**Cimarron Corporation** 

Groundwater Decommissioning Plan Cimarron Site, Crescent, OK

License No. SNM-928, Docket No. 70-925

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March 2009

# CIMARRON CORPORATION

P.O. BOX 315 • CRESCENT, OK 73028

# March 26, 2009

Mr. Kenneth Kalman Office of Nuclear Materials Safety & Safeguards U.S. Nuclear Regulatory Commission Washington, D.C. 20555

Re: Docket No. 70-925; License No. SNM-928 License Amendment Request for Groundwater Decommissioning

# Dear Mr. Kalman:

Cimarron Corporation (Cimarron) has completed the decommissioning of buildings and soils at the Cimarron site, and anticipates completing decommissioning by reducing the concentration of uranium in groundwater to comply with the current license criterion of 180 pCi/l total uranium. Cimarron proposes to remediate groundwater by converting dissolved uranium to the solid phase, and establishing geochemical conditions that prevent its remobilization at concentrations exceeding the license criterion.

In 1999, NRC approved a site decommissioning plan (combining the April 1995 Site Decommissioning Plan and the July 1998 Decommissioning Plan Groundwater Evaluation Report) requiring additional groundwater assessment, and committing to additional action should it be determined that natural attenuation would not reduce groundwater concentrations to acceptable levels. Subsequent evaluation indicated that it would take decades for groundwater to attain the stipulated release criteria by natural attenuation. Consequently, Cimarron now submits the enclosed Groundwater Decommissioning Plan as an amendment to the NRC approved Site Decommissioning Plan.

This submittal supersedes submittals dated June 2, 2008, September 4, 2008, and January 30, 2009. The June 2, 2008 submittal provided information showing that the Groundwater Decommissioning Plan satisfies the requirements of NUREG-1757 and Reg. Guide 4.15, as well as where technical issues previously identified are addressed in the plan. These issues have been addressed repeatedly in teleconferences, and it is not necessary to revisit these issues in this letter of submittal.

Section 7 of the enclosed Groundwater Decommissioning Plan provides a cost estimate for the work as proposed. The cost estimate, with the detailed backup included in Appendix H, complies with decommissioning cost estimation guidance contained in NUREG-1757, "Consolidated NMSS Decommissioning Guidance". This plan does not provide for financial assurance, which will be addressed separately.

Jeff Lux, Senior Project Manager 

Tronox Worldwide, LLC
One Leadership Square 

211 N. Robinson Ave.

Oklahoma City, OK 73126-8859

405.775.5194 Fax - 405.302.4637 In addition to the submittal of a Groundwater Decommissioning Plan, this license amendment request addresses three license conditions related to the decommissioning of the site; each of these conditions cites documents which are no longer relevant to this decommissioning project. Cimarron believes this is the appropriate time to revise these three license conditions so the license accurately reflects the requirements which will apply to this final step in the decommissioning of the site.

Condition 10 of the current license cites numerous documents relating to the decommissioning of the Cimarron site, primarily addressing decommissioning of soils. Only a few of those documents are still relevant to the completion of decommissioning. Cimarron provides herein Attachment 1 describing the content and status of the documents referenced in License Condition 10. Cimarron requests that License Condition 10 be revised to read:

For use in accordance with statements, representations, and conditions contained in letters dated September 14, 1990; July 25, 1995; January 28, 1997; February 10, 1998, and March 26, 2009, as amended in accordance with License Condition 27(e).

Condition 26 of the current license addresses the development of a radiation protection program applicable to the decommissioning of the site. The last document referenced in Condition 26 was dated December 11, 1998. Since that time, Cimarron has made significant changes to the Radiation Protection Plan (RPP), and NRC has repeatedly reviewed the RPP during annual and biannual inspections. In addition, NRC added Condition 27(e) authorizing Cimarron to change the "NRC-approved Radiation Protection Plan" provided those changes comply with specified requirements. Cimarron requests that NRC revise Condition 26 to read:

Cimarron shall conduct a radiation protection program in accordance with the Radiation Protection Plan dated March 2, 2009, as amended in accordance with License Condition 27(e).

Like Condition 10, Condition 27(a) of the current license addresses certain site-specific aspects of decommissioning, primarily addressing media other than soils. Cimarron provides herein Attachment 2 describing the content and status of the documents referenced in License Condition 27(a). Cimarron requests that License Condition 27(a) be revised to read:

The licensee is authorized to remediate the Cimarron facility in accordance with the "Decommissioning Plan for Cimarron Corporation's Former Nuclear Fuel Fabrication Facility at Crescent, Oklahoma" dated April 19, 1995, with supplemental correspondence dated July 30, 1998, March 4, 1999, January 29, 2009, August 10, 2005, August 11, 2005, and March 26, 2009, as amended in accordance with License Condition 27(e).

Jeff Lux, Senior Project Manager 

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405.775.5194 Fax - 405.302.4637 Cimarron and its contractors have been pursuing the implementation of an effective, cost-efficient approach to remediate the groundwater at the Cimarron site for more than five years through an in situ bioremediation program. We believe that such an approach is consistent with NRC's "Principles of Good Regulation". Cimarron also believes it is in both NRC's and Cimarron's best interest to revise certain license conditions at this time so the license accurately reflects the remaining requirements for decommissioning.

NRC approval of this license amendment request is respectfully requested. If you have any questions regarding this license amendment request, please call me at 405-775-5194 (OKC) or 405-642-5152 (mobile).

Sincerely,

Jeff Lux Project Manager

Cc: Jack Whitten, NRC Region IV David Cates, DEQ Mike Broderick, DEQ

Jeff Lux, Senior Project Manager 

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# Attachment 1

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# **Cimarron License SNM-928 – Condition 10 References**

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# Attachment 1 Cimarron License SNM-928 - Condition 10 References

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Document Date	Description	Recommendation
11/19/1985	Request to possess 6,000 kg Thorium	License Item 6(D) authorizes possession of 6,000 kg Thorium - delete from license.
3/3/1986	Request to increase authorized quantity of <5% U-235 from 1,200 g to 6,000 g	License Item 6(A) authorizes possession of 1,200 g of U-235 - delete from license.
9/4/1987	Request to bury Option 2 material on site	Disposal of Option 2 material is complete - delete from license.
11/2/1989	Final release survey for Pu plant	Subarea I, in which the Pu plant resides, has been released for unrestricted use - delete from license.
8/22/1990	Request to discontinue filing 70.59 reports	9/14/90 letter from NRC (next citation) approves request - delete from license.
9/14/1990	NRC approval to discontinue 70.59 reports	See 8/22/90 above - Retain in condition 10
6/24/1992	Request for information from NRC - Organization chart, detail on invoice, status of Pu plant license termination, status of on site disposal cell approval, status of adequacy of disposal area and lagoon cleanup (Subarea L).	Organization has changed multiple times since this submittal, financial detail was provided, Subarea with Pu plant was released for unrestricted use, disposal is complete and Subarea L was released for unrestricted use - delete from license.
2/25/1993	Response to 1/8/93 RAI on disposal cell - Subsidence, Wind and water erosion, Deed notice and location markers, Commitment to complete decommissioning	Disposal and associated work is complete, condition 23 still requires continuing inspections - delete from license.
4/19/1994	Onsite Disposal Plan - Responsibilities, Definitions, Precautions, Characterization, Transportation, Disposal, Determination of activity in cell, Run-on and run-off control, Cap placement, Record of disposal	Decommissioning and disposal of soils is complete - delete from license.
5/31/1994	Response to 4/19/94 RAIs - Final survey of material in cell, Average concentration determination, Reg Guide 1.86 criteria, Option 2 limit, Hot spot averaging, Final survey of excavations, Final survey of cap, Use of NUREG/CR-5849	Decommissioning and disposal of soils is complete, issues addressed. Subarea N demonstrated releasable, but not released due to groundwater in Subarea K - delete from license.
7/20/1994	Response to 7/18/94 RAI - How to sample and analyze for Kd of soil in disposal cell	Decommissioning and disposal of soils is complete - delete from license.
9/21/1994	Response to 8/12/94 RAIs - Hot spot averaging of soil in disposal cell, QC samples, NUREG/CR-5849 calculations, Soil counter calibration	Disposal is complete, soil counter calibration has changed since this time and has been inspected repeatedly - delete from license

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# Attachment 1 Cimarron License SNM-928 - Condition 10 References

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Document Date	Description	Recommendation
11/3/1994	Follow up on telephone conversation - Exposure to workers placing soil in disposal cell	Decommissioning and disposal of soils is complete - delete from license.
11/15/1994	License Amendment Request - Changes to Appendix A and Annex A	Appendix A and Annex A have changed substantially since this submittal. This submittal is no longer relevant - delete from license.
12/16/1994	License Amendment Request - Cimarron desires to designate Karen Morgan as RSO	License Condition 24 designates Karen Morgan as RSO - no longer needed - delete from license.
4/12/1995	Soil density test results for waste in and cap on disposal cell, Cell 2	Decommissioning and disposal of soils is complete - delete from license.
6/5/1995	Resume for Karen Morgan	License Condition 24 designates Karen Morgan as RSO - no longer needed - delete from license.
7/5/1995	Response to telephone inquiry on hot spot averaging in South Uranium Yard	The subject area (Subarea K) has been released for unrestricted use - delete from license.
7/25/1995	Submittal of Final Status Survey Plan for Phase II Areas	FSSR for Subarea F, a Phase II area, is in NRC review - retain in Condition 10.
8/9/1995	Submittal of Final Status Survey Report for Unaffected Areas (Phase I)	All Phase I areas have been released for unrestricted use -delete from license.
11/13/1995	Response to NRC comments on Final Status Survey Report for Phase I Areas	All Phase I areas have been released for unrestricted use -delete from license.
1/23/1996	License Amendment Request - Organization Change	Organization has changed since this submittal - it is no longer appropriate - delete from license
4/25/1996 (Listed twice)	Option 2 materal disposal procedure change from stockpiling to direct transportation to cell	Decommissioning and disposal of soils is complete - delete from license.
6/10/1996	RAIs regarding 4/25/96 proposal	Decommissioning and disposal of soils is complete - delete from license.
8/28/1996	Hot spot averaging in stockpiles and cell - not performed in five pond areas	Decommissioning and disposal of soils is complete - delete from license.
9/20/1996	Response to 8/16/96 RAIs - License Amendment Request - Changes to Appendix A and Annex A	Appendix A and Annex A have changed substantially since this submittal - delete from license.
11/20/1996	Proposed lung fluid solubility test	Decommissioning and disposal of soils is complete - delete from license.

# Attachment 1 Cimarron License SNM-928 - Condition 10 References

Document Date	Description	Recommendation
1/2/1997	Response to 12/2/96 RAIs on Annex A	Appendix A and Annex A have changed substantially since this submittal - delete from license.
1/28/1997	Response to 10/31/96 NRC Comments on Final Status Survey Plan for Phase II Areas	FSSR for Subarea F, a Phase II area, is in NRC review - retain in Condition 10.
5/6/1997	Response to 2/25/97 NRC Comments - Volumetric averaging and groundwater contamination at Ponds 1 and 2, Averaging of paved areas, concrete in drainageways.	Issues all addressed except groundwater. Groundwater is addressed in Condition 27(b) - delete from license.
5/16/1997	Response to 3/5/97 NRC Comments on RPP -	Appendix A and Annex A have changed substantially since this submittal - delete from license.
12/5/1997	Response to 10/3/97 NRC Comments on Phase III Final Status Survey Plan	FSSRs for all Phase III areas have been approved by NRC. This is no longer needed - delete from license.
2/10/1998	Agenda for 2/17/98 Meeting w/ NRC - includes information on dose calculations	Provides basis for limits now stipulated in the license. Includes information on dose calculations - retain in Condition 10.
6/26/1998	Response to 2/9/98 NRC Comments on Phase III Final Status Survey Plan	FSSRs for all Phase III areas have been approved by NRC. This is no longer needed - delete from license.
7/2/1998	Responses to 7/1/98 Conference Call - Resolving questions about inspection report #70-925/97-02 - soil counter "traceability" and typographical error	Issues raised during conference call have been addressed - delete from license.
2/15/2000	Submittal of Final Status Survey Report for Phase III, Subarea K	Subarea K has been released from license - delete from license.
2/20/2001	Response to 1/29/01 NRC Comments on FSSR for Phase III, Subarea K - Hot spot averaging, revise Table 4.1	Subarea K has been released from license - delete from license.
4/17/2002	Decommissioning Schedule	Schedule no longer relevant - delete from license.
5/10/2002	Revised Decommissioning Schedule	Schedule no longer relevant - delete from license.

Attachment 2

Cimarron License SNM-928 – Condition 27(a) References

# Attachment 2 Cimarron License SNM-928 - Condition 27(a) References

Document Date	Description	Recommendation
4/19/1995	Decommissioning Plan for Cimarron Corporation's Former Nuclear Fuel Fabrication Facility at Crescent, Oklahoma	Foundational document for decommissioning retain in Condition 27(a).
9/10/1996	Response to 7/11/96 NRC Comments on Decommissioning Plan	Work complete for all media except groundwater, which is addressed more fully in later documents - delete from license.
5/6/1997	Response to 2/25/97 NRC Comments on Cimarron's 9/10/97 Response	Work complete for all media except groundwater, which is addressed more fully in later documents - delete from license.
8/26/1997	Response to 7/1/97 NRC Comments on Decommissioning Plan - Waste Ponds #1 and #2, Concrete rubble	Waste Ponds released. Rubble addressed as per March 1, 1999 NRC letter - delete from license.
3/10/1998	Final Status Survey Report for Concrete Rubble in Sub-Area "F"	Rubble addressed as per March 1, 1999 NRC letter - delete from license.
3/12/1998	Final Status Survey Report for Phase III Sub Area "O" Uranium Waste Ponds #1 and #2 (Subsurface)	Waste Ponds released - delete from license.
6/15/1998	Response to 5/20/98 NRC Comments on Final Status Survey Report for Concrete Rubble in Sub-Area "F"	Rubble addressed as per March 1, 1999 NRC letter - delete from license.
7/30/1998	Decommissioning Plan Ground Water Evaluation Report	Amends 4/19/95 decommissioning to address groundwater issues identified since 1995 - add to Condition 27(a).
10/6/1998	Response to 9/10/98 NRC Comments Regarding Residential Inhalation Dose from Concrete Rubble in Sub-Area "F"	Rubble addressed as per March 1, 1999 NRC letter - delete from license.
3/4/1999	Response to 1/19/99 NRC Comments on "Decommissioning Plan Groundwater Evaluation Report"	Retain in Condition 27(a).
1/29/2003	Burial Area #1 Groundwater Assessment Report	Reports hydrogeology and delineates groundwater impact in Burial Area #1 add to Condition 27(a).
8/10/2005	Site-Wide Groundwater Assessment Review	Provides description of site-wide source identification and investigation, and delineates areas requiring monitoring and/or remediation - add to Condition 27(a).
8/11/2005	Refined Conceptual Site Model	Provides site-wide and area-specific hydrogeological and geochemical information for areas requiring groundwater remediation - add to Condition 27(a).



**Cimarron Corporation** 

# Groundwater Decommissioning Plan

License SNM-928; Docket Number 70-925

March 2009

## 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

Date: March 2009

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# Acronyms and Abbreviations

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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<sup>2</sup>/sec centimeters squared per second cm<sup>3</sup> 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<sub>3(s)</sub> siderite FeS iron sulfide FeS<sub>(s)</sub> mackinawite Fe<sub>3</sub>O<sub>4</sub> magnetite  $Fe_3S_4$ greigite ft/day feet per day ft/ft feet per foot grams g g/cm<sup>3</sup> grams per cubic centimeter g/kg grams per kilogram 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 Μ molar m/day meters per day mg/kg milligrams per kilogram mg/L milligrams per liter

# Acronyms and Abbreviations

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 <sub>2</sub>	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
тос	total organic carbon
U	uranium
UCL	upper confidence limit
UO <sub>2</sub>	uraninite
UO <sub>3</sub>	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 Site 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 uranium in 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 the 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 ( $\mu$ g/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.

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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, as demonstrated by eight quarters of groundwater monitoring results with uranium below the Criteria and no increasing trends based on Environmental Protection Agency (EPA) statistical evaluation methods (Mann-Kendall test/Sen's estimate of slope).
- 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, as demonstrated by a round of soil sampling to confirm the presence of iron to uranium ratio of at least 80:1 (as specified by the results of the geochemical model) completed at the end of the Remedy Completion Demonstration Testing phase.
- Geochemical modeling results will be updated with site-specific data to demonstrate the 1,000-year stability of the remedy.
- Column testing will be conducted with results that show that re-oxidation of the aquifer will not result in remobilization of the uranium above the Criteria.

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 the <u>Site Decommissioning Plan</u> (SDP) (Chase Environmental Group, April 1995). The SDP was supplemented by the <u>Site Decommissioning Plan –</u> <u>Groundwater Evaluation Report</u> (GER) (Chase Environmental Group, 1998). NRC approved the SDP and GER on August 23, 1999.

The <u>Radiological Characterization Report for Cimarron Corporation's Former Nuclear</u> <u>Fuel Fabrication Facility</u> (Chase Environmental Group, 1994) divided the Cimarron Site into Subareas A through O (Figure 2-1). Subareas A through E were surveyed as unimpacted 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.

<u>Site-Wide Groundwater Assessment Review</u> (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 <u>Conceptual Site Model, Revision 1</u> (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); and
- 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 <u>Guidelines for</u> <u>Decontamination of Facilities and Equipment Prior to Release for Unrestricted Use or</u> <u>Termination of Licenses for Byproduct, Source, or Special Nuclear Material</u> for the release of materials. Condition 27(c) also stipulates the use of the October 1981 <u>Disposal or Onsite Storage of Thorium or Uranium Wastes from Past Operations</u> 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 Cimarron Corporation Vice President, 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;

- Re-injection 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)

Appendix G: Column Testing Procedure

Appendix H: Bioremediation Cost Estimate Detail (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 <u>Conceptual Site</u> <u>Model, Revision 1</u> (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. The 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 <u>Conceptual Site</u> <u>Model, Revision 1</u> (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), from the WAA transition zone (sample T-64), and from 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).

Sample ID	SiO₂ %	Al <sub>2</sub> O <sub>3</sub> %	Fe <sub>2</sub> O <sub>3</sub> %	MgO %	CaO %	Na <sub>2</sub> O %	K₂O %	TiO₂ %	P <sub>2</sub> O <sub>5</sub> %	MnO %	Cr <sub>2</sub> O <sub>3</sub> %	V <sub>2</sub> O <sub>5</sub> %	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

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

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

	Crystalline Mineral Assemblage (relative proportions based on peak height)							
Sample	Major	Moderate	Minor	Тгасе				
T-64	quartz	potassium-feldspar	plagioclase-feldspar	*mica, *calcite, *dolomite, *pyroxene, *amphibole				
Т-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				

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

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

## 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 waterbearing 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 <u>Conceptual Site</u> <u>Model</u>, <u>Revision 1</u> (ENSR, 2006). The area-specific hydrogeologic considerations 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-high 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 3.1.2).

## 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 above mean sea level (msl) 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 insitu 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 (GWB) (Professional Version 6.04; 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 involves 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.

The following description provides the conceptual model used to assemble the geochemical model (there are a variety of mechanisms that will prevent uraninite from oxidizing and remobilizing, however this reaction was modeled to evaluate the ability of iron (hydro) oxides to sorb uranium and control the concentration of dissolved uranium even under fully oxidized conditions).

