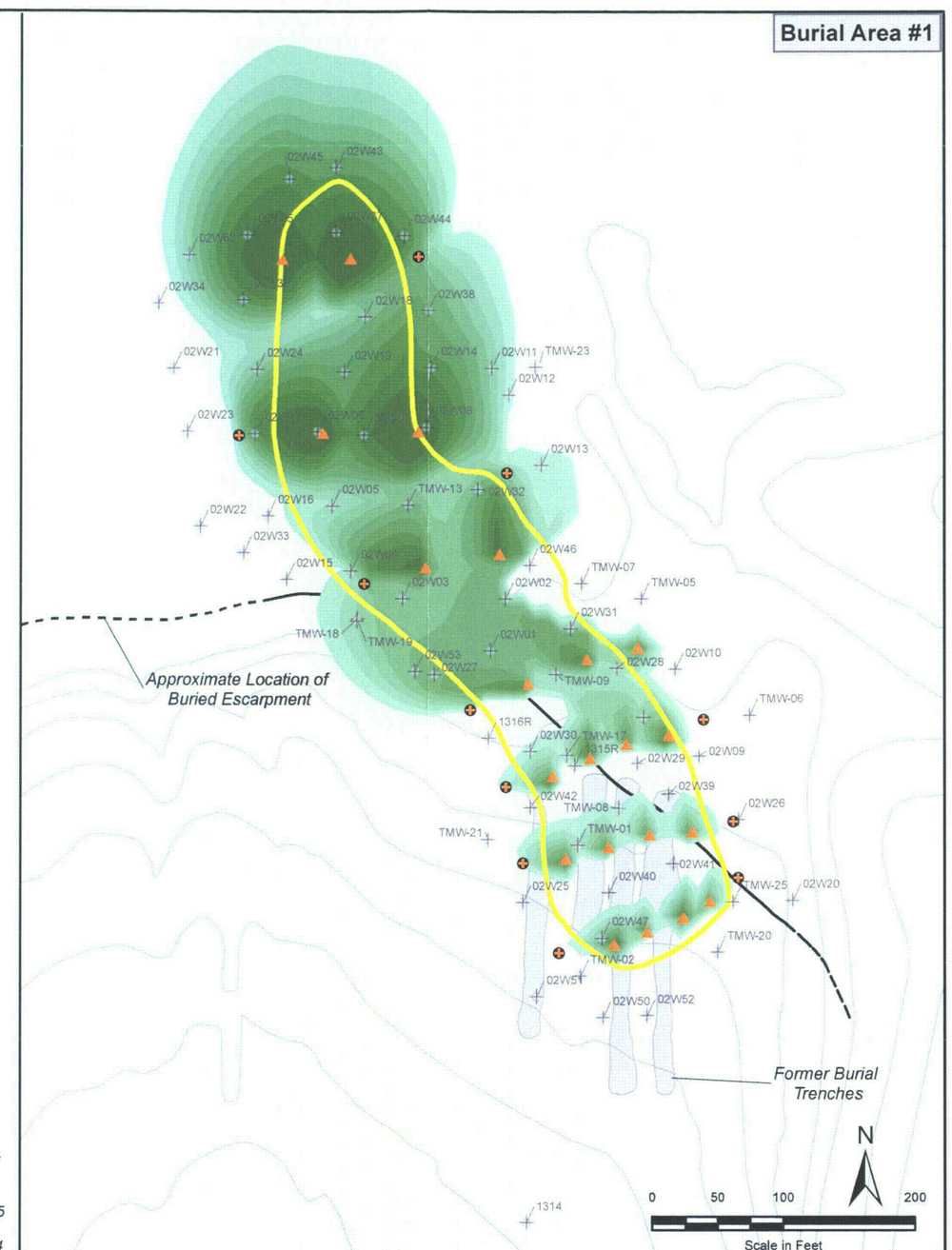
Relative TOC Concentration $\frac{C}{Co}$ %

Co - TOC concentration at injection location
C - TOC concentration projected at downgradient location

- 10
- 20
- 30
- 40
- 50
- 60
- 70
- 80
- 90
- 100

Notes:

- *Objective of TOC distribution modeling was to show complete lateral coverage between injection and extraction wells in each transect during the recirculation period; downgradient locations will then fill in as a result of solute transport under ambient flow conditions.*
- *Western Alluvial area of impact: July 2005*
- *Burial Area #1 area of impact: 3rd Q 2004*



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Drafter: MPD

Program Manager	Erhardt Werth
Project Manager	Sara Handy
Task Manager	Janis Lutrick
Technical Review	Jeff Gillow

