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COPY NO.	DATE	DESCRIPTION
1	Oct. 2003	<b>Docket # 70-925; License No. SNM-928</b> DRAFT Work Plan—In Situ Bioremediation Treatment of Uranium in Groundwater in Burial Area #1

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# CIMARRON CORPORATION

P.O. BOX 315 • CRESCENT, OK 73028

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October 22, 2003

Mr. Kenneth Kalman  
Low-Level Waste & Decommissioning Projects Branch  
Division of Waste Management  
Office of Nuclear Materials Safety & Safeguards  
U. S. Nuclear Regulatory Commission  
Washington, D.C. 20555

Re: Docket No. 70-925; License No. SNM-928  
Addendum to Site Decommissioning Plan

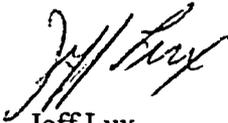
Dear Mr. Kalman:

Cimarron Corporation (Cimarron) submits the enclosed document entitled, "DRAFT Work Plan – In Situ Bioremediation Treatment of Uranium in Groundwater in Burial Area #1" for NRC's information. This work plan addresses groundwater that contains uranium in excess of the license release criteria of 180 pCi/L in Subareas C and F. It is submitted as an addendum to the Site Decommissioning Plan as referenced in condition 27(a) of license SNM-928.

As you are aware, most decommissioning activities have been completed; only groundwater assessment and/or remediation activities remain. This draft document is provided for your information prior to a meeting in Rockville, tentatively scheduled for November 20, 2003. Cimarron anticipates that any regulatory or technical issues associated with the remediation of groundwater in Burial Area #1 by in situ bioremediation will be identified and discussed at that meeting. Cimarron does not anticipate formal comments or requests for additional information prior to that meeting.

If you have questions or comments, please call me at 405-282-5680, ext. 120 (Cimarron) or 918-223-2522 (Cushing).

Sincerely,



Jeff Lux  
Manager, Planning and Regulatory Compliance

xc: D. Blair Spitzberg, NRC Region IV  
Saba Tahmassebi, Oklahoma DEQ

**DRAFT**  
**Work Plan –**  
**In Situ Bioremediation**  
**Treatment of Uranium in**  
**Groundwater in Burial Area #1**

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Cimarron Corporation  
Crescent, Oklahoma

October 2003

**PREPARED FOR:** \_\_\_\_\_

Cimarron Corporation

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**Jim Harrington**  
Technical Director

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**Mike M. Gates**  
Project Advisor

**Draft  
Work Plan –  
In Situ Bioremediation  
Treatment of Uranium in  
Groundwater in Burial Area  
#1**

**Cimarron Corporation  
Crescent, Oklahoma**

**Prepared for:  
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**Our Ref.:  
OK001376.0001**

**Date:  
October 2003**

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## Table of Contents

<b>1.0</b>	<b>Summary</b>	<b>1</b>
<b>2.0</b>	<b>Introduction</b>	<b>3</b>
2.1	Plume Status	3
2.2	Remedial Goals	3
2.3	License Termination Conditions	3
2.4	ARCADIS Remedial Approach	4
2.4.1	In Situ Bioremediation Process	4
2.4.2	Scientific Basis for the ARCADIS Process	5
2.5	Ecological and Human Health Impacts	11
<b>3.0</b>	<b>Work Plan</b>	<b>11</b>
3.1	Existing Geochemical Groundwater Data and Additional Baseline Data Collection	11
3.2	Treatment Injection/Application	13
3.2.1	Development of a Forward IRZ	13
3.2.2	Surface Application of TOC	14
3.2.3	Remediation of the Plume	14
3.2.4	Upgradient Sandstone Injection	15
3.2.5	Surface Ecosystem Creation	16
3.3	ARCADIS Treatment Monitoring and QA/QC During Remedial Activities	16
3.4	Groundwater Uranium Compliance Monitoring and Stability Demonstration Monitoring	18
3.5	Timeline	19
3.6	Well Abandonment	19
<b>4.0</b>	<b>Sampling and Analysis Plan</b>	<b>20</b>

## Table of Contents

<b>5.0 Health and Safety Plan</b>	<b>21</b>
<b>6.0 References</b>	<b>22</b>

### List of Figures

Figure 1	Cimarron Site Map
Figure 2	Uranium Plume
Figure 3	Remedial Elements Location
Figure 4	Cross-Section Location
Figure 5	Geological Cross-Sections & Injection Point Spacing
Figure 6	Proposed Compliance Monitoring Wells
Figure 7	Proposed Timeline

## **1.0 Summary**

This workplan describes the steps to be taken at the Cimarron Facility near Crescent, OK, to remediate the groundwater plume in Burial Area #1. This summary description highlights the activities to be performed during plume remediation. The rest of the workplan describes each step in greater detail, provides a background for the bioremediation process that will be employed, and references the other steps that ARCADIS, as Cimarron's subcontractor, will take to perform this work in a safe, efficient, and timely manner.