Upon cessation of treatment, oxidizing groundwater will flow into the treated area causing oxidative dissolution of the iron sulfides and the uraninite. Consumption of oxidants influent to the treated area will occur through reaction with the reduced iron minerals. Iron sulfides will be oxidized to amorphous iron oxides, and the uraninite will gradually dissolve to form soluble uranyl carbonates. 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: 1) a batchmodel that simulates the chemical reactions occurring during reduction and reoxidation of the aquifer; and 2) 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.

during August/September 2004; Conservative Values Provided for Uraniu and Oxygen		
Species	Concentration [mg/L]	Comment
- 2+		

Composition of Average Groundwater Samples Collected from BA#1

	[mg/L]	
Ca <sup>2+</sup>	139.15	Average (ENSR, 2006, Table 4-1)
Cľ	44.26	Average (ENSR, 2006, Table 4-1)
Fe	1.00x10 <sup>-07</sup>	Not detected, a concentration below analytical detection limit was used
рН	7.11	Average (ENSR, 2006, Table 4-1)
Alkalinity	404.65	Average (ENSR, 2006, Table 4-1)
Mg <sup>2+</sup>	54.50	Average (ENSR, 2006, Table 4-1)
NO₃ <sup>-</sup>	0.44	Average (ENSR, 2006, Table 4-1)
Na⁺	56.47	Average (ENSR, 2006, Table 4-1)
O <sub>2</sub> (aq)	2.92	95% UCL (ENSR, 2006, Table 4-1)
SO4 <sup>2-</sup>	186.20	Average (ENSR, 2006, Table 4-1)
SiO <sub>2</sub> (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<sub>2</sub>).

Table 3-4

Uranium Isotope	Specific Activity (pCi/g)	Mass Abundance (%)	pCi isotope/µg
<sup>238</sup> U	3.33 x 10 <sup>5</sup>	97.38	0.324
<sup>234</sup> U	6.19 x 10 <sup>9</sup>	0.0197	1.22
<sup>235</sup> U	2.14 x 10 <sup>6</sup>	2.6	0.0556
·		Total:	1.6

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

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<sub>3</sub>) (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.

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.
UO₃(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.

	Table 3-6	Mass of Minerals Used in the Geochemical Model
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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 <u>Conceptual Site Model, Revision 1</u> (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 seven cells, 39 meters (129 feet) 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 ( $\alpha_L$ ), 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.

$$D = \alpha_{I} \cdot v + D^{*} \tag{5-1}$$

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 <sup>-8</sup> cm <sup>2</sup> /s	Model input
Longitudinal dispersivity	1x10 <sup>-5</sup> m	Model input
Linear groundwater velocity	0.18 m/d (0.6 ft/day)	ENSR, 2006

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

The average linear groundwater velocity in Sandstone B was calculated to 0.6 feet per day (ft/day) in the <u>Conceptual Site Model</u>, <u>Revision 1</u> (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  $(CaUO_2CO_3 \text{ and } Ca_2UO_2[CO_3]_3)$  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 into the 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).

$$> (s)FeOH + H^{+} \iff (s)FeOH_{2}^{+} \qquad \log K = 6.51$$
$$> (s)FeOH \iff (s)FeO^{-} + H^{+} \qquad \log K = -9.13$$

Carbonate and bicarbonate surface complexation are described by:

$$>(s)FeOH + H^+ + HCO_3^- \iff (s)FeCO_3H^0 + H_2O$$
 logK = 3.47

 $>(s)FeOH + HCO_3^- \leftrightarrow >(s)FeCO_3^- + H_2O$  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:

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

$$> (w)Fe(OH)_2 + UO_2^{2+} \iff (w)Fe(O)_2UO_2 + 2H^+$$
 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.

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

$$>(w)FeOH + UO_2^{2+} \leftrightarrow > (w)FeOUO_2^+ + H^+$$
 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):

$$> (s)Fe(OH)_{2} + UO_{2}^{2+} + CO_{3}^{2-} \iff (s)Fe(O)_{2}UO_{2}CO_{3}^{2-} + 2H^{+} \log K = 3.67$$
$$> (w)Fe(OH)_{2} + UO_{2}^{2+} + CO_{3}^{2-} \iff (w)Fe(O)_{2}UO_{2}CO_{3}^{2-} + 2H^{+} \log K = -0.42$$

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

$$> (s)FeOH + UO_2^{2^+} + HCO_3^- \iff (s)FeOUO_2CO_3^- + 2H^+ \log K = 0.33$$
$$> (w)FeOH + UO_2^{2^+} + HCO_3^- \iff (w)FeOUO_2CO_3^- + 2H^+ \log K = -3.76$$

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<sub>2</sub>SO<sub>4</sub>) and 8,100 mg/L ferrous sulfate (FeSO<sub>4</sub>) were added during the remediation injections while reducing conditions were 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 the 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<sub>3</sub>[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.

Mineral	Composition	Mass [g]	Density [g/cm <sup>3</sup> ]	Volume [cm <sup>3</sup> ]	Fraction [% volume]
Quartz .	SiO <sub>2</sub>	7,885	2.648	2978	74.44
Calcite	CaCO <sub>3</sub>	53.7	2.71	19.8	0.4952
Mackinawite	FeS	2.001	4.17	0.480	0.0120
Siderite	FeCO <sub>3</sub>	1.006	4.047	0.249	0.00621
Uraninite	UO <sub>2</sub>	0.048	10.97	0.00439	1.079x10 <sup>-4</sup>

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

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Species	Concentration [mg/L]	Comment
SiO <sub>2</sub> (aq)	NA	In equilibrium with quartz
HCO3 <sup>-</sup>	NA	In equilibrium with calcite.
U	NA	Highest measured concentration (ENSR, 2006, Table 4-1)
Fe	NA	In equilibrium with siderite.
SO4 <sup>2-</sup>	NA	In equilibrium with mackinawite.
рН	7.11	Average (ENSR, 2006, Table 4-1)
O <sub>2</sub> (aq)	$\log f(O_2) = -74$	Reducing conditions during IRZ.
Ca <sup>2+</sup>	2,586.86	Calcite dissolved during reduction.
Cľ	44.26	Average (ENSR, 2006, Table 4-1)
Mg <sup>2+</sup>	54.71	Average (ENSR, 2006, Table 4-1)
NO <sub>3</sub> <sup>-</sup>	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 one 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% 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 ( $0.00001 \mu g/L$ ). 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  $\mu$ g/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 ten 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 six 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 six 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 (2,422 pCi/L at well 1351 in the WUA, and 1,058 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.

 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<sub>2[s]</sub>). 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 coprecipitate. 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<sub>3</sub>O<sub>4</sub>) 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 laboratory column 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 in 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<sub>2</sub>S) and becomes volatile, while at circumneutral to high pH, it takes the form of the bisulfide ion (HS<sup>-</sup>). 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<sub>3</sub>S<sub>4</sub>) 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 reoxidation.

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<sup>-8</sup> percent 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 two 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<sub>2</sub>).

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

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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 reoxidation 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<sup>3</sup>, 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 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%). 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 the 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:

- Uranium in groundwater in all areas undergoing treatment is below the Criteria; and
- 2) Iron sulfide mass is accumulated to the target for maintaining treatment longevity (mass ratio of 1 part uranium to at least 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 nonuniform 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 reinjection 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 5.2.1.2 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. Results of monitoring conducted during the initial treatment area implementation, as well as laboratory column testing will be evaluated to ensure that the four success criteria described below are met prior to proceeding with full-scale treatment. 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<sub>2</sub>). 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 1,000-year compliance period (Step 6).

Remedy completion demonstration testing includes soil and groundwater sampling and analysis as described in Section 5.2.3 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 implementation 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 the 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. A total of 12 soil borings will be installed across the three areas of impact, with up to two soil samples collected from each boring based on material types encountered in the borings, for a total of up to 24 soil samples. 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 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;
- 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; and
- 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 extraction well will provide the make-up water that will be amended for re-injection in the injection wells. 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 <u>Conceptual Site Model, Revision 1</u> (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 seven-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 seven days of continuous TOC injection were completed; contour maps of resulting TOC concentration are presented in Figure 5-3. These contours show that seven 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 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, nondegradable) dye tracer into each injection well at a continuous flow rate. The tracer will move through the water-bearing zone in a manner similar to the amendments, but is not susceptible to degradation as are the TOC and ferrous sulfate. 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 duration of the tracer injection will be determined based on the tracer arrival and achievement of steady state concentrations for the tracer at the extraction well. Steady state concentrations will be determined through observation of at least two to three tracer concentrations of very similar value.

At this point, tracer injection will be discontinued but monitoring of the tracer will continue in the cross-gradient and downgradient monitoring wells through declining concentrations to evaluate the stability of the tracer. 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 re-injection 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, specific conductivity, and ferrous iron (Fe<sup>2+</sup>); and
- Groundwater chemistry parameters (laboratory analysis): TOC, total dissolved solids (TDS), sulfate, sulfide, nitrate, nitrite, total iron (unfiltered and acid preserved) and dissolved iron (0.45 micron-filtered and acid preserved), alkalinity, and uranium (both mass and activity).

Collectively, the field parameters and groundwater parameters analyzed in the laboratory are referred to as groundwater performance indicators.

The data collection frequency for water level and field parameters will be daily until field conditions stabilize or until conditions dictate a less frequent interval. Uranium activity will also be analyzed with a short turn-around time. Evaluation of these parameters will provide the information needed to determine when to collect groundwater samples for laboratory analysis. Groundwater samples for laboratory analysis will be collected approximately monthly during the initial treatment testing phase. Analytical methods and DQOs for the initial treatment area operation are included in Appendix C.

The groundwater monitoring results from the initial testing phase will be reviewed and statistically evaluated to demonstrate that uranium concentrations are decreasing while reducing conditions are being established. The uranium data will undergo statistical analysis using the software ProUCL Version 4.0 (EPA's statistical analysis software). This software can calculate the significance of the decline in concentration of uranium in groundwater in monitoring wells across the initial treatment areas as compared to the baseline (pre-treatment) data set.

In addition to groundwater sampling, soil sampling will be conducted at the end of the initial treatment testing phase. Groundwater data (groundwater performance indicators) obtained during the operation of the initial treatment system are expected to provide assurance that the required geochemical conditions have been established in soil. Consequently, it was assumed that soil sampling will only need to be performed one time – at the conclusion of operation of the initial treatment system. Of course, if the success criteria as described below are not demonstrated in a single soil sampling event, initial treatment will continue and the sampling will be repeated.

Soil samples will be collected from one boring near one injection well and one boring near one monitoring well in each of the six initial treatment areas, for a total of 12 borings. Sampling techniques will be used to minimize the disturbance to the area adjacent to the wells; the volume of soil that is retrieved will be minimized to prevent large void volumes. Sampling techniques will also be used to prevent air oxidation of the soil samples (samples will be collected in core-sleeves and handled at the surface in a nitrogen-flushed bag and immediately frozen on dry ice, as per EPA procedures (Wilkin, 2006)). If a boring yields two different types of material within the saturated zone (e.g., clay from 10 to 12 feet and sand from 14 to 16 feet), more than one sample may be collected from a boring. This determination will be made based on the boring log generated during installation of the wells, or the logs of existing nearby wells. A

maximum of two samples will be collected from each boring, for a maximum of 24 total soil samples.

Soil samples will be analyzed for:

- Uranium (total activity, isotopic, mass concentration);
- Bulk iron mineralogy determined by selective chemical extraction and x-ray diffraction;
- Iron sulfide content; and
- Changes in iron mineralogy determined by microprobe methods that include SEM, micro-x-ray fluorescence analysis (μ-XRF), and micro-x-ray absorption near edge structure (μ-XANES).

These parameters are shown in Table 5-1 (page 3 of Figure 5-1) and are referred to as the soil performance indicators.

Analytical results will be evaluated to determine that iron sulfide is being developed in all material types at all locations. In addition, analytical results need to demonstrate that iron sulfide concentrations are generated at multiples of uranium concentrations, such that a reduction in uranium concentration corresponds to an increase in iron sulfide concentration. The iron sulfide and uranium data will undergo statistical analysis using the software ProUCL version 4.0 (EPA's statistical analysis software). This software can compare two data sets to determine if the difference is significant and it also has the ability to handle "non-detect" data as well as non-parametric data sets.

## Laboratory Column Testing

Concurrently with the initial treatment testing phase, ARCADIS will run column tests utilizing site soils and site groundwater, Cimarron River water, and rainwater to demonstrate that, even if infiltrating water generates an oxidizing environment, the concentration of uranium in the column test effluent will not exceed the release Criteria. The column testing procedure is summarized below and described in detail in Appendix G.

ARCADIS will collect soil from borings located in four of the six initial treatment areas. The column tests can only be practically performed on samples of unconsolidated

soils, so sandstone from Burial Area #1 and the Western Upland area will not be collected for column testing. This is reasonable because the fine-grained soil in the two transition zones and the cleaner sands of the deeper alluvium represent "ends of the spectrum", with the silty sandstone being in the middle of the spectrum. It is reasonable to presume that if the fine-grained soil and clean sands yield acceptable results in column tests, the silty sandstone would yield acceptable results.

Groundwater samples corresponding to the groundwater in each of these four soil samples will be collected from impacted and unimpacted wells yielding water quality similar to that of the corresponding soil sample (based on information presented in <u>Conceptual Site Model, Rev. 01</u>). For instance, referring to Figure 4-7 of the CSM, Rev. 01, if a soil sample were collected for a column test near TMW-13, groundwater for this column test would be collected from this well and an unimpacted well yielding high sulfate (similar to Sandstone C) water. ARCADIS will ensure that site groundwater used in tests reflects the chemistry of groundwater associated with the soil sample used in the column test.

The soil samples collected from the initial treatment areas will likely have some amount of increased iron sulfide from the initial treatment activities, but will not have the required 80:1 ratio of iron to uranium in this reduced treatment time frame. As a result, reducing conditions will be created in the laboratory in each batch of soil samples and corresponding groundwater from an impacted well until the required ratio of iron sulfide to uranium is achieved. Once this ratio is achieved, the soil will be packed into columns for the column tests. Unimpacted site groundwater will be run through the column until oxidizing conditions are created within the column. In addition, the column tests will be conducted using Cimarron River water with water quality representative of river water at flood stage and rainwater to simulate oxidizing conditions produced by infiltration of either river water or rainwater. River water will be used because it potentially has a higher concentration of nitrate than groundwater; this will be verified through analysis. Both during leaching and after oxidizing conditions are established, samples of the effluent from each column will be analyzed for uranium to demonstrate that the iron sulfide has retarded the remobilization of uranium at concentrations exceeding the release criteria.

Soil mineralogical analyses will be performed of the soil samples collected for column testing prior to starting the column test, and at the end of the establishment of oxidizing conditions in the column. These analyses will also be performed in the field during operation of the initial treatment system as described above. The results of the mineralogical analyses of the soil used in the column tests will serve as a data set for comparison with the field results. In this manner, fingerprints in the soil mineralogy will

be established and then compared to the mineralogical analyses of soil samples collected from the field.

The goal of the laboratory column 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; and
- 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.

#### 5.2.1.3 Success Criteria for Initial Treatment Area Phase

In discussions with the NRC, Cimarron has developed four success criteria that must be met prior to advancing from the initial treatment area implementation to full-scale implementation. These four success criteria are discussed in detail below.

#### Success Criterion #1 - Reactant Must be Distributed Throughout the Impacted Area

ARCADIS must demonstrate that amendments can be distributed throughout each of the impacted areas, including the alluvial areas, the finer-grained materials present in the transition zones of both Burial Area #1 and the Western Alluvial Area, and the sandstone of both Burial Area #1 and the Western Upland Area. In monitoring wells within the initial treatment areas, both the attainment of a steady-state tracer concentration and subsequent decline in tracer concentration after shutting down the injection system must be determined prior to moving on to full-scale remediation.
Success Criterion #2 – Uranium Concentrations Must be Reduced Through Achievement of Reducing Conditions

ARCADIS must be able to demonstrate that uranium concentrations are statistically significantly decreasing while reducing conditions are being established in the initial treatment areas. Groundwater sampling results will be assessed using EPA's ProUCL software to demonstrate that a statistically significant reduction in uranium concentration is observed in all six initial treatment areas as reducing conditions are achieved. The presence of reducing conditions will be demonstrated by DO, iron, nitrate, and sulfate monitoring results.

# Success Criterion #3 – A "Bank" of Iron Sulfide Must be Created in the Soil to Prevent Remobilization

To demonstrate longevity of the remediation effort, ARCADIS must establish a bank of iron sulfide sufficient to yield an iron sulfide to uranium ratio of no less than 80:1. However, it is neither practical nor necessary to develop this ratio during the initial treatment phase. In fact, it is not necessary that this ratio be developed at each and every spot; this ratio must be averaged volumetrically in each material type throughout the areas of impact. ARCADIS must demonstrate that a bank of iron sulfide is being built up in both low- and high-permeability material in each of the initial treatment system areas.

Iron sulfide concentrations must exhibit a statistically significant increase in samples collected from borings within the initial treatment areas relative to corresponding samples collected from borings at a similar location during baseline analysis prior to initiating treatment. Finally, it must be demonstrated that increases in iron sulfide concentrations correspond to reductions in uranium concentrations for associated wells as determined for Success Criterion #2.

# Success Criterion #4 – Uranium Must not Remobilize if Water Bearing Zone Becomes Oxic

ARCADIS will conduct laboratory column testing using site soils and groundwater, Cimarron River water, and rainwater to demonstrate that, even under oxidizing conditions, leaching of uranium above the Criteria will not occur. This will be demonstrated in the column test by obtaining uranium activity levels in leachate from all columns of less than 180 pCi/L in all samples collected after reducing conditions are established through the attainment of oxidizing conditions in the column.

#### 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 microand macronutrients in molasses and other carbohydrates promotes microbial cell reproduction and growth, thus increasing the microbial biomass in the aquifer; and
- 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 re-injected into the aquifer. While the re-injection 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 consisting 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 5.2.1.2, 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 a 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 sandstone, with these distances 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 of 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 performance indicators:

- <u>Groundwater performance indicators</u>: field parameters (pH, temperature, dissolved oxygen, specific conductivity), TOC, TDS, alkalinity, sulfate, sulfide, nitrate, nitrite, total iron (unfiltered and acid preserved), dissolved iron (0.45 micron-filtered and acid preserved), ferrous iron (determined colorimetrically in the field), and uranium (both mass and activity); and
- <u>Soil performance indicators</u>: Bulk iron mineralogy, including selective chemical extraction and XRD, quantification of iron sulfide content, and 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). The sampling program will be flexible when seeking to accommodate extremes in seasonal fluctuations in the water table or after extreme rain events. Event-driven groundwater performance indicator sampling will be performed when seasonal precipitation or river stage is outside of the norm (as described in the Hydrology Addendum included in Appendix B). 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 indicators 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 levels in groundwater in all areas undergoing treatment (32 wells) are below the Criteria; and
- Iron sulfide mass has accumulated to the target mass ratio of 1 part uranium to at least 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. The initial target ratio of 80:1 iron to uranium will be evaluated throughout the remediation phase, and although likely this will not change, the remediation system is flexible and adaptive so that it can accommodate a revised target for the mineralogy if the updated model dictates that revision is necessary.