ARCADIS
630 Plaza Drive, Suite 100
Highlands Ranch, Colorado 80129
Tel: 720-344-3500
Fax: 720-344-3535
www.arcadis-us.com

Legend

- Extraction Well
- Injection Well
- Monitoring Well
- Contours (5 foot interval)
- Approximate Location of Buried Escarpment
- Former Sanitary Lagoon
- Uranium Area of Impact (≥180 pCi/L)

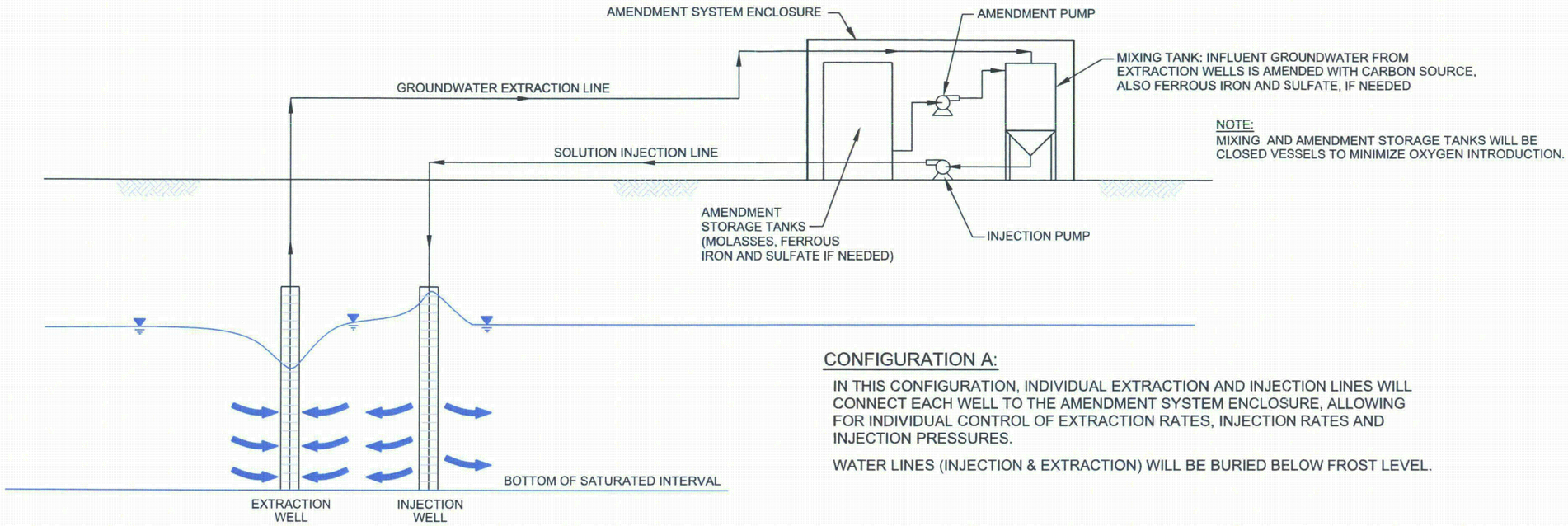
Estimated TOC Distribution and Proposed IRZ Well Layout