In order to accomplish the project performance goal, ARCADIS will perform the following activities:

- 1) Create a chemically reduced, in-situ reactive zone beyond the forward (downgradient) edge of the uranium groundwater plume through the injection of carbohydrates and alcohols (collectively referred to as organic carbon) directly into the groundwater. This forward in-situ reactive zone will be referred to in this work plan as the FIRZ. By starting remediation efforts at this location, ARCADIS can quickly refine its understanding of the site specific nutrient application rates and concentrations necessary to achieve uranium and sulfate reduction in situ. In addition, the FIRZ will effectively remediate any uranium-contaminated groundwater that migrates into the area due to subsequent treatment applications of nutrient bearing water applied to the surface and injected into the groundwater plume.
- 2) Enhance the strongly reducing conditions in the FIRZ by the addition of iron and/or sulfate with additional organic carbon. This addition will encapsulate uranium precipitated in Step 1, and will also lead to the formation of a bank of reduced iron and reduced sulfur compounds, primarily iron sulfides such as greigite, mackinawite and pyrite. Also, other reduced compounds including sulfur, and microbial biomass and stored microbial organic carbon will be formed in the FIRZ that will also contribute to long-term uranium stability.
- 3) Monitor uranium concentrations (as well as other parameters that indirectly indicate treatment progress, such as iron, sulfate, and redox potential) in the groundwater in the FIRZ for three to six months. This will be followed by the collection of soil cores after several months of FIRZ operation with the soil cores analyzed for total reduced iron and reduced sulfur content to demonstrate that the bank of reduced iron and sulfur compounds is being formed.

**DRAFT  
Work Plan – In Situ  
Bioremediation  
Treatment of  
Uranium in  
Groundwater in  
Burial Area #1**

Cimarron Corporation  
Crescent, Oklahoma

- 4) Initiate surface application treatments of organic carbon over the remaining body of the groundwater plume to provide treatment of uranium in the vadose and capillary zone immediately above the groundwater. This will prevent the mobilization of uranium in concentrations exceeding 50 pCi/L by the leaching of infiltrating rainwater. ARCADIS will also inject organic carbon treatment reagents into and around the groundwater plume and in upgradient areas through existing wells and/or through temporary injection points.
- 5) Create a strongly reducing zone in the body of the plume as described in steps 1, 2, and 3 above. This area will be referred to in this work plan as the plume in situ reactive zone, or pIRZ.
- 6) Monitor both the groundwater and vadose zone for uranium and additional parameters, such as iron and sulfur compounds, to evaluate the progress of the treatment in the groundwater plume. Soil pore waters from the vadose zone will also be extracted to evaluate the formation of reduced compounds within the vadose zone and the concentration of oxygen and oxidizing compounds (such as ferric iron) in the vadose zone solids and pore water.
- 7) As optional activities, apply additional reagents during the approximately 12 to 18 months of treatment, as deemed necessary to meet the required remediation time frame. Optional additional activities may include greater application rates of the primary remediation agents (organic carbon, iron, and sulfate) and/or spot application (in high uranium concentration areas) of alternative treatment technologies such as treatment with nano-scale zero valent iron and/or in-situ hydroxyapatite formation.
- 8) Establish positive drainage and native vegetation over the plume area. While not necessary for uranium immobilization or for maintaining uranium stability, this step will enhance the uranium stability by reducing the potential for the infiltration of oxygen-bearing water originating as rainfall.

At the end of this process, ARCADIS will demonstrate that license closure conditions have been met. Specifically, uranium concentrations will be measured for 8 quarters in wells within the plume at less than 180 pCi/L. Other reduced compounds will be measured and shown to have been coprecipitated with the uranium, providing stable conditions that will prevent the reoxidation of uranium at concentrations exceeding 180 pCi/L for over 1000 years. ARCADIS will measure concentrations of in situ reduced materials, compare those concentrations with other geochemical systems in which uranium has remained stable for periods in excess of 1000 years. Finally,

ARCADIS will use groundwater and vadose zone transport and geochemical models to show that the intrusion of oxygen from natural systems will not be able to alter these geochemical conditions sufficiently to re-mobilize uranium at concentrations exceeding license criteria.