### 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 levels in the monitored wells must be below the Criteria for eight quarters. 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 (USEPA, 2000). Trend analysis will be conducted to assure there are no increasing trends in the data as described below. As noted below, up to 12 quarters of monitoring will be conducted, if needed, to provide statistically defensible trend information. It should also be noted that a robust data set of two to three years of monitoring data in 32 set wells that confirm all wells have uranium levels below the Criteria will be obtained prior

to initiating the eight quarters of remedy completion demonstration groundwater monitoring.

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 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 (USEPA, 1992). 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 the increase 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 16 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, 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, remediation has been demonstrated. If the trend is still positive and significant, 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 ( $\alpha$ ) is the probability that the test will falsely identify a trend. Since these proposed tests have  $\alpha = 0.05$  means 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,  $\alpha$ , and the number of tests, n, using the following relation:

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

Given that n = 16 and  $\alpha = 0.05$ , 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 (up to four quarters of additional monitoring) 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.

An additional round of soil sampling for mineralogical analyses will be conducted at the end of the remedy completion demonstration testing phase when the eight quarters of groundwater monitoring has been completed. 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). The results of these analyses will be evaluated to confirm that the required ratio of 80 parts iron to 1 part uranium is still present at the end of the Remedy Completion Demonstration Testing phase.

#### 5.3 Compliance with Requirements for License Termination

The following criteria must be satisfied to achieve license termination:

- A. Eight quarters of groundwater monitoring results with uranium below the Criteria and no increasing trends based on EPA statistical evaluation methods (Mann-Kendall test/Sen's estimate of slope);
- B. A round of soil sampling to confirm the presence of iron to uranium ratio of at least 80:1 completed at the end of the remedy completion demonstration testing phase;
- C. Geochemical modeling results updated with site-specific data to demonstrate the 1,000-year stability of the remedy; and
- D. Column testing results that show that re-oxidation of the aquifer will not result in remobilization of the uranium above the Criteria (from column testing completed during the initial treatment area phase).

Treatment completion will be 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 32 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

- 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.
- Iron mineralogy testing demonstrating that the required soil mineralogy continues to be present following completion of the eight quarters of remedy completion demonstration monitoring of groundwater.

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 baseline, 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. The results of the laboratory column testing performed during the initial treatment testing phase which demonstrate that re-oxidation of the treated soils will not result in leaching of uranium above the Criteria will also be incorporated into the completion report. Analytical laboratory reports documenting the analytical results can be provided upon request.

A final dose assessment will also be included with the License Termination Request. Cimarron will demonstrate for scenarios such as a resident farmer that the remaining dose is below 25 mRem on average with no exceedence of the 100 mRem level. The dose assessment will be based upon uranium concentrations in groundwater as observed during the groundwater monitoring, specifically the eight quarters of remedy completion demonstration monitoring. In addition, the concentration of uranium in groundwater as predicted by the geochemical modeling, over the 1,000-year period, will be used as the basis for the dose assessment.

#### 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. Laboratory column testing will also be conducted during the initial treatment area phase. 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 (discussion check-point as indicated on Figure 5-1). Cimarron will continue to provide updates to the NRC on a minimum annual basis throughout the active remediation phase to present data collected, review results to date, and provide an assessment of the bioremediation treatment success and planned path forward.

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 5.2.2.4, 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; this information will be shared with the NRC and ODEQ at the end of the first full year of full-scale remediation (discussion check-point as indicated on Figure 5-1).

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 5.2.2.4, 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 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. A discussion check-point will be held at this point with the NRC and ODEQ to present the data supportive of ceasing active treatment and initiating the remedy demonstration completion testing phase.

Stage 4 includes the remedy demonstration completion testing phase as described in detail in Section 5.2.3. This phase will consist of eight 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 earlier if the active treatment phase is less than the maximum expected duration of three years. License termination is then anticipated to occur no later than one year from submission of the treatment completion report and final dose assessment.

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## 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 the 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; and

• 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; and
- 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 activity. The ODEQ criterion for groundwater is 110  $\mu$ g/L total uranium on a mass basis. 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; and
- Section 5.3: Remedy Completion Demonstration Testing.

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

## 7. 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 5.4. ARCADIS' offer and the total fixed price offer amount are contingent upon NRC approval of this <u>Site Decommissioning</u> <u>Plan – Groundwater Decommissioning Amendment</u>.

The following table summarizes the cost estimate prepared for completion of the groundwater decommissioning in accordance with the approach presented in this document. Should NRC require modification of this <u>Site Decommissioning Plan –</u> <u>Groundwater Decommissioning Amendment</u> in ways that change the substance of the plan, both the cost and schedule may be impacted. Detailed backup for the estimated groundwater decommissioning costs (excluding the NRC oversight costs and assumed 25% contingency) is provided on CD-ROM in Appendix H.

# Table 7-1 Groundwater Decommissioning Cost Estimate

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Task/Component	Cost	Percentage	Notes
Planning and Preparation	\$1,374,868	12%	
Decontamination and/or Dismantling of Radioactive Facility Components	\$7,163,919	62%	Groundwater Remediation
Restoration of Contaminated Area on Facility Grounds	\$236,074	2%	Site Closure and Decommissioning of Treatment Systems
Final Radiation Survey	\$65,000	1%	Additional RSO Costs
Site Stabilization and Long-Term Surveillance	\$ -	0%	
Packing Material Costs	\$ -	0%	Included in Laboratory Costs
Shipping Costs	\$ -	0%	Included in Laboratory Costs
Waste Disposal Costs	\$13,857	. 0%	
Equipment/Supply Costs	\$152,005	1%	Capital Expenditures
Laboratory Costs	\$459,279	4%	
Miscellaneous Costs	\$2,000,000	. 17%	NRC Oversight Costs
SUBTOTAL	\$11,465,000	100%	
25% Contingency	\$2,866,250		· ·
TOTAL DECOMMISSIONING COST ESTIMATE	\$14,331,250		

## 8. References

- Abdelouas, A., W. Lutze, and H. Nuttall. 1999. Oxidative dissolution of uraninite precipitated on Navajo sandstone. Journal of Contaminant Hydrology, 36:353-375.
- Abdelouas, A., W. Lutze, W. Gong, E. Nuttall, B. Strietelmeier, and B. Travis. 2000. Biological reduction of uranium in groundwater and subsurface soil. Science of the Total Environment, 25: 21-35.
- Adams and Bergman. 1995. Geohydrology of Alluvium and Terrace Deposits, Cimarron River from Freedom to Guthrie, Oklahoma. USGS WRI 95-4066.
- ARCADIS. 2006. Work Plan for In-situ Bioremediation of Groundwater. Cimarron Facility. Crescent, OK.
- Baer. J. 1972. Dynamics of Fluids in Porous Media. New York: Dover Publications, Inc. pp. 165-167.
- Barnett, M.O., Jardine, P.M., and Brooks, S.C., 2002. U(VI) adsorption to heterogeneous subsurface media: Application of a surface complexation model. Environmental Science and Technology 36, pp. 937–942.
- Bethke, C. M., 1996. Geochemical Reaction Modeling Concepts and Applications, Oxford University Press, New York, 397p.
- Carr and Marcher. 1977. Preliminary Appraisal of the Garber-Wellington Aquifer, Southern Logan and Northern Oklahoma Counties. USGS OFR 77-278.
- Casas, I., J. De Pablo, J. Gimenez, M. Torrero, J. Bruno, E. Cera, R. Finch, and R.
   Ewing. 1998. The role of pe, pH, and carbonate on the solubility of UO<sub>2</sub> and uraninite under nominally reducing conditions. Geochimica et Cosmochimica Acta, 62, 2223-2231.
- Chang, Y., A. Peacock, P. Long, J. Stephen, J. McKinley, S. Macnaughton, A.
   Hussain, A. Saxton, and D. White. 2001. Diversity and Characterization of Sulfate-Reducing Bacteria in Groundwater at a Uranium Mill Tailings Site.
   Applied and Environmental Microbiology, 67: 3149-3160.

Chao, T.T., and L. Zhou. 1983. Extraction techniques for selective dissolution of amorphous iron oxides from soils and sediments. Soil Science Society of America Journal. 47: 225-232.

Chase Environmental Group, 1994, Radiological Characterization Report for Cimarron Corporation's Former Nuclear Fuel Fabrication Facility.

Chase Environmental Group, April 1995, Site Decommissioning Plan.

Chase Environmental Group, 1998, Site Decommissioning Plan – Groundwater Evaluation Report.

Cimarron Corporation. 1998. Decommissioning Plan Ground Water Evaluation Report, July 1998.

Cimarron Corporation. 2003. Burial Area #1 Groundwater Assessment Report, January 2003.

Cimarron Corporation. 2005. Site-Wide Groundwater Assessment Review. August 2005.

Cimarron Corporation. 2007. Burial Area #1 Subsurface Soil Assessment. November 2007.

Cooper, D.C., and J.W. Morse. 1999. Selective extraction chemistry of toxic metal sulfides from sediments. Aquatic Geochemistry 5(1): 87-97.

Davis, J. A., D. E. Meece, M. Kohler, and G. P. Curtis, 2004. Approaches to surface complexation modeling of uranium (VI) adsorption on aquifer sediments, Geochimica Cosmochimica Acta, 68, pp. 3621–3641.

Davis, J.A., and G.P. Curtis. 2007. Consideration of geochemical issues in groundwater restoration at uranium in-situ leach mining facilities. NUREG/CR-6870.

Dodge, C.J., Francis, A.J., Gillow, J.B., Halada, G.P., Eng, C., and Clayton, C.R. 2002. Association of uranium with iron oxides typically formed on corroding steel surfaces. Environmental Science and Technology 36(16): 3504-3511.

Dzombak, D.A., Morel, F.M.M., 1990. Surface complexation modeling, hydrous ferric oxide. John Wiley and Sons., New York, 393 pp.

ENSR, 2006. Conceptual Site Model, Revision 1.

Ferris, F., R. Hallberg, B. Lyhven, and K. Pedersen. 2000. Retention of strontium, cesium, lead and uranium by bacterial iron oxides from a subterranean environment. Applied Geochemistry, 15: 1035-1042.

Fetter, C.W., 1994. Applied Hydrology. Prentice-Hall, Inc., Englewood Cliffs, New Jersey.

Francis, A.J., C.J. Dodge, J.B. Gillow, J. Cline. 1991. Microbial Transformations of Uranium in Wastes, Radiochimica Acta 52/53, pp. 311-316.

Francis, A. J., C. J. Dodge, F. Lu, G. P. Halada, and C. R. Clayton. 1994. XPS and XANES studies of uranium reduction by Clostridium sp. Environ. Sci. Technol. 28:636–639.

Fuhrmann, M., and A. Lanzirotti. 2005. <sup>241</sup>Am, <sup>137</sup>Cs, Sr and Pb uptake by tobacco as influenced by application of Fe chelators to soil. Journal of Environmental Radioactivity. 32: 33-50.

J.L. Grant and Associates, 1989. Site Investigation Report for the Cimarron Corporation Facility, Logan County, Oklahoma.

Gillow, J.B. In-preparation. Biotransformation of plutonium associated with iron (hydr)oxide colloids.

Gleyzes, C., S. Tellier, and M. Astruc. 2002. Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures. Trends in Analytical Chemistry 21(6,7): 451-467.

Guilbert, J., and C. Park. 1986. The Geology of Ore Deposits. W.H. Freeman and Co, New York. NY.

Harrington, J. 2002. In-situ treatment of metals in mine workings and materials. Tailings and Mine Waste 251-261. Hartog, N., J. Griffioen, P. Van Bergen, and C. Van Der Weijden. 2001. Determining the reactivity of reduced components in Dutch aquifer sediments. Impacts of Human Activity on Groundwater Dynamics, Publication no. 269.

- Lack, J., S. Chaudhuri, S. Kelly, K. Kemner, S. O'Connor, and J. Coates. 2002. Immobilization of Radionuclides and Heavy Metals through Anaerobic Biooxidation of Fe (II). Applied and Environmental Microbiology, 68: 2704-2710.
- Lanzirotti, A., and S. Sutton. 2006. Synchrotron X-ray microbeam techniques in assessing metal bioavailability in the environment. Geochimica et Cosmochimica Acta, 70: 343-346.
- Leventhal, J., and E. Santos. 1981. Relative importance of organic carbon and sulfide sulfur in a Wyoming roll-type uranium deposit. Open File Report (US Geological Survey) 81-580.
- Liu, C., J.M. Zachara, L. Zhong, R. Kukkadupa, J.E. Szecsody, and D.W. Kennedy. 2005. Influence of sediment bioreduction and re-oxidation on uranium sorption. Environ. Sci. Technol. 39: 4125-4133.
- Lloyd, J., and L. Macaskie. 2000. Bioremediation of Radionuclide-Containing Wastewaters. *In* Environmental Microbe-Metal Interactions, D. Lovley, Ed. ASM Press, Washington, DC.
- Lovley, D., E. Phillips, Y. Gorby, and E. Landa. 1991. Microbial reduction of uranium. Nature, 350, 413-416.
- Lovley, D., and E. Phillips. 1992. Bioremediation of Uranium Contamination with Enzymatic Uranium Reduction. Environmental Science and Technology, 26, 2228-2234.
- Lutes, C.C., Frizzell, A., Palmer, P., and Suthersan, S.S., 2005. Summary of 200 Field Applications of Enhanced Anaerobic Biological Treatment; Oral Presentation at the Eighth International In-situ and On-site Bioremediation Symposium; Baltimore, MD.
- Madden, A.S., A.C. Smith, D.L. Balkwill, L.A. Fagan, and T.J. Phelps. 2007. Microbial uranium immobilization independent of nitrate reduction. Environmental Microbiology, 9(9): 2321-2330.

- Marsili, E., H. Beyenal, L. Di Palma, C. Merli, A. Dohnalkova, J.E. Amonette, and Z. Lewandowski. 2007. Uranium immobilization by sulfate-reducing biofilms grown on hematite, dolomite, and calcite. Environmental Science and Technology, 41: 8349-8354.
- Martin, T., and H. Kempton. 2000. In Situ Stabilization of Metal-Contaminated Groundwater by Hydrous Ferric Oxide: An Experimental and Modeling Investigation. Environmental Science and Technology, 34, 3229-3234.
- Morse, J.W., and Rickard, D. 2004. Chemical dynamics of sedimentary acid volatile sulfide. Environmental Science and Technology. 38(7): 131A-136A.
- NEA, 2007. Thermochemical Database Project, Nuclear Energy Agency. http://www.nea.fr/html/dbtdb/. Accessed February 2008.
- Nextep Environmental, Inc, 2005, Final Status Survey Report, Subarea F, Cimarron Facility, Crescent, OK.
- N'Guessan, A.L., H.A. Vrionis, C.T. Resch, P.E. Long, and D.R. Lovley. In-press. Sustained removal of uranium from contaminated groundwater following stimulation of dissimilatory metal reduction. Environmental Science and Technology. Web release date March 6, 2008.
- Nyer, E., P. Palmer, E. Carman, G. Boettcher, J. Bedessem, F. Lenzo, T. Crossman, G. Rorech, D. Kidd. 2001. In Situ Treatment Technology, 2nd Ed. ARCADIS Geraghty & Miller Environmental Science and Engineering Series, Lewis Publishers, Boca Raton.
- O'Loughlin, E.J., S.D. Kelly, R.E. Cook, R. Csencsits, and K.M. Kemner. 2003. Reduction of uranium(VI) by mixed iron(II)/iron(III) hydroxide (green rust): formation of UO<sub>2</sub> nanoparticles. Environ. Sci. Technol. 37(4): 721-727.
- Ortiz-Bernard, I., Anderson, R.T., Vrionis, H.A., and Lovley, D.R. 2001. Resistance of solid-phase U(VI) to microbial reduction during in situ bioremediation of uranium-contaminated groundwater. Applied and Environmental Microbiology, 70, pp.7558-7560.
- Otero, X., and F. Macias. 2002. Variation with depth and season in metal sulfides in salt marsh soils. Biogeochemistry, 61: 247-268.

Pauwels, H., W. Kloppmann, J. Foucher, A. Martelat, and V. Fritsche. 1998. Field tracer test for denitrification in a pyrite-bearing schist aquifer. Applied Geochemistry, 13: 767-778.

- Poutlon, S.W., and D.E. Canfield. 2005. Development of a sequential extraction procedure for iron: implications for iron partitioning in continentally derived particles. Chemical Geololgy 214: 209-221.
- Reeder, R.J., M. Nugent, C.D. Tait, D.E. Morris, S.M. Heald, K.M. Beck, W.P. Hess, and A. Lanzirotti. 2001. Coprecipitation of uranium(VI) with calcite: XAFS, micro-XAS, and luminescence characterization. Geochimica et Cosmochimica Acta 65(20): 3491-3503.
- Rickard, D.T. 1975. Kinetics and mechanism of pyrite formation at low temperatures. American Journal of Science. 275: 636-652.
- Rickard, D., A. Griffith, A. Oldroyd, I.B. Butler, E. Lopez-Capel, D.A.C. Manning, and D.C. Apperley. 2006. The composition of nanoparticulate mackinawite, tetragonal iron(II) monosulfide. Chemical Geology 235(3-4): 286-298.
- Schroeder, P.R., T.S. Dozier, P.A., Zappi, B.M. McEnroe, J.W. Sjostrom, and R.L.
   Peyton. 1994. The Hydrologic Evaluation of Landfill Performance (HELP)
   Model: Engineering Documentation for Version 3. EPA/600/R-94/168a and b.
   U.S. Environmental Protection Agency Risk Reduction Engineering
   Laboratory, Cincinnati, OH.
- Senko, J., J. Istok, J. Suflita, and L. Krumholz. 2002. In Situ Evidence for Uranium Immobilization and Remobilization. Environmental Science and Technology, 36, 1491-1496.
- Spear, J., L. Figueroa, and B. Honeyman. 2000. Modeling Reduction of U (VI) under Variable Sulfate Concentrations by Sulfate-Reducing Bacteria. Applied and Environmental Microbiology, 66: 3711-3721.
- Suthersan, S. 2002. Natural and Enhanced Remediation Systems. ARCADIS Geraghty & Miller Environmental Science and Engineering Series, Lewis Publishers, Boca Raton.

Tesoriero, A., H. Liebscher, and S. Cox. 2000. Mechanism and rate of denitrification in an agricultural watershed: Electron and mass balance along groundwater flow paths. Water Resources Research, 36: 1545-1559.

Tessier, A., P.G.C. Campbell, M. Bisson. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Analytical Chemistry, 51: 844-851.

Thornton, E.C., L. Zhong, M. Oostrom, and B. Deng. 2007. Experimental and theoretical assessment of the lifetime of a gaseous-reduced vadose zone permeable reactive barrier. Vadose Zone Journal 6: 1050-1056.

Tortorelli, Robert L. and McCabe, L.P., 2001, Flood frequency estimates and documented and potential extreme peak discharges in Oklahoma: U.S. Geological Survey Water-Resources Investigations Report 01-4152, 59 p.

USEPA, 2000. Guidance for Data Quality Assessment – Practical Methods for Data Analysis. USEPA QA/G-9.

USEPA, 1992. Methods for Evaluating Attainment of Cleanup Standards - EPA 230-R-92-014, July.