Cimarron Corporation
Crescent, Oklahoma

Date: 04/18/2008

FIGURE

5-3

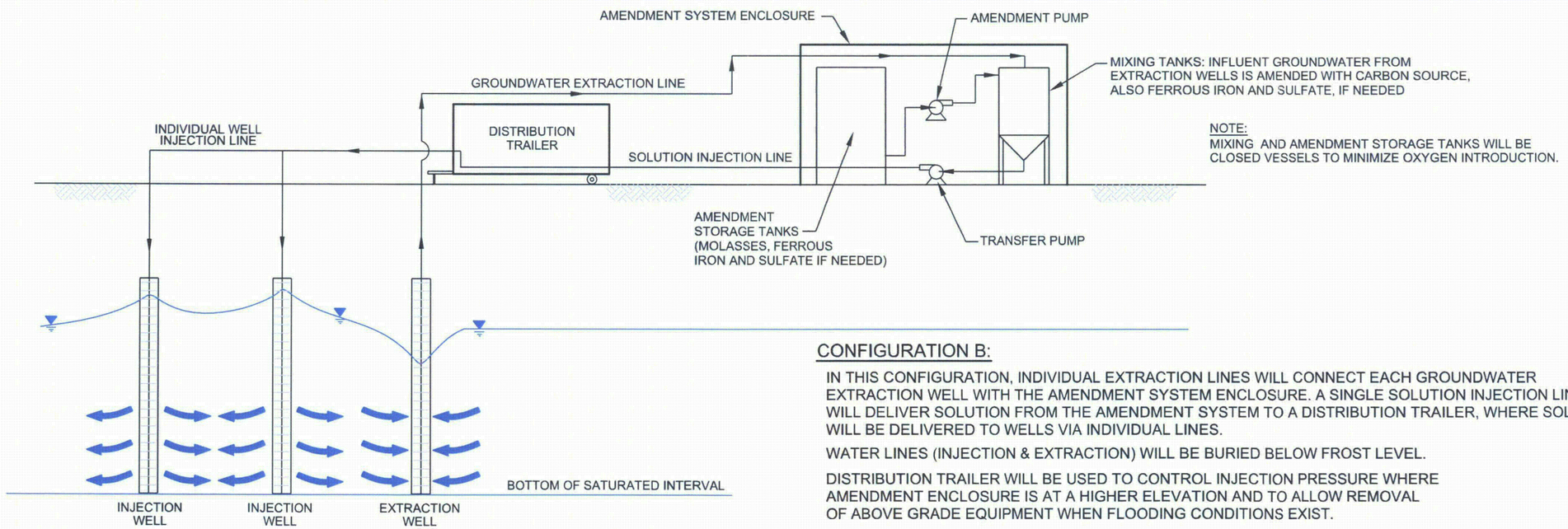


NOTE:
MIXING AND AMENDMENT STORAGE TANKS WILL BE CLOSED VESSELS TO MINIMIZE OXYGEN INTRODUCTION.

CONFIGURATION A:

IN THIS CONFIGURATION, INDIVIDUAL EXTRACTION AND INJECTION LINES WILL CONNECT EACH WELL TO THE AMENDMENT SYSTEM ENCLOSURE, ALLOWING FOR INDIVIDUAL CONTROL OF EXTRACTION RATES, INJECTION RATES AND INJECTION PRESSURES.

WATER LINES (INJECTION & EXTRACTION) WILL BE BURIED BELOW FROST LEVEL.



NOTE:
MIXING AND AMENDMENT STORAGE TANKS WILL BE CLOSED VESSELS TO MINIMIZE OXYGEN INTRODUCTION.

CONFIGURATION B:

IN THIS CONFIGURATION, INDIVIDUAL EXTRACTION LINES WILL CONNECT EACH GROUNDWATER EXTRACTION WELL WITH THE AMENDMENT SYSTEM ENCLOSURE. A SINGLE SOLUTION INJECTION LINE WILL DELIVER SOLUTION FROM THE AMENDMENT SYSTEM TO A DISTRIBUTION TRAILER, WHERE SOLUTION WILL BE DELIVERED TO WELLS VIA INDIVIDUAL LINES.

WATER LINES (INJECTION & EXTRACTION) WILL BE BURIED BELOW FROST LEVEL.

DISTRIBUTION TRAILER WILL BE USED TO CONTROL INJECTION PRESSURE WHERE AMENDMENT ENCLOSURE IS AT A HIGHER ELEVATION AND TO ALLOW REMOVAL OF ABOVE GRADE EQUIPMENT WHEN FLOODING CONDITIONS EXIST.

COCRS-0319.DWG

Program Manager	Erhardt Werth
Project Manager	Sara Handy
Task Manager	Janis Lutrick
Technical Review	Sara Handy

ARCADIS

ARCADIS U.S., Inc.
630 Plaza Drive, Suite 200
Highlands Ranch, Colorado 80129
Tel: 720.344.3500 Fax: 720.344.3535
www.arcadis-us.com