## **2.0 Introduction**

### **2.1 Plume Status**

A groundwater plume containing soluble uranium in excess of 180 pCi/L currently exists in Burial Area #1, crossing the boundary of Sub Areas C and F. This plume has been documented and mapped in prior correspondence with the Nuclear Regulatory Commission (NRC). Details of the recent comprehensive assessment are contained in "Burial Area #1 Groundwater Assessment Report" (Cimarron Corp, 2003). Figure 1 shows an overview of the Cimarron site, and Figure 2 shows the extent of the uranium plume (defined as groundwater exceeding 180 pCi/L) in Burial Area #1.

### **2.2 Remedial Goals**

The uranium plume outlined in Figure 2 encompasses an area of approximately 1.6 acres. ARCADIS proposes to perform remedial activities in an area of approximately 3 to 4 acres. The area of remediation extends beyond the existing plume to achieve groundwater conditions less than 50 pCi/L in the entire area. Additional reduced materials will be emplaced in this area around the edges of the 180-pCi/L plume. These additional reduced materials will act to provide geochemical stability for the precipitated uranium, to ensure that uranium will not remobilize after plume remediation is completed. (For the purpose of this document, plume remediation refers to reduction of dissolved uranium concentrations in the plume defined in Figure 2; the "additional stabilization area" is defined as the forward IRZ and the reduced zones around the edges and upgradient of the plume that will serve to provide additional long-term protection against uranium remobilization and will reduce the uranium outside of the plume to below 50 pCi/L.)

### **2.3 License Termination Conditions**

The Cimarron Facility Groundwater Decommissioning Plan (Cimarron Corporation, 1998) proposed a site groundwater standard of 180 pCi/L for total uranium. The NRC incorporated this standard into License SNM-928 as condition 27(b), in License Amendment 15. Condition 27(b) requires 8 consecutive quarters of monitoring to demonstrate that uranium concentrations are maintained at or below 180 pCi/L. This

Work Plan provides an in situ treatment approach that will not only meet, but also exceed this license termination condition.

## **2.4 ARCADIS Remedial Approach**

### **2.4.1 In Situ Bioremediation Process**

The bioremediation process that ARCADIS proposes has been used extensively to degrade chlorinated solvents and to stabilize metals within contaminated aquifers. As of May 2003, more than 180 sites have been stabilized by the IRZ technology (Nyer and others, 2001; Suthersan, 2002; Harrington, 2002). The proposed process consists of the following steps:

- 1) Determination of the background biogeochemical conditions within the plume to be remediated, with special emphasis on the current rate of migration of oxygen into the plume, and the concentrations of dissolved and solid phase electron acceptors present in the plume area. These electron acceptors are typically comprised of 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 contaminated plume area. This will be accomplished by the injection of organic carbon, which will be oxidized and degraded by microbial activities (fermentation and organic carbon oxidation).
- 3) Precipitation of the uranium as a reduced uranium (IV) oxide ( $UO_2$  (solid)). This is a microbially mediated redox reaction, where organic carbon is oxidized, and uranium is reduced (organic carbon is the electron donor, and uranium is the electron acceptor). With time, the freshly precipitated uranium will become increasingly crystalline and insoluble (Casas and others, 1998).
- 4) Precipitation of other reduced compounds adjacent to and around the uranium precipitated in step (3). These other reduced compounds will primarily be iron sulfides, formed as a result of microbial sulfate reduction, where organic carbon is oxidized and sulfate is reduced to sulfide. Typically, organic carbon injected into groundwater will sequentially deoxygenate the aquifer, and then support the reduction of uranium followed by the reduction of structural iron compounds and dissolved sulfate (Zehnder and Stumm, 1989). All of these

reactions are microbially performed redox reactions. The process is designed to precipitate iron sulfides such that the molar concentrations will be more than 1,000 times the molar concentration of precipitated uranium oxides. For example, at Cimarron, the mass of sulfide that ARCADIS proposes to create in this workplan is about 2 million pounds. The mass of uranium in the existing plume is estimated at approximately 200 pounds.

- 5) Determine that sufficient reduced minerals have been deposited in the plume to deoxygenate the plume area for a sufficient time frame to maintain uranium stability. This typically will involve recovery of solid phase materials and determination of the mass of reduced compounds.