United States Geological Survey (USGS). 2007b. StreamStats. http://streamstats.usgs.gov/gages/viewer.htm

Waite, T.D., Davis, J.A., Payne, T.E., Waychunas, G.A., and Xu, N., 1994. Uranium(VI) adsorption to ferrihydrite: Application of a surface complexation model. Geochmica et Cosmochimica Acta, 58, pp.5465-5478.

Walker, S.R., H.E. Jamieson, A. Lanzirottie, C.F. Andrade, and G.E.M. Hall. 2005. The speciation of arsenic in iron oxides in mine wastes from the Giant Gold Mine, N.W.T.: Application of synchrotron micro-XRD and micro-XANES at the grain scale. The Canadian Mineralogist, 43(4): 1205-1224.

 Waste Isolation Systems Panel. 1983. A Study of the Isolation System for Geologic Disposal of Radioactive Wastes. Board on Radioactive Waste Management, Commission on Physical Sciences, Mathematics, and Resources, National Research Council. National Academy Press, Washington DC.

Wilkin, R.T. 2006. Mineralogical Preservation of Solid Samples Collected from Anoxic Subsurface Environments. EPA Ground Water Issue, National Risk Management Research Lab, Cincinnati, OH, EPA/600/R-06/112.

- Wilkin, R.T., and H.L. Barnes. 1996. Pyrite formation by reactions of iron monosulfides with dissolved inorganic and organic sulfur species. Geochimica et Cosmochimica Acta 60(21): 4167-4179.
- Wu, W., J. Carley, M. Fienen, T. Mehlhorn, K. Lowe, J. Nyman, J. Luo, M. E. Gentile, R. Rajan, D. Wagner, R. F. Hickey, B. Gu, D. Watson, O. A. Cirpka, P. K. Kitanidis, P. M. Jardine, and C. S. Criddle. 2006a. Pilot-scale bioremediation of uranium in a highly contaminated aquifer I: conditioning of a treatment zone. Environ. Sci. Technol. 40: 3978-3985.
- Wu, W., J. Carley, T. Gentry, M. A. Ginder-Vogel, M. Fienen, T. Mehlhorn, H. Yan, S. Carroll, J. Nyman, J. Luo, M. E. Gentile, M. W. Fields, R. F. Hickey, D. Watson, O. A. Cirpka, S. Fendorf, J. Zhou, P. Kitanidis, P. M. Jardine, and C. S. Criddle. 2006b. Pilot-scale bioremediation of uranium in a highly contaminated aquifer II: geochemical control of U(VI) bioavailability and evidence of U(VI) reduction. Environ. Sci. Technol., 40: 3986-3995.
- Wu, W., Carley, J., Luo, J., Ginder-Vogel, M.A., Cardenas, E., Leigh, M.B., Hwang, C., Kelly, S.D., Ruan, C., Wu, L., Van Nostrand, J., Gentry, T., Lowe, K., Melhorn, T., Carrol, S., Luo, W., Fields, M.W., Gu, B., Watson, D., Kemner, K., Marsh, T., Tiedje, J., Zhou, J., Fendorf, S., Kitanidis, P.K., Jardine, P.M., and Criddle, C.S. 2007. In Situ bioreduction of uranium(VI) to submicromolar levels and reoxidation by dissolved oxygen. Environmental Science and Technology 41: 5716-5723.
- Zehnder, A., and W. Stumm. 1989. Geochemistry and Biogeochemistry of Anaerobic Habitats. In: Anaerobic Microbiology, 2nd Ed. A. Zehnder, Ed.
- Zheng, C. and P.P. Wang. 1999. MT3DMS: A Modular Three-Dimensional Multispecies Transport Model for Simulation of Advection, Dispersion, and Chemical Reactions of Contaminants in Groundwater Systems: Documentation and User's Guide.



## 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 (urany! [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  $\mu$ g/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 re-injection 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 solidphase (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.







	1327 1327 1327B UNNAMED STREET	1319 C-3       AOC         1319 C-2       1319 B-4         1319 C-2       1319 B-4         1319 A-1       1319 B-1         1319 A-2       1319 B-1         1319 A-3       1319 C-1         1319 A-3       0         1322       0         1322       0         1328       Scale in Feet	oact (≥180 pCi/L) topes (pCi/L) 400 N
Program Manager Erhardt Werth Project Manager Sara Handy		Western Alluvial and Western Upland Areas of Impact	Date: 04/18/2008
Task Manager Janis Lutrick Technical Review Jeff Gillow	630 Plaza Drive, Suite 100 Highlands Ranch, Colorado 80129 Tel: 720-344-3500 Fax: 720-344-3535 www.arcadis-us.com	Cimarron Corporation Crescent, Oklahoma	3-2



**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 Reoxidation 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.







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.





aricas	st ou parts iron.		
C. Geoc	nemical modeling results updated with site-specific data demo	Instrate 1,000-year stability for the remedy.	
D. Colum initial	nn testing results demonstrated that reoxidation of the aquifer treatment area phase).	will not remobilize U above 180 pCi/L (from column testing comple	ted during
License Te	rmination Process:		
Submit lice of year 7 or Achieve lice	ense termination request including final dose assessment bas earlier based upon remedial performance) cense termination (no later than one year from submission of t	eed on modeled long-term U concentrations (estimated submission the final dose assessment).	at the start
* Minimum a	nnual meetings with NRC to present data collected, review res	sults to date, and provide assessment of bioremediation	
Program Manager	d planned path forward.		
Program Manager Erhardt Werth	d planned path forward.		Date: 02/10/2009
Program Manager Erhardt Werth Project Manager Sara Handy	A planned path forward.	Bioremediation Implementation Process	Date: 02/10/2009 FIGURE
Program Manager Erhardt Werth Project Manager Sara Handy ask Manager Janis Lutrick	630 Plaza Drive, Suite 100 Highlands Banch Colorado 80129	Bioremediation Implementation Process	Date: 02/10/2009 FIGURE

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

# of Sampling Locations	Sampling Frequency	Analyses to be Conducted
	camping requery	(See Appendix C of GDP for Data Quality Objectives for each analysis)
Stage 2: Baseline Monitoring	·	: •
5-1a: Groundwater Monitoring:		
32 weils across all 3 areas: BA#1, WAA, WUA	One-time sampling event	Water levels
•		Oranium – total activity, isotopic, mass concentration     Performance indicators:
· .		<ul> <li>Field parameters (pH, temperature, dissolved oxygen</li> </ul>
		specific conductivity, ferrous iron)
		• Total dissolved solids
		o Alkalinity
	· · · ·	o Nitrate/nitrite
	•	<ul> <li>Total/dissolved iron</li> </ul>
5-1b: Soil Monitoring:		
12 soil borings installed across all 3 areas in different	One-time sampling event	Performance indicators:
geologic materials with 1 to 2 soil samples per boring	•	<ul> <li>Bulk iron mineralogy including:</li> </ul>
(total of up to 24 soil samples)		<ul> <li>Selective chemical extraction</li> <li>X-ray diffraction</li> </ul>
		o Iron sulfide content quantification
· · · · · · · · · · · · · · · · · · ·		<ul> <li>Induced mineralogy changes including microprobe methods to examine soil mineralogy changes induced</li> </ul>
		by TOC additional and anaerobic microbial processes
•	• • • •	using:
	· · · · ·	
		<ul> <li>μ-XANES</li> </ul>
Stage 2: Initial Treatment System Installation	· · · · · · · · · · · · · · · · · · ·	
5-1c: Groundwater Monitoring:		Minter lough
12 wells - 2 wells within each of the 6 Initial Treatment	Initially daily, then weekly for tracer.	Vvater levels     Tracer
Areas	water levels, and field parameters for first	<ul> <li>Uranium – total activity, isotopic, mass concentration</li> </ul>
	month; monthly for other parameters	Performance indicators:     Eicld normation (obl. tompomtum, dissolved on/gar
	Treatment System Installation testing	specific conductivity, ferrous iron)
	phase.	<ul> <li>Total organic carbon</li> </ul>
		o Total dissolved solids
		o Sulfate/sulfide
,	· · · ·	<ul> <li>Nitrate/nitrite</li> <li>Total/dissolved iron</li> </ul>
5-1d: Soil Monitorina:		
Two soil borings installed within each of the 6 Initial	Minimum of one sampling event based	Uranium – total activity, isotopic, mass concentration
Treatment Areas with 1 to 2 soil samples per boring (total	on observed results.	Performance indicators:     Bulk iron mineralogy including:
of up to 24 soil samples)		Selective chemical extraction
· · · · · · · · · · · · · · · · · · ·		X-ray diffraction
· · · · ·		<ul> <li>Induced mineralogy changes including microprobe</li> </ul>
· · · · ·		methods to examine soil mineralogy changes induced
		by TOC additional and anaerobic microbial processes
	· · ·	SEM with EDS
		<ul> <li>μ-XRF</li> <li>μ-XANES</li> </ul>
5-te: Laboratory Column Testing:		- Proneo
Laboratory Column Studies	During Initial Treatment System	Column testing to asses:
	Installation testing phase	Oxygen consumption     Iron oxidation
		Laboratory column testing to be conducted using a PNNL methodology
	· .	Chomton et al 2007) as described in Attachment A to the September 2000 GDP Addendum
Stage 3: Performance Monitoring:		
5-1f: Groundwater Monitoring:		
32 wells across all 3 areas: BA#1, WAA, WUA	Monthly for the first 6 months of IRZ	Water levels
•	operation	Uranium – total activity, isotopic, mass concentration     Performance indicators
		<ul> <li>Field parameters (pH, temperature, dissolved oxyger</li> </ul>
· · · · ·		specific conductivity, ferrous iron)
	start of IRZ operation and continuing until	o Total dissolved solids
	the start of remedy completion	<ul> <li>Alkalinity</li> </ul>
	demonstration testing for groundwater	o Sulfate/sulfide
· · · · · · · · · · · · · · · · · · ·		o Total/dissolved iron
5-1g: Soil Monitoring:		T
12 soil borings installed across all 3 areas in different	Minimum of one sampling event based	Uranium – total activity, isotopic, mass concentration
geologic materials with 1 to 2 soil samples per boring	on observed results	<ul> <li>renormance indicators:</li> <li>Bulk iron mineralogy including:</li> </ul>
(total of up to 24 soil samples)		<ul> <li>Selective chemical extraction</li> </ul>
		X-ray diffraction
	1	<ul> <li>Induced mineralogy changes including microprobe</li> </ul>

Stage 4: Remedy Completion Demonstration Monitorin	<b>o</b> :	methods to examine soil mineralogy changes induced by TOC additional and anaerobic microbial processes using: SEM with EDS µ-XRF µ-XANES
5-1h: Groundwater Monitoring:	9	
16 wells across all 3 areas: BA#1, WAA, WUA	Quarterly for 8 quarters	<ul> <li>Water levels</li> <li>Uranium – total activity, isotopic, mass concentration</li> <li>Performance indicators:         <ul> <li>Field parameters (pH, temperature, dissolved oxygen, specific conductivity)</li> </ul> </li> </ul>
<b><u>5-11: Soil Monitoring:</u></b> 12 soil borings installed across all 3 areas in different geologic materials. 1 to 2 soil samples per boring (total of up to 24 soil samples)	One-time sampling event	<ul> <li>Uranium - total activity, isotopic, mass concentration</li> <li>Performance indicators:         <ul> <li>Bulk iron mineralogy including:                 <ul> <li>Selective chemical extraction</li> <li>X-ray diffraction</li> <li>Iron sulfide content quantification</li> <li>Induced mineralogy changes including microprobe methods to examine soil mineralogy changes induced by TOC additional and anaerobic microbial processes using:</li></ul></li></ul></li></ul>

a - Sampling and analyses to be performed in accordance with Cimarron's Quality System Manual and the Data Quality Objectives (DQOs) established for this project as included in Appendix C of the June 2008 GDP.

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MIXING TANK: INFLUENT GROUNDWATER FROM EXTRACTION WELLS IS AMENDED WITH CARBON SOURCE, ALSO FERROUS IRON AND SULFATE, IF NEEDED

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

MIXING TANKS: INFLUENT GROUNDWATER FROM EXTRACTION WELLS IS AMENDED WITH CARBON SOURCE, ALSO FERROUS IRON AND SULFATE, IF NEEDED

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

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 5.2.1.1).

### Appendix A

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Groundwater Flow Modeling Report, Cimarron Site (ENSR) Prepared for: Cimarron Corporation (Tronox) Oklahoma City, Oklahoma



ENSR Corporation October 2006 Document No.: 04020-044



ENSR AECOM

Prepared for: Cimarron Corporation (Tronox) Oklahoma

## Groundwater Flow Modeling Report

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ENSR AECOM

## **ENSR**

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## **1.0 INTRODUCTION**

#### 1.1 Overview

In order to depict and predict groundwater flow and to evaluate groundwater remediation alternatives, two groundwater flow models were developed for the Cimarron Site. These two models address two of the three areas on site that require remediation of Uranium (U) in the groundwater. The two models included Burial Area #1 (BA #1) and the Western Alluvial (WA) area.

Calibration was evaluated by comparing measured groundwater elevations, flow path data, and water budgets, with simulated elevations, paths, and budgets. Both flow models achieved adequate calibration to the observed groundwater elevation data, to observed flow path trajectories, and to the estimated water budgets. Discrepancies between observations and predictions are considered reasonable. The overall water table configuration for each model was consistent with expectations based on observations of U concentrations. Overall hydrogeological concepts as presented in the Conceptual Site Model (CSM), Rev 01 (ENSR, 2006) were captured by the numerical models.

The resulting models are useful tools to evaluate groundwater flow characteristics (velocities, flux rates, etc.) and to evaluate different remediation scenarios including, but not limited to, understanding the permanence of the proposed remedial technique and to design the injection of reagents.

#### 1.2 Background and Objectives

Cimarron Corporation's site near Crescent, Oklahoma is a former nuclear fuel manufacturing facility. Since stopping operations, the site has been undergoing decommissioning under the oversight of the Nuclear Regulatory Commission (NRC) and the Oklahoma Department of Environmental Quality (ODEQ). As a result of the facility processes there are several areas at the Cimarron Site that have residual concentrations of Uranium (U) in the groundwater. Cimarron Corporation is currently considering remedial actions in Burial Area #1, the Western Alluvial Area, and the Western Uplands area. To support the design of these remedial systems, numerical groundwater flow models were developed for two of these areas. These models, based largely on data and concepts presented in the Conceptual Site Model (Rev 01, ENSR, 2006), serve as tools to evaluate remediation strategies.

The overall objective of this modeling effort was to provide tools by which remediation alternatives could be evaluated. This objective was achieved by setting up the numerical models to include geologic and hydrologic conditions as observed and documented in the CSM-Rev 01 (ENSR, 2006). The models were then calibrated to specific targets. This calibration process yielded two models that compared well to observations and therefore could provide a frame of reference with which to evaluate impacts from remediation alternatives.

These models were initially developed to support ENSR's remediation via pump and treat. While Cimarron was considering remediation via pump and treat, they were also considering bioremediation. In this latter process, via additives, the geochemical conditions in the aquifer would be converted to a reducing environment which would immobilize the U. This process has been conceptualized and proposed by Arcadis. Data from these calibrated models and simulations using these numerical models can help to design either these or other remediation alternatives.

Note that even though there are detectable concentrations of U in the Western Upland area of the site, a numerical model was not constructed for that area. The conceptual site model for the WU area is presented in the CSM Rev 01 (ENSR, 2006). This conceptual site model forms the basis for ARCADIS' evaluation and selection of remedial design for this area. Given the extent of the U concentrations, complex numerical modeling for this area may not be necessary based on the remedial approach.



## 2.0 HYDROGEOLOGIC FRAMEWORK

Much of the following has been extracted and paraphrased from the CSM-Rev 01 Report (ENSR, 2006). This section largely focuses on the parts of the CSM that were directly used in the modeling effort:

#### 2.1 Site Setting

The Cimarron Site lies within the Osage Plains of the Central Lowlands section of the Great Plains physiographic province, just south of the Cimarron River (**Figure 1**). The topography in the Cimarron area consists of low, rolling hills with incised drainages and floodplains along major rivers. Most of the drainages are ephemeral and receive water from storms or locally from groundwater base flow. The major drainage included in the models was the Cimarron River, which borders the site on the north. This river drains 4,186 square miles of Central Oklahoma from Freedom to Guthrie, Oklahoma (Adams and Bergman, 1995). The Cimarron River is a mature river with a well-defined channel and floodplain. The stream bed is generally flat and sandy and the river is bordered by terrace deposits and floodplain gravels and sands (Adams and Bergman, 1995). In the area of the Cimarron Site, the ancestral Cimarron River has carved an escarpment into the Garber-Wellington Formation. Floodplain alluvial sediments currently separate most of the river channel from the escarpment. Surface elevations in the Cimarron area range from 930 feet above mean sea level (amsl) along the Cimarron River to 1,010 feet amsl at the former plant site. Between the river and the escarpment, the ground surface is flat relative to the variable topography of the escarpment and leading up to the uplands. Vegetation in the area consists of native grasses and various stands of trees along and near drainages. Soil thickness in the project area ranges from about one to eight feet.

#### 2.2 Precipitation

Adams and Bergman (1995) summarized the precipitation for the Cimarron River Basin from Freedom to Guthrie, Oklahoma. Their study showed that precipitation ranges from an average of 24 in/yr near Freedom, Oklahoma, in the northwest part of the Cimarron River floodplain in Oklahoma, to 32–42 in/yr at Guthrie, Oklahoma. Wet weather years occurred between 1950 and 1991, 1973–1975, 1985–1987, and 1990–1991. The wettest months of the year are May through September, while the winter months are generally the dry months. The period from 1973 through 1975 had a total measured rainfall that was 23 inches above normal (Carr and Marcher, 1977). Precipitation data collected by the National Oceanic and Atmospheric Administration (NOAA) for Guthrie County, Oklahoma, from 1971 to 2000 indicates that the annual average precipitation is 36.05 inches.

#### 2.3 General Geology

The regional geology of the Cimarron area and the site-wide stratigraphic correlations for the project area can be combined into a general geological model for the Cimarron Site (Figure 2). The site consists of Permianage sandstones and mudstones of the Garber-Wellington Formation of central Oklahoma overlain by soil in the upland areas and Quaternary alluvial sediments in the floodplains and valleys of incised streams. The Garber sandstones dip gently to the west and are overlain to the west of the Cimarron Site by the Hennessey Group. The Wellington Formation shales are found beneath the Garber sandstones at a depth of approximately 200 feet below ground surface in the project area. The Garber Formation at the project site is a fluvial deltaic sedimentary sequence consisting of channel sandstones and overbank mudstones. The channel sandstones are generally fine-grained, exhibit cross-stratification, and locally have conglomeratic zones of up to a few feet thick. The sandstones are weakly cemented with calcite, iron oxides, and hydroxides. The silt content of the sandstones are clay-rich and exhibit desiccation cracks and oxidation typical of overbank deposits. Some of the mudstones are continuous enough at the Cimarron Site to allow for separation of the sandstones into three main units, designated (from top to bottom) as Sandstones A, B, and C. Correlation of these three sandstone units is based primarily on elevation and the presence of a thick mudstone unit at the

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base of Sandstones A and B that can be correlated between borings. Within each sandstone unit, there are frequent mudstone layers that are discontinuous and not correlative across the project area.