IRZ TREATMENT PROCESS FLOW DIAGRAM

Cimarron Corporation
Cresent, Oklahoma

Project Number	GPTRONOX.0004
Drawing Date	04/18/2008
Figure	5-4

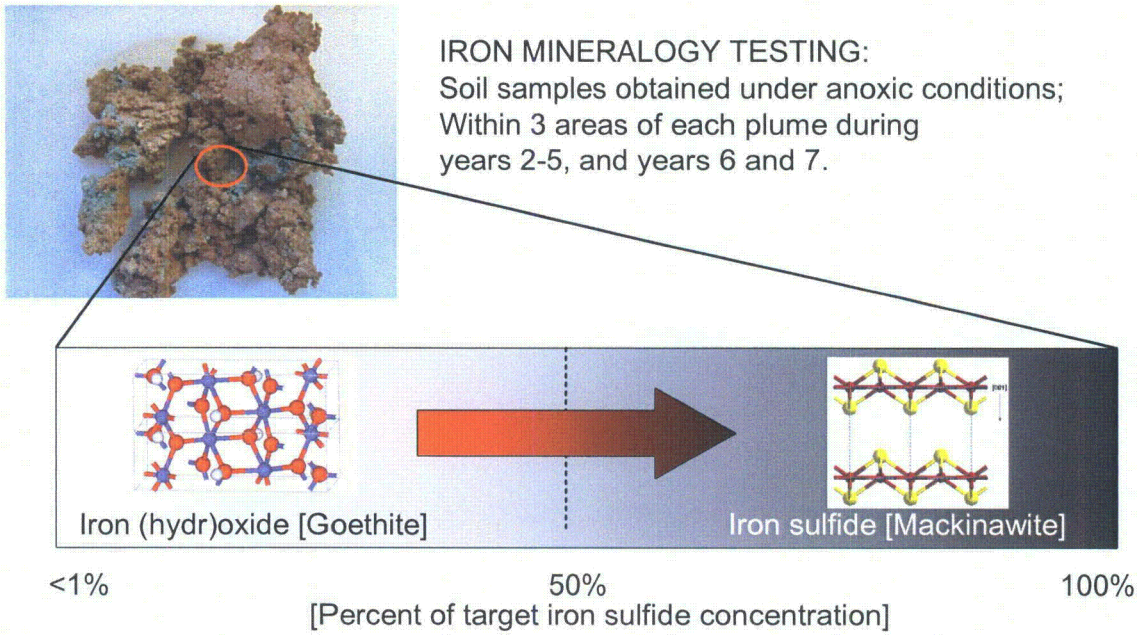
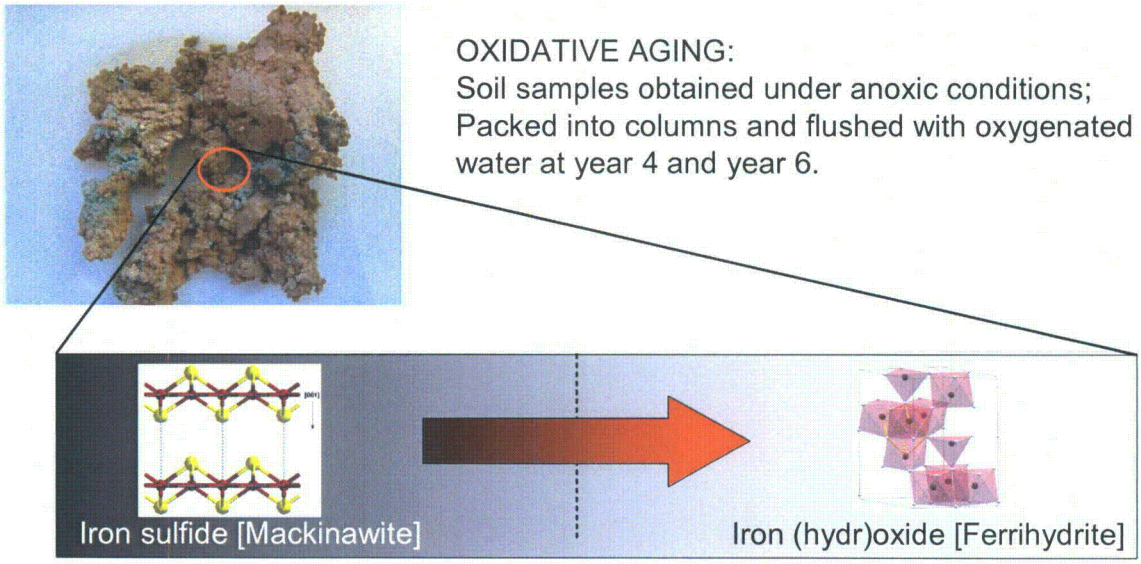


Figure 5-5. Iron Mineralogy Testing to Determine the Mass of Iron Sulfide Created in the Aquifer. Iron (hydr)oxide and iron sulfide will be determined by selective chemical extraction, acid-volatile sulfide-simultaneously extractable metals (AVS-SEM), and electron and x-ray microprobe methods (as detailed in Section 5.2.1.2).



[Conversion of iron sulfide after oxidizing conditions are established]

Figure 5-6. Oxidative Aging Testing to Demonstrate and Characterize the Conversion of Iron Sulfide in Aquifer Soil to Iron (Hydr)oxide Through Oxidation. This testing will proceed according to the methods described in Thornton et al., 2007; quantification of iron sulfide and iron (hydr)oxide will be performed by selective chemical extraction and AVS-SEM, as well as electron and x-ray microprobe methods.