The Cimarron Site is located on part of an upland or topographic high between Cottonwood Creek and the Cimarron River. The project site is dissected by shallow, incised drainages that drain northward toward the Cimarron River. Groundwater base flow and surface water runoff during storms have been ponded in two reservoirs (Reservoirs #2 and #3) on the project site. The Cimarron River is a mature river that has incised the Garber Formation, forming escarpments that expose the upper part of the Garber sandstones. Within the Cimarron River has developed a floodplain of unconsolidated sands, silts, and clays that separate the Garber sandstones exposed in an escarpment from the main river channel. Surface drainages within the project site flow toward the Cimarron River. Geological features of each modeled area of the Cimarron Site are as follows:

- BA #1 Area The upland is underlain by a sequence of sandstone and mudstone units, namely, from top to bottom, Mudstone A, Sandstone B, Mudstone B, and Sandstone C. The alluvium can be divided into a transitional zone located within the erosional drainage area and an alluvial zone located north of the escarpment line. The transitional zone consists predominantly of clay and silt and overlies Sandstone B or Mudstone B. A paleochannel appears to exist in the transitional zone, which may control the flow of groundwater in the vicinity of the upland in this area. The alluvium consists of mainly sand and overlies Sandstone C and Mudstone B. Additional descriptions of the geology of this area are included in the CSM-Rev 01 Report (ENSR, 2006).
- Western Alluvial Area Alluvial sediments in this area consist of predominantly sand with minor amounts of clay and silt. Sandstone B and Mudstone B exist beneath the alluvial sediments near the escarpment and Sandstone C underlies the alluvial sediments farther out in the floodplain. Additional descriptions of the geology of this area are included in the CSM-Rev 01 (ENSR, 2006).

#### 2.4 Site-Specific Geology

#### 2.4.1 BA #1 Area

Geologic logs from seventy-five boreholes were used to describe the subsurface geology in the immediate vicinity of the Uranium (U) plume at the BA #1 area. The lithologic logs collected from borehole cuttings described the subsurface geology as a sequence of interbedded layers of near surface unconsolidated alluvial material and deeper consolidated sandstones and mudstones. The logs identified twenty-seven unique material types, which included unconsolidated materials of varying degrees of sand, silt, and clay, anthropogenically disturbed surficial deposits, and sedimentary rock. In an effort to simplify the conceptualization of the subsurface geology these twenty-seven different material types were collapsed into nine distinct material types representing strata with significantly different hydrogeologic characteristics. The four unconsolidated materials include, fill, sand, silt, and clay, and the underlying consolidated units include Sandstone A, Sandstone B, and Sandstone C, interbedded with two distinct mudstone layers (Figure 3). The simplified lithologic units describe, from the surface downward, fill material in the uplands and widely scattered silt in the upland and alluvial areas. In the alluvial areas this is underlain by a thick sandstone unit with a relatively thick bed of clay within the unit. The upland areas and beneath the alluvium consist of interbedded sandstone and mudstone. Because of varied topography and elevation the exposure of materials at the site varies widely. In the upland areas most of the exposed material is either sandstone or mudstone while in the alluvium most of the exposed material is either sand or to a lesser extent silt and clay. All data in the lithologic logs was used in the development of the model

#### 2.4.2 Western Alluvial Area

The subsurface geology at the WA area was depicted by geologic logs from twenty boreholes near the escarpment. In contrast to the geology of the BA#1 area, the subsurface of the WA area is a relatively flat, "pancake" geology where Sandstone C, the lowest sandstone indicated in the BA #1 area, is overlain by a continuous unit of unconsolidated alluvial sand, which is overlain by a intermittent unit of unconsolidated clay

(Figure 4). A simplification of the information from the lithologic logs was not necessary for the WA and the inconsistent distribution of clay around the site was largely due to topography and the erosion of the clay in the low lying areas. All data in the lithologic logs was used in the development of the model

#### 2.5 Hydrogeology

Groundwater flow through above-described regional geologic units is governed by recharge areas and discharge areas.

Regionally, recharge is precipitation (rain, snow, etc) that infiltrates past the root zone to the water table. As discussed above, the average annual precipitation rate is approximately 30 in/yr. Recharge to the alluvium and terrace deposits along the Cimarron River was estimated to be 8 percent of precipitation based on baseflow calculations and the assumptions of steady-state equilibrium in the alluvium and terrace sands (Adams and Bergman, 1995). Rainfall recharge to groundwater is therefore estimated to be approximately 2.4 in/yr ( $5.5 \times 10^4$  ft/day).

Discharge of groundwater occurs at low points in the watershed and generally coincides with streams and lakes. At this site the Cimarron River is a local and regional discharge boundary. Average annual baseflow in the Cimarron River should equal average annual recharge indicating that the recharge and discharge rates are balanced.

Recharge to the groundwater system typically occurs at topographic highs. The application of this water to the groundwater system results in downward gradients in the recharge areas; that is, there is a component of flow downward in addition to horizontal. Conversely, discharge from the groundwater system occurs at the topographic low points in any given watershed, for instance at a stream, river, or lake. Because of this, groundwater gradients tend to be upward in these areas; that is, there is component of flow upward in addition to horizontal. The flow path of any given unit of groundwater depends on where in the watershed it originates as recharge and how far it has to flow to discharge.

#### 2.6 Hydrologic Implications

The site-specific geology suggests several hydrologic implications including:

- The alluvial material was largely deposited by the historical meandering of the Cimarron River and the
  deposition of overbank deposits that result from intermittent floods on the river. This inconsistent and
  repeating depositional cycle resulted in a series of inter-bedded unconsolidated material types that are
  collectively referred to as alluvium, which on a small scale can exhibit variable hydrogeologic
  characteristics but on a larger scale can be considered collectively.
- Groundwater discharged from the Garber-Wellington formation largely discharges through the alluvial deposits on its way to its final destination, the Cimarron River.
- Since both the WA and the BA #1 areas are within the Cimarron River alluvial valley, both areas
  receive groundwater from both upgradient discharge of groundwater to the alluvial deposits and from
  subsurface discharge of water from the deeper aquifer to the alluvium and river system. In general,
  flow from the southern upgradient sandstones to the alluvium is characterized as horizontal flow and
  flow from the sandstone underlying the alluvium is characterized as having a component of vertical
  (upward) flow.
- The sandstone and siltstone/mudstones of the Garber-Wellington formation are relatively impermeable when compared to the unconsolidated alluvial sands adjacent to the river. This suggests that the water table gradient in the sandstone would be relatively steep when compared to the alluvial sand. This would further suggest that water could be more easily withdrawn from the alluvial sand than from the consolidated sediments occurring both beneath, and upgradient of the alluvial material.

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 In addition, within the bedrock, the sandstone units have higher permeability relative to the mudstones. Therefore, more groundwater flow is expected to take place horizontally within these water bearing units, with less flow between the units.

The hydrogeologic characteristics of the Cimarron River alluvial system are typical of a relatively permeable aquifer system receiving groundwater from an adjacent, less permeable bedrock aquifer and transferring the groundwater to the discharge zone, in this case the Cimarron River.

#### 2.7 Conceptual Model of Site Groundwater Flow

The Conceptual Site Model (CSM) of the Cimarron River flow system was developed prior to the development of groundwater models for the WA area and the BA #1 area. The CSM was incorporated into the groundwater models to ensure that the models used existing information and an accepted interpretation of the site-wide geology. The conceptual models for the WA area and the BA #1 area were developed separately and as such are discussed separately. However, it is recognized that the conceptual models for the two areas must be consistent.

#### 2.7.1 The Cimarron River

The Cimarron River is a significant hydrogeologic boundary for the entire Cimarron Site. The headwaters of this river are in New Mexico and from there it flows through Colorado, Kansas, and Oklahoma. In the vicinity of the Site (Freedom to Guthrie, OK) the Cimarron River is a gaining river. That is, it is a discharge zone for groundwater. Groundwater flow into the river is controlled by the difference in elevation of groundwater and in the river and by the conductivity of the river bottom sediments. The elevation of the river changes seasonally, but this can be represented as an average annual elevation for this steady-state modeling effort. Changes in the elevation of the river may result in short-term changes in the groundwater flow directions and gradients in the nearby alluvial materials. However, over the long-term, an average elevation is appropriate to reflect the average groundwater flow system. Cimarron River streamflows and associated water level elevations in the immediate vicinity of the Western Alluvial area and BA#1 model domains has not been historically measured. The variability in river water levels at the site were estimated using long term flow records (1973 through 2003) from the USGS stream gages at Dover (30.0 miles upstream to the west) and Guthrie (10.3 miles downstream to the east). Daily averaged water level elevations at each of the two sites were averaged and the average water level elevation for the area of the model domains was determined through linear interpolation to be 925.0 feet. A further statistical evaluation indicated that the 5<sup>th</sup> percentile of water level elevations at the site was 924.1 feet and the 95th percentile of water level elevations was 927.7 feet; therefore, 90% of the time the Cimarron River water level at the site varies within a range of 3.60 feet.

#### 2.7.2 BA #1 Area

Groundwater in the vicinity of the BA #1 Area originates as precipitation that infiltrates into the shallow groundwater in recharge zones, both near the BA #1 area and in areas upgradient of the BA #1 area. The amount of water flowing from the sandstones into the modeled area and into the alluvial material is controlled by the changes in groundwater elevation and hydraulic conductivities between the two units.

Local to the BA #1 area, infiltrated rainwater recharges the shallow groundwater in the area of the former disposal trenches and then flows into Sandstone B. The reservoir also contributes water to the groundwater system. This groundwater then flows across an escarpment that is an interface for the Sandstone B water-bearing unit and the Cimarron River floodplain alluvium, and finally into and through the floodplain alluvium to the Cimarron River. Flow in Sandstone B is mostly northward west of the transitional zone and northeastward along the interface with the transitional zone. Flow is driven by a relatively steep hydraulic gradient (0.10 foot/foot) at the interface between Sandstone B and the floodplain alluvium. Once groundwater enters the transition zone of the floodplain alluvium, the hydraulic gradient decreases to around 0.023 foot/foot and flow is refracted to a more northwesterly direction. The decrease in hydraulic gradient is due in part to the much higher overall hydraulic conductivity in the floodplain alluvium compared to Sandstone B (10–3 to 10–2 cm/s in

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alluvium versus 10–5 to 10–4 cm/s in Sandstone B). The refraction to the northwest is primarily due to a paleochannel in the floodplain alluvial sediments. The direction of this paleochannel is to the northwest near the buried escarpment and then is redirected to the north as it extends farther out into the floodplain. Once groundwater passes through the transitional zone, it enters an area where the hydraulic gradient is relatively flat. Data indicates that the gradient in the sandy alluvium is approximately 0.0007 ft/ft. **Figure 3-4** in the CSM-Rev 01 Report (ENSR, 2006) presents a potentiometric surface map of Sandstone B and the alluvium for the BA #1 area based on groundwater level measurements during August/September 2004. Seasonal data between 2003 and 2005 indicate that although groundwater levels may change seasonally, the hydraulic gradients and groundwater flow directions do not change significantly over time (ENSR, 2006).

#### 2.7.3 Western Alluvial Area

Groundwater in the vicinity of the WA area originates as precipitation that infiltrates into the shallow groundwater in recharge zones both near the WA area and in areas upgradient of the WA area. Most of the groundwater in the WA area comes from the discharge of groundwater from Sandstones B and C to the alluvial materials. The amount of water flowing from the sandstones to the alluvial material is controlled by the difference in groundwater elevation and hydraulic conductivities between the two geologic units. Groundwater flow in the WA area is generally northward toward the Cimarron River; flow is driven by a relatively flat hydraulic gradient of 0.002 foot/foot. **Figure 3-6** in CSM-Rev 01 Report (ENSR, 2006) presents a potentiometric surface map of the alluvium for the WA area based on groundwater level measurements during August/September 2004. As with the BA#1 Area, although groundwater levels may change seasonally, there is little change over time in hydraulic gradient and groundwater flow directions.

## 3.0 MODELING APPROACH

Groundwater flow at the two Cimarron sites (BA #1 and WA areas) was simulated using the three-dimensional MODFLOW model (McDonald and Harbaugh, 1988). The MODFLOW model uses a block-centered finitedifference method to simulate groundwater flow in three dimensions. The MODFLOW model was selected because of its wide acceptance by the technical community, because of its robustness, and because several Windows® based applications support the model, including the GMS 6.0<sup>®</sup> modeling package, which was used for this project. The GMS 6.0<sup>®</sup> software package is a visualization package that facilitates easy manipulation of the MODFLOW input and output files. In addition to using the MODFLOW groundwater model, the MODPATH particle tracking program was used to simulate the transport of groundwater particles within the model domain as a direct result of a flow field predicted by MODFLOW.

#### 3.1 Groundwater Model Domain

The domains of the BA #1 area and WA groundwater models were set up to include the specific areas of interest and all important boundary conditions.

For the BA #1 area, the specific area of interest was located northwest of the Reservoir #2 from the source area in the uplands, downgradient through the transition zone, and into the alluvial sands (**Figure 5**). The downgradient boundary was the Cimarron River and the upgradient boundary was along an east-west line coincident with the Reservoir #2 dam. Groundwater flow is primarily northward, so boundaries parallel to groundwater flow were set up at locations upstream and downstream along the Cimarron River far enough away from the high U concentrations and parallel to flow lines to not influence the interior of the model domain during pumping simulations. The lower boundary (i.e., bottom) of the BA #1 model domain was fixed at elevation 900 feet, well below the lower extent of the alluvial aquifer.

In the case of the WA area, the specific area of interest was located just downgradient of the escarpment along a north-trending line of high U concentrations (**Figure 6**). The downgradient boundary was the Cimarron River and the upgradient boundary was set at the escarpment. Groundwater flow is primarily northward so boundaries parallel to groundwater flow were set up at locations upstream and downstream along the Cimarron River far enough away from the high U concentrations to not influence the interior of the model domain during pumping simulations. The lower boundary (i.e., bottom) of the WA area model domain was fixed at 870 feet, well below the lower extent of the alluvial aguifer.

The model domain for the BA #1 area was set up to include the area from the upgradient reservoir to the south, to the Cimarron River to the north, and to distances east and west adequate enough to have a negligible effect on the interior of the model domain. The model was developed with grid cells that are 10 feet square in the X-Y plane and with 12 layers extending from the land surface down to a depth of elevation 900 feet, resulting in approximately 270,000 grid cells within the model domain.

The model domain for the WA area was set up to include the area from the escarpment to the south to the Cimarron River to the north and east and west to distances adequate enough to have a negligible effect on the interior of the model domain. The model was developed with grid cells that are 10 feet square in the X-Y plane and with 2 layers extending from the land surface down to a depth of elevation 870 feet, resulting in 97,830 grid cells within the model domain. The high density of grid cells within each model domain was selected for two reasons including: 1) to provide for a finely discretized model within the area of the U plume for testing the effects of groundwater pumping, and 2) to provide for adequate representation of the subsurface geology into discrete geologic material types, particularly for the BA#1 area.

#### 3.1.1 BA #1 Area

The model layers for the BA #1 area were developed directly from the lithologic information from the seventytwo boreholes that were available for the site. A simplification of the original borehole data, which had originally described 27 unique lithologic types, was imported directly into the GMS 6.0® modeling platform, as the basis for the groundwater model. The simplified geology included the following geologic units/materials: 1) fill, 2) silt, 3) an upper sand unit, 4) clay, 5) a lower sand unit, 6) an upper sandstone unit (Sandstone A), 7) an upper mudstone (A), 8) a middle sandstone unit (Sandstone B), 9) a lower mudstone (B), and 10) a lower sandstone unit (Sandstone C). Each of the boreholes was reviewed in light of the surrounding boreholes to ensure that the inter-relationships between boreholes were realistic and representative of the CSM-Rev 01 (ENSR, 2006) developed for the site. Following the importation and adjustment of the borehole information, each layer in each of the seventy-two boreholes was assigned a Horizon ID to indicate the layer's position in the depositional sequence at the Site. The GMS 6.0® modeling platform was then used to "connect" the boreholes to form cross-sections based on the Horizon IDs assigned to each of the boreholes. Since a crosssection was developed for every adjacent borehole, this resulted in a total of one hundred sixty-five crosssections; each of which was reviewed to ensure the sensibility of the interpretations. In cases where the cross-section did not make geologic sense, the cross-section was manually modified (**Figure 7**).

Once the cross-sections were developed and checked for accuracy, the GMS 6.0® program was used to develop three-dimensional solids of each material type within the intended model X-Y model domain. Each of the 3-D solids was represented by upper and lower TIN (triangularly integrated network) surfaces and was created using the previously developed cross-sectional data. Each of the solids types corresponded to the nine geologic units indicated by the lithologic information for the boreholes (**Figure 8**).

The model boundaries were identified and incorporated into the GMS 6.0® platform, including the location of the river boundary, the general head boundary, and the recharge boundary (discussed in the next section). One of the last steps in the development of the BA #1 area groundwater model was to develop a generic, twelve layer 3D grid that encompassed the model domain on a 10 ft by 10ft horizontal spacing. The next step in the development of the model was to assign hydrogeologic properties to each of the material types and boundaries and then transition all of the 3-D solids information to the 3-D grid that is used by the MODFLOW and MODPATH models (**Figure 9**). The final step was to make modifications to the distribution of material types (i.e., hydraulic conductivities) to adjust for the discrepancies between the mathematically interpreted version of the distribution of soil types and the interpretation of soil types based on the CSM (ENSR, 2006).

#### 3.1.2 WA Area

The model layers for the WA area were developed directly from the lithologic information from the twenty boreholes that were available for the site. The borehole data was imported directly into the GMS 6.0® modeling platform as the basis for the groundwater model. Each of the boreholes was reviewed in light of the surrounding boreholes to ensure that the inter-relationships between boreholes were realistic and representative of the CSM, Rev.1 (ENSR, 2006) developed for the site. Following the importation and adjustment of the borehole information, each layer in each of the twenty boreholes was assigned a Horizon ID to indicate the layer's position in the depositional sequence at the site. The GMS 6.0® modeling platform was then used to "connect" the boreholes to form cross-sections based on the Horizon IDs assigned to each of the boreholes. Since a cross-section was developed for every adjacent borehole, this resulted in a total of forty-one cross-sections; each of which was reviewed to ensure the sensibility of the interpretations. In cases where the cross-section did not make geologic sense, the cross-section was manually modified (Figure 10).

Once the cross-sections were developed and checked for accuracy, the GMS 6.0® program was used to develop three-dimensional solids of each material type within the intended model X-Y model domain. Each of the 3-D solids was represented by upper and lower TIN (triangularly integrated network) surfaces and was created using the previously developed cross-sectional data. Each of the solids types corresponded to the three geologic units indicated by the lithologic information for the boreholes (**Figure 11**). It should be noted that the geologic materials in the WA area consisted only of sandy alluvium and the underlying bedrock (Sandstone C), so this process was much simpler than for the BA#1 area.

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The model boundaries were identified and incorporated into the GMS 6.0® platform including the location of the river boundary, the general head boundary, and the recharge boundary (discussed in the next section). One of the last steps in the development of the WA area groundwater model was to develop a generic, two layer 3D grid that encompassed the model domain on a 10 ft by 10 ft horizontal spacing. The final step in the development of the 3-D solids information to the 3-D grid that is used by the MODFLOW and MODPATH models (**Figure 12**).

#### 3.2 Hydrogeologic Physical Properties

The physical property most commonly used to characterize subsurface permeability is the hydraulic conductivity. This parameter is applied to Darcy's Law as a proportionality constant relating groundwater flow rate to groundwater gradient and cross-sectional area, and is a measure of the ability of a soil matrix to transport groundwater through the subsurface. Hydraulic conductivity values are required to describe the permeability of each cell in the MODFLOW groundwater model because Darcy's equation is used by the model to solve for groundwater head in each model cell. If hydraulic conductivity values in the model area were spatially the same, the multiple model layers could act as a single layer. However, this degree of uniformity is not evident at the Cimarron site, so each model layer was assigned a unique horizontal and vertical hydraulic conductivity value consistent with the geology assigned to that layer.

In the case of the BA #1 area model, the MODFLOW model represents the complicated ten layer geologic system of largely continuous material types with twelve model layers. From the surface downward these include, 1) fill, 2) silt, 3) an upper sand unit, 4) clay, 5) a lower sand unit, 6) an upper sandstone unit (Sandstone A), 7) an upper mudstone (A), 8) a middle sandstone unit (Sandstone B), 9) a lower mudstone (B), and 10) a lower sandstone unit (Sandstone C). A single, constant hydraulic conductivity value was assigned to each of these 10 material types.

In the case of the WA area model, the MODFLOW groundwater model represents the (simple relative to the BA #1 model) subsurface by assigning the two dominant material types (sand and sandstone) to two different model layers. (Note: even though clay was present in the boring logs, it was not saturated, therefore was not modeled). These are 1) a sandy alluvium layer beneath the clay layer and exposed at several locations throughout the site and 2) an underlying sandstone layer beneath the sandy alluvial aquifer (Sandstone C). A single, constant hydraulic conductivity value was assigned to each of the two layers.

Hydraulic conductivity values for both the alluvium and the sandstone were derived from slug and pumping tests conducted during the field investigations, as described in the Burial Area #1 Groundwater Assessment Report (Cimarron Corporation, 2003). **Table 1** summarizes the findings from these tests. Results for the alluvium ranged from 0.04 to 312 ft/day with a median value of 38 ft/day. Results for the sandstones ranged from 0.07 to 2.83 with a median value of 0.35 ft/ day. The conductivity values are consistent with literature (Freeze & Cherry, 1979).

In general, the vertical hydraulic conductivity is assumed to be less than the horizontal because of the interbedding that occurs during sedimentary deposition. While relatively small layers and lenses of fine material do not significantly effect the lateral movement of groundwater they can effect the vertical movement by creating more tortuous pathway for groundwater flow, and resistance to vertical flow. In general, the vertical hydraulic conductivity in sedimentary or alluvial deposits can be 1 to 30% of the horizontal hydraulic conductivity.

The alluvial materials (sand, clay, silt) were assumed to have vertical components of flow consistent with a sedimentary environment. Therefore, the vertical hydraulic conductivity of the alluvial materials was set to 10% of horizontal hydraulic conductivity. For the sandstones and mudstones, the vertical hydraulic conductivity was set to 5% of horizontal hydraulic conductivity. The groundwater flow in sandstone and mudstone may be controlled not only by primary (matrix) pathways, but also secondary (remnant fracture) pathways. However, there is no data (i.e., groundwater elevation data) to suggest that fractures flow is significant at this site, especially on the scale of the entire model domain. Note that the conceptual

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understanding of fractures at this site is that most of fractures occur on bedding planes (i.e., in the horizontal direction); thus, flow in the stone fractures would be controlled by horizontal hydraulic conductivity, not the vertical.

Anisotropy values are used if there is some reason to believe that the aquifer has a substantially different permeability along one horizontal axis than another. This is not believed to be the case in either the WA area or the BA #1 model domain and therefore the horizontal anisotropy was assumed to be unity.

#### 3.3 Boundary Conditions

The boundary conditions at the perimeter of the model domain play an important role in the outcome of a groundwater simulation because of the dependence of hydraulic behavior within the interior of the model on the water levels and fluxes fixed at the model boundaries. Ideal model boundaries are natural hydrogeologic features (i.e., groundwater divides, rivers). Recharge to groundwater is also a boundary condition. Model predictions can be inaccurate when the areas of interest in the model domain are too close to a poorly selected boundary condition. In the absence of natural hydrogeologic boundaries, boundaries are chosen at distances great enough such that they do not affect the outcome of simulations in the area of interest. In the groundwater models of the Cimarron Site, the downgradient boundary was selected to coincide with the Cimarron River, a natural hydrogeologic boundary. Since there are no nearby natural features for the other boundaries, the domain was extended to distances sufficient such that simulations would not be significantly affected by the model boundaries.

#### 3.3.1 Recharge

Recharge to groundwater is simulated using the MODFLOW Recharge Package. This package can be used to apply a spatially and temporally distributed recharge rate to any layer within a model domain. In general, the recharge package is used to represent the fraction of precipitation that enters the subsurface as rainfall recharge directly to the groundwater water table. In model domains representing relatively small geographic regions, and without significant variability in site wide precipitation, the recharge package is applied uniformly throughout the model domain. The recharge package can be temporally varied in unsteady simulations to predict system response to unique or seasonal events but can be applied at a constant rate for steady state simulations. For the steady-state simulation of groundwater flow at the two Cimarron sites the recharge package was applied uniformly over the entire model domains at a constant rate. Since the model was steady-state and no losses of groundwater were assumed, the recharge rate, determined through model calibration, was expected to be similar to the rate indicated in the CSM-Rev 01 (ENSR, 2006) of 8% of precipitation or 2.4 in/yr.

#### 3.3.2 Surface Water/Groundwater Interactions

The Cimarron River is included in each of the models, as it is the regional groundwater discharge point. The Cimarron River is represented in the model domain using the MODFLOW River Package. The channel bed elevations at these sites were linearly interpolated from the gage datum of 999.2 feet at the USGS stream gage at Dover, OK (#07159100) located about 30 miles upstream, and the gage datum of 896.5 feet at the USGS stream gage at Guthrie, OK (#07160000) located about 10 miles downstream. The resulting value of 922.8 feet was assigned as the river bed elevation for both the BA #1 and WA areas. The surface water elevations were assumed to be 2 feet higher than the bed elevations at both locations resulting in a constant water surface elevation of 924.8 feet.

Depending on the difference between the measured river surface elevation and the predicted groundwater elevation in the cells adjacent to the river cells, the river will either be simulated to lose water to the aquifer or gain water from the aquifer. Based on the topography and hydrogeology of the site, the streams and rivers are generally expected to gain groundwater. The rate of water gain or loss from the Cimarron River is represented in MODFLOW using three parameters that include (1) the river bed area, (2) the channel bottom thickness, and (3) the hydraulic conductivity of the river bed sediments. While the product of the hydraulic conductivity

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and the riverbed area divided by the bed thickness results in a conductance term (C), this value was established through model calibration rather than being calculated, due to a lack of site-specific information.

Model cells that were assigned river properties are shown with blue dots on Figures 9 and 12 for the BA #1 and WA models, respectively.

The reservoir south of the BA#1 area was incorporated into the General Head Boundary condition as described below. None of the other intermittent surface waters, such as the drainageways, were included in the model, as their influence on the groundwater system is local and sporadic.

#### 3.3.3 Upgradient General Head Boundary

The upgradient boundaries for both the BA #1 and the WA area were represented as a General Head Boundary (GHB) in MODFLOW. Unlike a constant head boundary, which holds the water level constant and offers no control over the amount of water passing through the boundary, the GHB offers a way to limit the supply of upgradient water entering the model domain. This limitation provides a better representation of the system that is limited by the transfer of groundwater from the upgradient aquifer to the upgradient model boundary, and conductivity. The head assigned to the GHB defines the groundwater level at the boundary and largely dictates the downgradient water levels and the gradients. The conductivity of the GHB defines the permeability of the boundary and controls the amount of water that can pass through the boundary. Water can pass into or out of the model domain through the general head boundary, depending on the relative hydraulic heads.

#### 3.3.4 Underlying General Head Boundary

In addition to representing the upgradient boundary using a GHB, the upward hydraulic gradient from the underlying bedrock described in the site CSM-Rev 01 (ENSR, 2006) can also be represented this way. Because the Cimarron River is a major discharge area, the discharge of deep groundwater through the alluvium and into the river is an expected phenomenon. To simulate this upward flow of groundwater a GHB was used in both model domains to varying degrees to represent a higher water level at depth than in the alluvial aquifer. The volumetric flow rate of water into the alluvial aquifer was limited by adjusting to a relatively low conductance during the calibration process.

Some of the model cells that were assigned general head boundary properties are shown with brown dots on **Figures 9** and **12** for the BA #1 and WA models, respectively. Other cells were also assigned this boundary type, but are not visible in this view of the model domain. Basically, all cells at the base of the models and at the southern limit were assigned GHB boundaries.

#### 3.4 Summary of Modeling Approach

Model parameters used to setup the groundwater models for the BA #1 and WA areas were developed from measured information and from interpretations made based on material characteristics. These parameters largely control the predictions made by the groundwater and pathline models.

## 4.0 MODEL CALIBRATION

#### 4.1 Calibration Approach

Once the model domain was established, the model grid developed, and the model inputs entered, the calibration process began. The calibration process is a quality control step used to provide a frame of reference for evaluating simulation results. The calibration of groundwater models proceeds by making adjustments to the boundary conditions and the hydraulic conductivities until the simulated groundwater elevations adequately match the observed groundwater elevations. In addition to comparing model predicted elevations to observed elevations, a good calibration was also dependent on capturing gradients and flow directions such that simulated flow paths were congruent with inferred flow paths from U concentration data. The overall regional water balance was also considered. The following sections (4.1.1, 4.1.2, and 4.1.3) discuss the three ways the model calibration was evaluated.

#### 4.1.1 Measured and Predicted Water Levels

Comparing model predicted groundwater levels with measured levels is a rigorous, obvious, and straightforward way to evaluate the ability of a groundwater model to meet the project objectives. In steady-state models the groundwater predictions are generally compared with representative average groundwater water levels at several locations around the site. Since a single round of groundwater elevation measurements may not be representative of the average water table due to seasonal variations, it is preferable to use the results of several temporally distributed water level surveys to provide a better representation of the average water table.

The water level data used to evaluate the BA #1 and WA groundwater model calibrations was from each of the wells/boreholes used to develop the models. Water levels from each of four surveys including September 2003, December 2003, during August and September of 2004, and in May of 2005 were averaged to arrive at a set of average water levels for comparison to model predictions. **Table 2** summarizes the average groundwater elevations from four sampling rounds. This data set served as the calibration data set.

During the calibration, the model calibration parameters were adjusted in order to reach a quantitative target: the mean absolute difference between the predicted and measured water levels within 10% of the measured site-wide groundwater relief.

For the BA #1 area, the maximum groundwater elevation was 950.96 feet at Well 02W51 and the minimum elevation was 925.37 feet at Well 02W17; therefore, the calibration target is 10% of that difference or approximately 2.6 feet.

For the WA area, the maximum groundwater elevation in the model domain is 931.75 feet (at T-63) and the minimum elevation is 930.35 feet (at T-82), then the calibration target of 10% of the difference is approximately 0.14 feet.

In addition, it is recognized that the two models, although developed separately, must be consistent with each other. That is, values for inputs between the two models cannot be significantly different from each other.

#### 4.1.2 Volumetric Flow-Through Rate

Both of these models are dominated by the boundary conditions, that is, the boundary conditions have a strong influence on the model results. Therefore, in addition to simply matching steady-state water levels in the model domain by successive adjustment of aquifer properties and boundary conditions, comparing estimated steady-state flow-through rates was also considered as a means for evaluating calibration. There are a variety of ways to estimate a flow-through rate based on drainage area, baseflow, recharge, etc. This

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section discusses one of the methods using one set of input values. Though not a rigorous calibration target, it is important to be mindful of the water budget, or flow-through volumes for the models. Therefore, the estimate of flow-through rate presented here is intended to provide a general, again not rigorous, frame of reference by which to evaluate the calibration.

One estimate of the steady-state flow rate through each model domain was made by multiplying an estimate of rainfall recharge by the total drainage area to arrive at an annual recharge rate. This recharge volume represents the water that enters the groundwater system over the entire watershed -- not just the model domain and/or immediate site vicinity. However, this entire volume will pass through the model domain on its way to the regional discharge boundary - The Cimarron River. During the calibration process, the model boundary conditions were adjusted in consideration of this calculated annual flow-through rate. Note that in making this estimate, it is assumed that the surface water divides as represented from the topographic contours coincide with groundwater divides.

For the BA #1 area, the total drainage area upgradient and including the model domain is approximately 2.1 square miles. Based on an annual recharge rate of 2.4 in/yr over the BA #1 watershed, the total flow through rate for the BA #1 model domain was estimated to be approximately 32,000 ft<sup>3</sup>/day. For the WA area, the total upgradient drainage area and model domain is 0.32 mi<sup>2</sup> resulting in an estimated total flow through rate of the WA model domain of approximately 5,000 ft<sup>3</sup>/day.

During the calibration process, adjustments of hydrogeologic characteristics and boundary conditions were made in light of these estimates of flow. Comparing these estimates with the calibrated results provides one way to evaluate calibration.

#### 4.1.3 Plume Migration

In addition to accurately reproducing water levels and volumetric flow rate through the groundwater system, a pathline analysis was conducted to demonstrate an accurate representation of groundwater movement in the system. This was especially important for BA #1 area where there is ample water quality data by which to infer flow paths. In the case of the BA #1 site, the current distribution of the U plume was compared to predicted particle pathlines developed from particles initiated in the original U source area. By demonstrating that particles seeded in the source area would effectively follow the path of a measured plume, the pathline simulation can illustrate the accuracy of the model in representing flow directions and groundwater gradients.

For the BA #1 area, the MODPATH model was used to predict the fate of particles seeded at the approximate location of the initial U source. The results of the steady-state MODFLOW model were used as the groundwater flow driver for the MODPATH simulation and the predicted paths of the particles were compared with the plume map for U at the BA #1 area. For the simpler WA model, a pathline comparison was not required.

#### 4.2 Calibration Parameters

For both of these models there are strong boundary conditions. These are the general head boundary at the upgradient (south) edge of each of the models to simulate water entering the model domain from the sandstones, the general head boundary along the bottom of the models to simulate flow up from the sandstone into overlying soils, and the river where groundwater discharges. Flow and elevations in the model are dominated by the flow entering the model through the general head boundaries and flow leaving the model through the river. When models are so strongly influenced by these boundary conditions, calibrated solutions can result from a variety of non-unique combinations of boundaries and hydraulic conductivities.

Early in the calibration process, adjustments to hydraulic conductivity, recharge rate, and river conductance were made to simulate groundwater elevations similar to measured groundwater elevations. Once these initial adjustments were made, calibration focused on adjusting the head and conductance of the general head boundaries.





The general head boundary uses two variables to control the transfer of water across a model boundary including a water level (head) and a conductance term. The assigned groundwater elevation indicates the pressure head along the boundary. This is essentially the starting point for predicted heads along the boundary and adjacent water levels in the model are either higher or lower depending on boundary conditions and the additions or losses of water elsewhere within the model domain. The rate at which water enters the model through the general head boundary is controlled by the conductance term. A high conductance indicates a relatively limitless supply of water to the aquifer when the water table downgradient of the boundary is stressed and a low conductance indicates a limited supply of water to the aquifer. Limiting the conductance is of particular importance if only a portion of the total aquifer is included within the model domain and it is unrealistic to assume that the upgradient supply of water is limitless.

Each groundwater model was re-run several times with successive adjustment to the calibration parameters (general head boundaries) until the models were satisfactorily calibrated.

#### 4.3 Calibration Results

In the following sections the results of each model's calibration is discussed with respect to the calibration targets discussed in Section 4.1.

#### 4.3.1 BA #1

In the calibration process, hydraulic conductivity, recharge, and river elevation and conductance were adjusted; the final calibration values are summarized in **Table 3**. The other adjusted parameters were the elevation and the conductance of the general head boundaries both at the back edge and on the bottom of the model. **Table 3** also includes the calibrated values for these inputs.

Through successive adjustment of the general head boundary parameters, the mean absolute error (MAE) between the measured and predicted water levels was calculated to be 1.2 feet. This value is much less than the 2.6 feet which is 10% of the total water table relief at the site; this indicates an acceptable model calibration. Additional adjustments to the shape and orientation of the underlying general head boundary were made to simulate flow paths (using MODPATH) consistent with that which is inferred from the concentrations downgradient of the burial area. Finally, adjustments to the general head boundary were also made to simulate an approximate flow-through volume consistent with what is expected based on the drainage area size and recharge rate. The following are calibration results that indicate transfer rates of groundwater through the BA #1 model domain.

- Calibrated transfer rate of water from the model domain to the Cimarron River is 19,100 ft<sup>3</sup>/day.
- Calibrated inflow rate from upgradient sandstone/mudstone units to the model domain is 16,900 ft<sup>3</sup>/day.
- Recharge rate to the aquifer is 1,200 ft<sup>3</sup>/day.

The difference between the total inflow (18,100 ft<sup>3</sup>/day) and the total outflow (19,100 ft<sup>3</sup>/day) equals ~1,000 ft<sup>3</sup>/day, which represents less than a 5% error in the water balance and is considered acceptable. **Figure 13** summarizes the calibration results showing the measured versus predictefd groundwater elevations, the static simulated groundwater contours and a comparison of the particle pathlines originating from the burial area with the plume map as drawn from concentrations measured in August 2004. In the calibration process, targets with the best data (i.e., water level, flow path) are given preference over targets with less data (i.e., flow through rates). Thus, a good match of water levels, flow paths, and gradients is achieved, but justifiably at the expense, somewhat, of the flow-through match. The total calibrated flow through value above is less than the calculated flow-through rate based on drainage area and recharge presented in **Section 4.1.2**.

One of Arcadis' bioremediation design objectives is to estimate flux (dissolved oxygen) through the plume. Based on the calibrated flow-through rates, ZoneBudget (Harbaugh, 1990) was used in conjunction with the



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MODFLOW output to calculate the flux through the plume areas only. The 2004 plume area for the BA #1 area is depicted on Figure 4-11 (CSM, Rev.1, ENSR, 2006); the plume was assumed to extend to the bottom of model Layer 7, which coincides with the lowest elevation where concentrations over 180 pCi/L were detected in August 2004. The flux was estimated at 19 gpm.

#### 4.3.2 WA area

In the calibration process, hydraulic conductivity, recharge, and river elevation and conductance were adjusted and the final calibration values are summarized in **Table 4**. The other adjusted parameter was the elevation and the conductance of the general head boundaries both at the back edge and on the bottom of the model. **Table 4** also includes the calibrated values for these inputs.

Conceptually the interaction of the sandstones with the alluvial materials should be very similar regardless of model area. That is, the conductance of Sandstone B and Sandstone C should be the same for the BA #1 model and for the WA model. Because the BA #1 model is so much more complicated, it was calibrated first and then the calibrated conductance values were applied to the WA model. In effect, calibration of the WA model relied almost exclusively on changing the elevations assigned to the general head boundaries.

Through successive adjustment of the general head boundary elevation the average absolute error between the measured and predicted water levels was determined to be 0.31 feet. This value is more than the target of 0.14 feet, which is 10% of the total water table relief at the site. When the gradient is very flat as it is in this case measured groundwater elevation differences over short distances can be very difficult to simulate, especially when spatial variations in hydraulic conductivity are not considered. Furthermore, because the calibration data set is averaged over several rounds of data, seasonal differences may be more apparent.

The flow paths generated based on the MODFLOW head field and the MODPATH model indicates that groundwater flow paths are generally from the south to the north, consistent with the conceptual model and with the inferred flow paths based on U concentrations from August 2004.

The following are calibration results that indicate transfer rates of groundwater through the WA area model domain.

- Calibrated transfer rate of water from the aquifer to the Cimarron River is 57,000 ft<sup>3</sup>/day.
- Calibrated inflow rate from upgradient sandstone/mudstone units to the model domain is 54,300 ft<sup>3</sup>/day.
- Recharge rate to the aquifer is 2,600 ft<sup>3</sup>/day.

The difference between the total inflow (56,900 ft<sup>3</sup>/day) and the total outflow (57,000 ft<sup>3</sup>/day) equals ~100 ft<sup>3</sup>/day, which represents less than a 1% error and is considered acceptable. **Figure 14** summarizes the calibration results showing the measured versus predicted groundwater elevations and the static simulated groundwater contours. In the calibration process, targets with the best data (i.e., water level, flow path) are given preference over targets with less data (i.e., flow through rates). Thus, a good match of water levels, flow paths, and gradients is achieved, but justifiably at the expense, somewhat, of the flow through match. The total flow through value presented above is more than the flow-through rate calculated based on drainage area and recharge presented in **Section 4.1.3**.

One of Arcadis's bioremediation design objectives is to estimate flux (dissolved oxygen) through the plume. Based on the calibrated flow-through rates, ZoneBudget (Harbaugh, 1990) was used in conjunction with the MODFLOW output to calculate the flux through the plume areas only. For the WA model the total U distribution was assumed to be an area that extends from near the base of the escarpment northward toward the Cjmarron River, apparently originating where the western pipeline entered the alluvium north of the former Sanitary Lagoons. Uranium concentrations that exceeded 180 pCi/L in August 2004 are presented in Figure 4-15, CSM-Rev 01, ENSR, 2006). This impacted area extended only to the bottom of model Layer 1 since there were no concentrations of U detected in the sandstone (i.e., Layer 2). The flux for this plume area was 31 gpm.

#### 4.3.3 Discussion

In addition to evaluating the calibration of the model from the standpoint of quantitative targets, another way to evaluate the model is how well it aligns with the conceptual model. Because there is often aquifer test data (i.e., slug tests, pumping tests), comparison of calibrated and measured hydraulic conductivities is a good way to evaluate how well the model corresponds with the conceptual model. **Table 1** summarizes the measured hydraulic conductivities and **Tables 3** and **4** summarize the calibrated hydraulic conductivities. **Tables 3** and **4** also summarize the calibrated inputs for the river, recharge, and general head boundaries.

There are no measured hydraulic conductivity data for Fill, Silt, Clay, and Sandstone A. For Alluvium, the measured hydraulic conductivity values range from about 20 to more than 275 ft/day. Pumping tests generally provide a better estimate of aquifer hydraulic conductivity than slug tests. Focusing on just pumping test results, the hydraulic conductivity ranges from about 120 to about 275 ft/day. The calibrated value, 235 ft/day, is consistent with this range.

Slug test data was also available from four wells screened in Sandstone B. The hydraulic conductivity results ranged from approximately 0.1 to 2 ft/day. The calibrated value for Sandstone B was 5 ft/day. One slug test was completed in Sandstone C and the result was 0.2 ft/day, less than the calibrated value of 3 ft/day. In both instances, the calibrated values are higher than the measured. Values derived from pump tests and values from calibrated models are often higher than slug test data. The locations of slug tests represent only a tiny fraction of each Sandstone B and C. During model calibration, the values are adjusted upward and may ultimately be more representative of site conditions than just a few data points may indicate.

In some instances, the hydraulic conductivities were adjusted upward to provide numerical stability to the model. The model can become numerically unstable when there are large changes (in hydraulic conductivity, groundwater elevation, etc) over short distances. In the BA#1 model this happens, for instance where clay (hydraulic conductivity less than 1 ft/day) comes into contact with sand (over 200 ft/day). This instability can be mitigated by smoothing those contrasts. Sometimes this is done at the expense of making a perfect match with measured data. As long as the adjustments are consistent with the conceptual model, the conceptual understanding of how different soils transmit water, and are mindful of the project objectives, smoothing typically does not impact simulations. The model will simulate this general behavior whether the contrast is 100 or 1000 times different. This change was evaluated in the sensitivity analyses, discussed below.

In the absence of data for fill, silt, clay and Sandstone A, estimates were made based on literature values and on qualitative site observations. Adjustments to these values were made during the calibration to encourage a good match of simulated and measured groundwater elevation and to encourage numerical stability.

**Figures 13** and **14** summarize the calibration results. The graph shows the measured versus predicted groundwater elevations. Each point represents the groundwater elevation at a particular well. The closer the point is to the line, the less difference there is between the simulated and observed groundwater elevation. These figures also show the simulated groundwater contour map. Overall these match well for both models. For the BA#1 model, Figure 13 also shows a comparison of a particle pathline originating from the Burial Area with the plume map as drawn from U concentrations measured on August 2004. As discussed above, these pathlines are a good match for the groundwater flow paths suggested by the distribution of U in groundwater.

#### 4.3.4 Summary of Calibration Results

Three calibration targets were set as objectives prior to model calibration: achieve a good match between simulated and measured groundwater elevations and gradients, achieve a good match with the site conceptual model, and yield relatively consistent correlation of water budget estimates. For the most part, the first two objectives were achieved without difficulty. The measured and simulated groundwater elevations are in

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concert and especially for the BA#1 model, the simulated flow directions agree with flow directions indicated by U concentrations. Discrepancies between measured and simulated groundwater elevations, flow paths, and water budgets are explainable and can be accounted for when interpreting simulation results. Ultimately, the discrepancies in estimated flow-through volumes and simulated flow-through volumes are explained by ranges in recharge to and discharge from the site as well as uncertainties inherent in the modeling.

## 4.4 Sensitivity Analysis

In order to characterize the effects of uncertainty in the modeling parameters (recharge, hydraulic conductivity, and general head boundaries) on model predictions, sensitivity runs were conducted. In these runs, each parameter was varied from the base run (calibrated model). Differences were noted and these differences help in understanding the range of possible predictions, and how uncertainties in these parameters may affect model predictions.

Rainfall recharge, hydraulic conductivity and the general head boundary were the three primary variables tested in the sensitivity evaluation. Rainfall recharge has a direct impact on the amount of water moving through the aquifer and an impact on the amount of water that can be withdrawn from an aquifer. The conductivity is the fundamental parameter describing how effectively groundwater is transmitted in an aquifer. The sensitivity evaluation was focused on the hydraulic conductivity of the sand. The upgradient head boundary and the aquifer bottom boundary in the model of the BA #1 area were both represented using the general head boundary (GHB) in MODFLOW. This boundary fixes a water level at a specific group of cells in a model domain and uses a conductance term to facilitate the calculation of the volume of water that can be moved across the general head boundary. Like recharge, the general head boundary has a significant effect on the hydrologic budget and can largely control the amount of water entering or leaving the model domain. Therefore the models' sensitivity to this parameter was evaluated also.

One parameter was adjusted to complete the sensitivity analysis of the BA #1 area to enable this already complex and numerically sensitive model to iterate to a solution under the range of conditions imposed by the sensitivity analysis. During the sensitivity analysis, the horizontal hydraulic conductivity of the clay was increased from the 0.5 ft/day that was used during the model calibration, to 10 ft/day. By increasing the hydraulic conductivity of the clay, the gradients were decreased resulting in a smoother transition across adjacent model cells and therefore, a more stable model.

With the parameters selected for the sensitivity analysis a sequence of model scenarios were developed and run to evaluate the effect of varying the magnitudes of the selected parameters on the calibration. The results are as follows.

For the BA #`1 area, with the increased hydraulic conductivity of the clay, calibration results were marginally different results then when the original calibrated clay conductivity value was used.

Modification of the recharge rate by a factor of 50% and 200% resulted in only minor changes to the steadystate head calibration. This is largely because of the relatively small component of the hydrologic budget that surface recharge represents in the calibrated model, which is less than 10% of the overall budget.

Changing the hydrologic conductivity in the sand aquifer by a factor of 50% and 200% resulted in a relatively minor change to the steady state calibration. Small differences in the Mean Absolute Error (MAE) between the calibration run and the sensitivity runs are primarily because the Mean Absolute Error value is calculated using several wells outside of the sand aquifer that were relatively unaffected by the change and because the flow regime is so strongly controlled by the recharge and discharge boundary conditions.

Changes made independently to the head and the conductance of the subsurface general head boundary by factors of 50% and 200% resulted in fairly substantial changes to the steady state calibration. This is because water flowing into the model through the subsurface general head boundary represents a significant portion of

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the total water budget in the model. Both the elevation and the conductance are strong controllers of how much water is permitted to enter the model, thus have obvious impacts to model predictions.

## 4.5 Uncertainties and Assumptions

In order to fully understand the predictions and simulations, it is important to understand the factors that contribute to model uncertainty. Addressing these uncertainties allows users to understand and interpret the results of the simulations.

### Flow-Through Volumes

As discussed above, estimates of flow-through volume were made based on drainage area and recharge rates. Comparing these estimates to simulated flow-through volumes was one way calibration was evaluated. Other methods can also be used to estimate flow-through volumes. For instance, one method varies recharge rates based on the ranges of annual precipitation rates of 24 inches, 30 inches, 32 inches, and 42 inches (CSM-Rev 01, ENSR, 2006). Another method uses streamflow measurements collected by the USGS on the Cimarron River at Dover (upstream) and Guthrie (downstream) and basin scaling to estimate the rate of groundwater discharge from the Western Alluvial area and the Burial Area #1. These approaches indicated that flow-through volume estimates may range over more than an order of magnitude depending on the methodology for making the estimate. In turn, depending on the technique to calculate flow-through volumes, different groundwater fluxes through the plume areas may be calculated.

#### Equivalent Porous Media Assumption

The MODFLOW model assumes that flow is through a porous media. That is, MODFLOW is designed to model groundwater flow through unconsolidated materials. MODFLOW is often used to model consolidated soils and bedrock, but flow through these materials may be governed by fractured flow, not porous media flow. The presence of fractures may greatly affect the direction and rate of groundwater flow especially on a local scale. For example, if the local groundwater flow system is dominated by a single fracture, the orientation of the fracture will control the direction of travel. Depending on the fracture's size, groundwater velocity through the fracture may be higher than would occur in more diffuse flow through a porous media even if the flux is the same. There is no evidence that groundwater flow and contaminant transport at the Cimarron Site are necessarily controlled by fracture flow. However, there may be local effects associated with fracturing the bedrock units. It is beyond the capabilities of the current model to accurately predict the time of travel through fractures in the consolidated soils or bedrock. Travel times through the consolidated units (sandstones and mudstones) can be calculated by MODPATH based on the assumption that the consolidated units are an equivalent porous media. The use of equivalent porous media assumptions are best suited for predictions over the scale of the model and may not provide accurate predictions local to a fracture or fracture system. Despite this uncertainty, groundwater flow is still likely to coincide generally with the surface water catchments and groundwater will discharge to the surface waters located within and adjacent to the site.

#### Steady-State Assumption

If the model should be used to simulate either groundwater extraction or injection, it should be noted that the groundwater model assumes that steady-state is reached instantaneously. In fact, there will be some time that will elapse before steady-state will be reached. Simulated pumping or injection also assumes that groundwater will be extracted from or injected into the entire cell saturated thickness. In fact, depending on where the well screen is placed and where the pump is set, this may not hold true. Simulated pumping or injection also occurs throughout the entire 10 foot by 10 foot cell. For these reasons, pumping and injection scenarios implemented in the field may result in drawdown and flow rates different from what has been predicted. Because the model accurately represents the conceptual model and overall observed flow rates, directions, and gradients, overall capture zones should be relatively accurate. As field data become available, they may be used to update and refine the model.

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### Fate and Transport Issues

It should be noted that this application is a flow model and, as such, only considers the movement of water in the subsurface. Constituents dissolved in groundwater may be subject to processes that result in migration that cannot be explained exclusively by groundwater velocity (i.e., advection).

Groundwater velocities generated by the model and presented in the CSM, Rev.1 (ENSR, 2006) require input of a value for porosity for each of the geologic materials. There are no site-specific data on porosities, and they are likely to be very variable. Literature values were used. It should be recognized that the calculated velocities are directly dependent on these input values of porosity. Changes to the porosity values could potentially change estimate velocities by more than an order of magnitude.

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# 5.0 SUMMARY AND CONCLUSIONS

Numerical groundwater models for the BA #1 and the WA areas have been conceptualized, developed, and calibrated to provide tools by which groundwater flow can be evaluated and changes to groundwater flow can be assessed as different remedial alternatives are simulated. In particular, in consideration of a bioremediation approach, the model may be used design scenarios for injection of reagents that will enhance stabilization of U and to demonstrate the permanence of uranium stabilization in groundwater.

The objective was achieved by developing and calibrating the numerical models to include key data that characterize groundwater flow at the site consistent with the CSM-Rev 01 (ENSR, 2006). Specifically, the BA #1 model domain included portions of the uplands at the site, which are underlain by a series of sandstone and mudstone layers, the transition zone, which is characterized by silts and clays underlain by sandstone and mudstone, and the alluvial valley where the geology is predominantly sand with smaller fractions of silt and clay. The BA #1 model was bounded on the south, in part, by the reservoir and on the north by the Cimarron River. The WA model included only the alluvial materials (sands, silts, clay) from the escarpment that forms the northern edge of the uplands to the Cimarron River. In the WA area, the alluvial materials are underlain by sandstone. Upgradient sandstones in both models are assumed to contribute groundwater to the alluvial soils and overlying sandstone and mudstone units. The Cimarron River is a discharge boundary to which all modeled groundwater flows.

Calibration targets included measured groundwater elevations, flow budgets, and flow path data. The flow models achieved good calibration to the observed groundwater elevation data, to the estimated water budgets, and to observed flow path trajectories. Discrepancies between observed and predicted elevations were reasonable. The simulated water table configuration for each model was consistent with flow paths suggested by observations of U concentrations. Overall hydrogeological concepts as presented in the Conceptual Site Model, Rev 01 (ENSR, 2006) were captured by the numerical models. A sensitivity evaluation established that the model simulations will be most sensitive to boundary conditions, especially the recharge from upgradient sandstone units. Uncertainties, especially associated with boundary conditions, are important when interpreting and using model predictions in remedial designs.

Ultimately, the resulting numerical models have captured key hydrologic and geologic features that shape the groundwater flow directions, patterns, and rates, thus satisfying the objective to provide useful tools to consider remediation design options. For instance, groundwater extraction can be simulated to create capture zones that include areas of high U concentration. Injection scenarios can also be simulated to ensure adequate distribution of reagents. Even the calibrated model itself can yield valuable information about groundwater flow directions and rates. For instance, the design of the bioremediation system requires estimates of groundwater flux to the plume area, which can be extracted from the model. The calibrated BA #1 model indicates that there are 19 gpm to the plume area. The calibrated WA area model indicates that there are 31 gpm to the impacted area. ARCADIS will use the model further to help design the bioremediation effort; their uses of the model will be documented in their work plan.

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## 6.0 REFERENCES

Adams, G.P. and D.L. Bergman. 1995. Geohydrology of Alluvium and Terrace Deposits, Cimarron River from Freedom to Guthrie, Oklahoma. USGS WRI 95-4066.

Cimarron Corporation, 2003. Burial Area #1 Groundwater Assessment Report for Cimarron Corporation's Former Nuclear Fuel Fabrication Facility, January.

Freeze, R.A. and J. A. Cherry. 1979. Groundwater. Englewood Cliffs, NJ: Prentice-Hall.

Harbaugh, Arlen W., 1990. A computer program for calculating subregional water budgets using results from the U.S. Geological Survey modular three-dimensional ground-water flow model: U.S. Geological Survey Open-File Report 90-392, 46 p.

MacDonald, Michael G. and Arlen, W. Harbaugh. 1988. A Modular Three-Dimensional Finite-Difference Ground-Water Flow Model. U.S. Geological Survey Open File Report 83-875.

Pollock, David W. 1994. User's Guide for MODPATH/MODPATH-PLOT, Version 3:A particle tracking postprocessing package for MODFLOW, the U. S. Geological Survey finite-difference ground-water flow model. U. S. Geological Survey Open-File Report 94-464.

Weaver, J.C., 1998. Low-Flow Characteristics and Discharge Profiles for Selected Streams in the Cimarron River Basin, Oklahoma. U.S. Geological Survey Water-Resources Investigations Report 98-4135.

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# Tables

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### Table 1 Summary of Slug and Aquifer Test Results Cimarron Corporation Crescent, Oklahoma

			Hydraulic Conductivity (cm/s)								
			Analysis Methodology								
					Pumping		_				
					Test -		Pumping				
		Slug Test			Jacob		Test -		Cooper-		
		Bouwer &	Slug Test	Sieve	Straight	Pumping	distance-	Butler and	Bredehoeft-	Geometric	Geometric
Geology	Well	Rice	Hvorslev	Analysis	Line	Test - t/t'	drawdown	Garnett	Papadopulos	Mean (cm/s)	Mean (ft/day)
Alluvium	TMW-09***	6.01E-03	1.20E-03							2.69E-03	7.61
	TMW-13	6.99E-02	6.20E-02							6.58E-02	186.61
	02W2*	1.92E-05								1.92E-05	0.05
	02W10*	3.36E-04	2.80E-04							3.07E-04	0.87
	02W11***	3.24E-03	4.00E-03	1.70E-03						2.80E-03	7.95
	02W15	1.09E-02	1.80E-02	1.00E-02						1.25E-02	35.49
	02W16	3.66E-02	3.90E-02	1.10E-02						2.50E-02	70.98
	02W17	3.25E-02	6.00E-02	6.00E-03						2.27E-02	64.35
	02W22				8.90E-02					8.90E-02	252.28
	02W33	1.30E-02	1.90E-02	1.70E-03						7.49E-03	21.23
	02W46*	3.56E-05	1.37E-05							2.21E-05	0.06
	02W56**	4.20E-02	7.10E-02	1.70E-02	8.30E-02	8.30E-02	8.60E-02			5.58E-02	158.04
	02W58		•		9.60E-02	8.60E-02				9.09E-02	257.56
	02W59	1.40E-02	3.30E-02		9.60E-02	8.00E-02		•		4.34E-02	123.03
	02W60				1.10E-01	8.60E-02				9.73E-02	275.70
	02W61	2.20E-02	2.30E-02		1.10E-01	8.90E-02				4.72E-02	133.73
	02W62							2.80E-02		2.80E-02	79.37
	TMW-24							4.13E-02		4.13E-02	117.07
Sandstone B	TMW-01	6.35E-05	2.70E-05							4.14E-05	0.12
	TMW-20	9.97E-04	4.10E-04							6.39E-04	1.81
	02W40								5.50E-04	5.50E-04	1.56
	02W51	7.10E-05	2.39E-05							4.12E-05	0.12
Sandstone C	02W48		7.85E-05							7.85E-05	0.22

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### Notes:

All data presented is summarized from the Burial Area #1 Groundwater Assessment Report (Cimarron Corporation, 2003).

\* Clay present at or near this well; data excluded from calculating ranges, mean.

\*\* Pumping Well

\*\*\* Some clays/silts present in well screen; data excluded from calculating ranges, means.

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Cumment	9/16/03	12/16/03	Aug/Sep 04	5/24/05	Avg WL
Summary	Water Level	Water Level	Water Level	Water Level	Elevation
	(feet)	(feet)	(feet)	(feet)	(feet)
**1206				n/a-SEEP	·
**1206				n/a-SEEP	
**1208				n/a-SEEP	
**1208				n/a-SEEP	
1311	965.48	964.83	966.02	962.70	964.76
1312	962.66	963.64	964.48	964.66	963.86
1312				964.66	964.66
1313	963.60	963.19	964.04	963.97	963.70
1314	944.02	943.67	944.14	944.57	944.10
1315R	932.31	934.73	935.46	936.45	934.74
1315R				936.45	936.45
1316R	931.57	932.89	936.84	936.12	934.35
1319 A-1	969.86	969.63	970.37	969.88	969.93
1319 A-2	969.74	969.49		969.79	969.68
1319 A-3	968.46	968.56	968.45	968.35	968.45
1319 B-1	946.73	947.13	948.35	pumping	947.40
1319 B-1				pumping	
1319 B-2	947.73	948.25	949.44	950.06	948.87
1319 B-3	946.67	947.12	948.37	949.02	947.79
1319 B-4	946.18	946.52	947.84	948.54	947.27
1319 B-5	945.61	944.87	946.24	947.37	946.02
1319 C-1	942.27	943.81	946.01	pumping	944.03
1319 C-1				pumping	·
1319 C-2	939.80	940.69	941.94	941.50	940.98
1319 C-3	939.06	939.78	941.07	940.85	940.19
1320	967.04	966.58	968.34	968.20	967.54
1321	935.97	936.45	937.74	938.07	937.06
1322	967.97	966.43	967.95	968.48	967.71
1323	941.84	942.49	943.29	944.19	942.95
1324	968.10	967.45	969.20	969.28	968.51
1325	971.25	970.62	972.44	972.31	971.66
1326	970.85	970.49	971.45	971.54	971.08
1327	966.02	965.95		966.62	966.19
1327B	966.05	965.55	966.01	966.63	966.06
1328	948.85	950.79	950.71	?	950:12
1329	968.26	967.97	968.00	968.62	968.21
1330	967.97	967.72	969.37	970.07	968.78
1331	965.80	965.30	967.02	966.63	966.19
1332	940.00	940.47	941.75	942.43	941.16
1333	967.92	967.16	968.48	969.03	968:15
1334	966.51	966.58	968.20	967.72	967.25
1335A	969.81	969.07	970.78	970.45	970.03
1336A	959.65	959.57	960.53	960.08	959.96
1337	965.90	965.48		966.95	966.11



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Summon	9/16/03	12/16/03	Aug/Sep 04	5/24/05	Avg WL
Summary	Water Level	Water Level	Water Level	Water Level	Elevation
	(feet)	(feet)	(feet)	(feet)	(feet)
1338	943.71	943.62	945.25	939.32	942.98
1339	951.68	952.74	938.46	955.13	949.50
1340	961.49	961.42	-	962.42	961.78
1341	936.75	936.75		939.39	937.63
1342	929.95	930.13		930.40	930.16
1343	928.37	928.57		929.40	928.78
1344	925.84	926.22		928.62	926.89
1345	933.74	933.63	935.32	936.30	934.74
1346	937.60	937.31	938.81	939.22	938.23
1347	965.13	964.47		965.96	965.18
1348	975.27	975.26	977.96	977.50	976.49
1348			977.96	977.50	977.73
1349	971.74	971.23	973.71	973.83	972.63
1349			973.71		973.71
1350	974.98	974.69	977.08	980.01	976.69
1350			977.08		977.08
1351	969.93	969.78	971.33	970.80	970.46
1351			971.33		971.33
1352	966.49	966.06	967.89	967.50	966.99
1352			967.89	967.50	967.70
1352			967.89		967.89
1353	985.70	988.00	988.31	988.04	987.52
1353			988.31		988.31
1354	965.5 <u>1</u>	965.24	967.00	966.46	966.05
1354			967.00		967.00
1355	967.64	967.01	968.71	968.85	968.05
1355	1		968.71		968.71
1356	968.83	968.24	969.38	969.57	969.00
1356			969.38	969.57	969.47
1357	969.51	968.88	970.72	970.47	969.89
1357			970.72		970.72
1358	971.26	970.53	972.67	972.49	971.74
1358			972.67	972.74	972.71
1359			972.79		972.79
1359			972.79	974.82	973.80
1360			974.88		974.88
1360			974.88		974.88
02W01	930.56	932.92	934.49	934.51	933.12
02W02	928.87	930.72	932.30	932.25	931.03
02W03	926.43	927.99	930.33	930.40	928.79
02W04	927.64	928.09	929.64	929.81	928.79
02W04		·		929.81	929.81
02W05	927.43	927.86	929.56	929.77	928.65
02W06	927.37	927.77	929.56	929.78	928.62

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## Table 2

Summary of Groundwater Elevation Data used for Calibration Cimarron Corporation Crescent, Oklahoma

	9/16/03	· 12/16/03	Aug/Sep 04	5/24/05	Avg WL
Summary	Water Level	Water Level	Water Level	Water Level	Elevation
ן טו	(feet)	(feet)	(feet)	(feet)	(feet)
02W07	927.53	927.98	929.53	929.76	928.70
02W07.				929.76	929.76
02W08	927.57	928.02	929.57	929.80	928.74
02W08				929.80	929.80
02W09	933.09	935.51	936.32	936.57	935.37
02W10	931.73	934.39	935.54	935.62	934.32
02W11	927.27	927.85	929.57	929.73	928.61
02W12	927.29	927.83	929.69	929.71	928.63
02W13	927.41	927.91	929.71	929.89	928.73
02W14	927.27	927.77	929.50	929.70	928.56
02W15	927.34	927.81	929.60	929.80	928.64
02W16	927.37	927.81	929.50	929.77	928.61
02W17	914.25	927.87	929.55	929.80	925.37
02W18	927.30	927.75	929.47	929.69	928.55
02W19	927.56	927.95	929.47	929.41	928.59
02W19				929.41	929.41
02W20	936.42	937.88	938.04	937.99	937.58
02W21	927.43	927.84	929.46	929.74	928.62
02W22	927.42	927.85	929.50	929.72	928.62
02W23	927.42	927.74	929.56	929.79	928.63
02W23				929.79	929.79
02W24	927.32	927.75	929.53	. 929.75	928.59
02W25	940.60	941.84	947.51	946.01	943.99
02W26	934.13	936.34	937.00	937.14	936.15
02W27	930.37	931.97	934.48	933.97	932.70
02W28	931.52	934.17	935.30	935.41	934.10
02W29	932.59	935.12	936.19	936.65	935.14
02W30	932.19	934.13	937.03	937.17	935.13
02W31	931.19	933.83	934.97	935.02	933.75
02W32	927.31	927.84	929.61	931.65	929.10
02W33	927.44	927.85	929.52	929.77	928.65
02W33				929.77	929.77
02W34	927.44	927.71	929.39	929.66	928.55
02W35	938.70	927.92	929.36	929.60	931.39
02W36	927.42	927.83	929.46	929.71	928.60
02W37	934.00	934.40	935.82	936.03	935.06
02W38	926.67	927.10	929.47	929.64	928.22
02W39	933.00	935.46	936.43	936.90	935.45
02W40	938.36	939.05	940.18	940.18	939.44
02W41	936.42	937.80	938.62	938.66	937.88
02W42	934.42	936.09	941.05	940.34	937.98
02W43	927.35	927.91	929.29	929.53	928.52
02W43				929.53	929.53
02W44	929.23	927.77	929.35	929.55	928.97





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Cummon	9/16/03	12/16/03	Aug/Sep 04	5/24/05	Avg WL
Summary	Water Level	Water Level	Water Level	Water Level	Elevation
ן טו	(feet)	(feet)	(feet)	(feet)	(feet)
02W45	927.55	927.86	929.32	929.56	928.58
02W46	927.97	929.10	930.88	930.73	929.67
02W47	937.87	939.46	941.28	???	939.54
02W48	925.58	926.13		929.09	926.93
02W50	939.89	940.20	941.60	941.70	940.85
02W51	949.20	949.84	952.77	952.03	950.96
02W52	938.96	939.45	940.74	940.97	940.03
02W53	930.40	932.03	934.70	934.13	932.81
02W62	927.68	928.02	929.44	929.69	928.71
02W62				929.69	929.69
T-51	929.26	929.25		930.45	929.66
T-52	929.07	929.14		930.42	929.55
T-53	929.09	929.16		930.57	929.61
T-54	929.65	929.88	930.94	931.61	930.52
T-55	929.30	929.58		931.25	930.04
T-56	929.21	929.54		931.27	930.01
T-57	929.83	929.90	930.94	931.85	930.63
	929.87	929.83	930.77	931.87	930.58
T-59	928.94	929.04		930.60	929.53
T-60	928.89	969.49		930.89	943.09
T-61	928.65	928.65		930.79	929.36
T-62	930.14 ·	930.14	930.82	932.15	930.81
T-63			931.48	932.01	931.75
T-63	930.02	930.02	931.48	932.01	930.88
T-63		•	931.48		931.48
T-64	930.31	930.31	931.57	932.43	931.15
T-65	930.06	929.93	930.90	932.05	930.74
T-65				932.05	932.05
T-66			931.71		931.71
T-67			931.17		931.17
T-67			931.17		931.17
T-67			931.17		931.17
T-67			931.17		931.17
T-68	·		930.81		930.81
T-69			930.93		930.93
T-70					
T-70R			931.24		931.24
T-71					
T-72			930.96		930.96
T-73			931.02		931.02
T-74			931.20		931.20
T-75			930.88		930.88
T-76			931.04		931.04
T-77			930.82		930.82

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	9/16/03	12/16/03	Aug/Sep 04	5/24/05	Avg WL
Summary	Water Level	Water Level	Water Level	Water Level	Elevation
	(feet)	(feet)	(feet)	(feet)	(feet)
T-77			930.82		930.82
T-77			930.82		930.82
T-78			930.87		930.87
T-79			930.53	,	930.53
T-81			930.80		930.80
T-82			930.35		930.35
TMW-01	939.36	940.23	942.38	943.82	941.45
TMW-02	940.65	940.99	941.29	941.62	941.14
TMW-05	930.74	933.29	934.56	934.02	933.15
TMW-06	932.81	935.77	936.02	936.05	935.16
TMW-07	930.17	932.54	933.41	933.05	932.29
TMW-08	933.75	935.89	936.50	936.99	935.78
TMW-09	931.68	934.32	935.02	935.28	934.08
TMW-09	_			935.28	935.28
TMW-13	927.66	928.18	929.36	929.77	928.74
TMW-13				929.77	929.77
TMW-17	932.23	933.08	933.97	934.11	933.35
TMW-17			933.97		933.97
TMW-18	927.30	927.76	930.18	930.05	928.82
TMW-19	dry	dry		n/a	
TMW-20	938.43	939.35		939.91	939.23
TMW-21	936.45	937.09	944.33	942.49	940.09
TMW-23	928.33	928.87	929.94	930.37	929.38
TMW-24	927.71	928.05	928.73	929.19	928.42
TMW-25	936.83	938.41	938.42	938.32	937.99



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Table 3BA #1 Summary of Model InputsCimarron CorporationCrescent, Oklahoma

	Burial Area (BA#1)							
Sub	Subsurface Units: Value Units Reference							
	К <sub>н</sub>	3.30E+00	ft/day	Average of Silt, Sand, & Clay				
	Kv	3.30E-01	ft/day	10% of К <sub>н</sub>				
	Horozontal Anisotropy	1.0		No horizontal anisotropy				
	Vertical Anisotropy (Kh/Kv)	1.0		No vertical anisotropy				
╙	Specific Storage	NA .		Not required for steady-state simulation				
	Specific Yield	NA		Not required for steady-state simulation				
	Long. Disp.	NA		Not required for flow model				
	Porosity	30	%	Freeze & Cherry, 1979 Table 2.4				
	Кн	2.83E-01	ft/day	ENSR CSM Sec-3.2.1				
	Kv	2.83E-02	ft/day	10% of К <sub>н</sub>				
	Horozontal Anisotropy	1.0		No horizontal anisotropy				
=	Vertical Anisotropy (Kh/Kv)	1.0		No vertical anisotropy				
S	Specific Storage	NA		Not required for steady-state simulation				
	Specific Yield	NA		Not required for steady-state simulation				
	Long. Disp.	NA		Not required for flow model				
	Porosity	20	%	Freeze & Cherry, 1979 Table 2.4				
	Кн	2.53E+02	ft/day	Average of pumping tests in alluvial wells				
	K <sub>v</sub>	2.53E+01	ft/day	10% of К <sub>н</sub>				
	Horozontal Anisotropy	1.0		No horizontal anisotropy				
P	Vertical Anisotropy (K <sub>H</sub> /K <sub>v</sub> )	1.0		No vertical anisotropy				
Sa	Specific Storage	NA		Not required for steady-state simulation				
	Specific Yield	NA		Not required for steady-state simulation				
	Long. Disp.	NA		Not required for flow model				
	Porosity	30	%	Freeze & Cherry, 1979 Table 2.4				
	К <sub>н</sub>	5.00E-01	ft/day	Artificially high to improve model stability				
	κ <sub>v</sub>	5.00E-02	ft/day	10% of K <sub>H</sub>				
	Horozontal Anisotropy	1.0		No horizontal anisotropy				
ay	Vertical Anisotropy (K <sub>H</sub> /K <sub>v</sub> )	1.0		No vertical anisotropy				
Ö	Specific Storage	NA	·	Not required for steady-state simulation				
	Specific Yield	NA		Not required for steady-state simulation				
	Long. Disp.	NA		Not required for flow model				
	Porosity	20	%	Freeze & Cherry, 1979 Table 2.4				
	Кн	4.00E+01	ft/day	Calibrated to high end of range in ENSR CSM Sec-3.2.1				
	K <sub>v</sub>	2.00E+00	ft/day	5% of K <sub>H</sub>				
A-9	Horozontal Anisotropy	1.0		No horizontal anisotropy				
to D	Vertical Anisotropy (K <sub>H</sub> /K <sub>V</sub> )	1.0		No vertical anisotropy				
spu	Specific Storage	NA		Not required for steady-state simulation				
Sai	Specific Yield	NA		Not required for steady-state simulation				
	Long. Disp.	NA		Not required for flow model				
	Porosity	5	%	Freeze & Cherry, 1979 Table 2.4				

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	Burial Area (BA#1)							
Subsurface Units: Value Units				Reference				
	К <sub>н</sub>	8.43E+00	ft/day					
	K <sub>V</sub>	4.22E-01	ft/day	5% of K <sub>H</sub>				
a	Horozontal Anisotropy	1.0		No horizontal anisotropy				
ton	Vertical Anisotropy (K <sub>H</sub> /K <sub>V</sub> )	1.0	· · · · · ·	No vertical anisotropy				
Silts	Specific Storage	NA		Not required for steady-state simulation				
	Specific Yield	NA		Not required for steady-state simulation				
	Long. Disp.	NA		Not required for flow model				
	Porosity	1	%	Freeze & Cherry, 1979 Table 2.4				
	К <sub>н</sub>	5.00E+00	ft/day	Calibrated to high end of range in ENSR CSM Sec-3.2.1				
-	K <sub>v</sub>	2.50E-01	ft/day	5% of K <sub>H</sub>				
е- В-	Horozontal Anisotropy	1.0		No horizontal anisotropy				
to	Vertical Anisotropy $(K_H/K_V)$	1.0		No vertical anisotropy				
nds	Specific Storage	NA		Not required for steady-state simulation				
Sa	Specific Yield	NA	*	Not required for steady-state simulation				
	Long. Disp.	NA		Not required for flow model				
	Porosity	5	%	Freeze & Cherry, 1979 Table 2.4				
	К <sub>н</sub>	3.00E+00	ft/day	Slug test results at well 02W48				
	Kv	1.50E-01	ft/day	5% of K <sub>H</sub>				
U U	Horozontal Anisotropy	1.0	;	No horizontal anisotropy				
ton	Vertical Anisotropy $(K_H/K_V)$	1.0		No vertical anisotropy				
spu	Specific Storage	· NA		Not required for steady-state simulation				
Sa	Specific Yield	NA		Not required for steady-state simulation				
	Long. Disp.	NA		Not required for flow model				
	Porosity	5	%	Freeze & Cherry, 1979 Table 2.4				

Cimarron River:	Value	Units	Reference
Upstream Elevation	924.8	feet	Based on Dover and Guthrie gage datums
Downstream Elevation	924.8	feet	Based on Dover and Guthrie gage datums
Conductance	10,000	(ft²/day)/ft	Estimate to for high river/aquifer connectivity

Areal Boundaries:	Value	Units	Reference
Recharge	5.48E-04	ft/day	ENSR CSM Sec-3.1.1 & 3.1.4

## Table 4 WA Summary of Model Inputs Cimarron Corporation Crescent, Oklahoma

	Western Alluvial Area (WA)							
Sub	surface Units:	Value	Units	Reference				
	К <sub>н</sub>	5.00E-01	ft/day	ENSR CSM Sec-3.2.1				
	Kv	5.00E-02	ft/day	10% of K <sub>H</sub>				
	Horozontal Anisotropy	1.0		No horizontal anisotropy				
ay	Vertical Anisotropy (K <sub>H</sub> /K <sub>V</sub> )	1.0		No vertical anisotropy				
Ö	Specific Storage	0.001		Default				
	Specific Yield	0.001		Default				
	Long. Disp.	10		Default				
	Porosity	20	. %	Freeze & Cherry, 1979 Table 2.4				
	Кн	2.35E+02	ft/day	Average of pumping tests in alluvial wells.				
	Kv	2.35E+01	ft/day	10% of K <sub>H</sub>				
	Horozontal Anisotropy	1.0		No horizontal anisotropy				
р	Vertical Anisotropy (K <sub>H</sub> /K <sub>V</sub> )	1.0		No vertical anisotropy				
Sa	Specific Storage	0.001		Default				
	Specific Yield	0.001		Default				
	Long. Disp.	10		Default				
	Porosity	30	. %	Freeze & Cherry, 1979 Table 2.4				
	К <sub>н</sub>	3.00E+00	ft/day	Slug test results at well 02W48				
	K <sub>v</sub>	1.50E-01	ft/day	5% of K <sub>H</sub>				
	Horozontal Anisotropy	1.0		No horizontal anisotropy				
to to	Vertical Anisotropy (K <sub>H</sub> /K <sub>V</sub> )	1.0		No vertical anisotropy				
spu	Specific Storage	0.001		Default				
Sa	Specific Yield	0.001		Default				
	Long. Disp.	10		Default				
	Porosity	5	%	Freeze & Cherry, 1979 Table 2.4				

Cimarron River:	Value	Units	Reference
Upstream Elevation	924.8	feet	Based on Dover and Guthrie gage datums
Downstream Elevation	924.8	feet	Based on Dover and Guthrie gage datums
Conductance	20,000	(ft²/day)/ft	Medium estimate based on prior experience

Areal Boundaries:	Value	Units	Reference
Recharge	5.48E-04	ft/day	ENSR CSM Sec-3.1.1 & 3.1.4