## 2.4.2 Scientific Basis for the ARCADIS Process

### 2.4.2.1 Uranium Removal by Microbial Reduction in Groundwater

Lovley and others (1991; Lovley and Phillips, 1992) proposed the remediation of uranium in groundwater using an in situ bioremediation process similar to what is proposed in Step 3 in Section 2.4.1. Since that proposal, an extensive bibliography has been published documenting the removal of uranium by microbial processes in groundwater or simulated groundwater conditions. This bibliography is summarized in Lloyd and Macaskie (2000). The following papers are particularly relevant to documenting that injection of an organic carbon source into a typical uranium plume 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 and others (2002) show uranium reduction can be rapidly achieved in an aquifer containing excess organic carbon into which soluble uranium is introduced and acetate, lactate, and formate (organic carbon sources) is supplied. They also demonstrate the importance of excluding nitrate and denitrification intermediates from the aquifer following uranium reduction to prevent remobilization of the uranium.

Chang and others (2001) showed that Sulfate Reducing Bacteria (SRB) are abundant in groundwater in a zone containing high concentrations of uranium at the Shiprock, NM site, and that these bacteria are capable of both uranium reduction and sulfate reduction and iron sulfide precipitation. Microbial reduction of uranium was shown to result in soluble uranium concentrations as low as 1 pCi/L.

Abdelouas and others (2000) performed column studies that showed that excess iron sulfide is an optimal material to provide a redox buffer to prevent oxidative dissolution

of uranium. They state “the more iron sulfide present, the higher the stability of uraninite,” the mineral form we propose to create in this work. They documented a maximum concentration of 29 pCi/L dissolved uranium was formed during re-oxidation of freshly precipitated uranium where a  $10^4$  molar excess iron sulfide was precipitated along with the uranium. ARCADIS proposes to create approximately the same molar ratio at the Cimarron site during remediation, so that even if the aquifer became oxidized, uranium concentrations would not approach the groundwater limit.

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

Abdelouas and others (1999) also performed column studies where accelerated oxidation experiments documented uranium stabilization for simulated “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.

#### *2.4.2.2 Sulfate Reduction and the Role of Iron Sulfides*

SRB have been utilized to perform in situ bioremediation for a wide variety of contaminants, including hydrocarbons, chlorinated solvents, and heavy metals. To perform sulfate reduction, an electron donor, typically organic carbon, and sulfate (which acts as the electron acceptor) must be present. Many SRB have been shown to be capable of uranium reduction as well (Chang and others, 2001; Spear and others, 2000).

The ARCADIS process primarily relies on SRB to take soluble sulfate and iron and reduce the sulfate to sulfide. Sulfide then chemically reacts with iron to make iron sulfides. The sulfate reduction/iron sulfide formation process is a process that 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 nearly ubiquitous bacteria. 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).

**DRAFT  
Work Plan – In Situ  
Bioremediation  
Treatment of  
Uranium in  
Groundwater in  
Burial Area #1**

Cimarron Corporation  
Crescent, Oklahoma

In order to initially activate the sulfate reduction process at Cimarron, ARCADIS will add only organic carbon. However, the existing soluble sources of sulfate are limited to a few hundred mg/L (Section 3.1). In order to create iron sulfides in the percent range (more than 10,000 g iron sulfide/kg aquifer material), which is necessary to obtain the molar ratios with uranium needed for uranium stability, ARCADIS will inject sulfate to create concentrations in the plume of a few grams per liter. Section 3.1 documents the background biogeochemical parameters ARCADIS will determine prior to injection. Sulfate concentrations, both in the soluble and the solid phase, will be critical for determining the required sulfate addition rate.

In the absence of iron (and other oxidized minerals), sulfate reduction in aquifers will lead to accumulation of aqueous sulfide ( $HS^-$ ). In the Cimarron soils, however, where oxidized iron minerals (such as hematite) are abundant (grab samples range 1%-3%), sulfide will react with the iron, reducing the ferric iron to ferrous iron. Ferrous iron formed in this way is relatively soluble; however, additional sulfide formed will quickly react with the ferrous iron, and at pH greater than 6.5, iron sulfide minerals will rapidly precipitate. The temporary increase in iron concentrations will last for a period of a few months. ARCADIS will therefore monitor the pH to ensure that the iron sulfide precipitates from solution. The presence of the IRZ at the forward edge of the plume will prevent iron migration beyond the treatment area.

Iron sulfide has been recognized as being critical to maintaining uranium stability in groundwater during bioremediation (Abdelouas and others, 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 between uranium and sulfide sulfur was found, indicating both a role for sulfur in depositing the uranium as well as in maintaining its deposition. It is critical to note that the sulfide continues to perform a stabilizing function in this deposit, which has been measured at millions of years old. Guilbert and Park (1986) call these deposits "kinetically stable" where the sulfur acts to control uranium stability. In uranium ore geology terms, ARCADIS will be creating a "regionally reduced" host aquifer at Cimarron. In these geologic conditions, a very small fraction, typically less than  $10^{-8}$  of the uranium in the ore deposit is made soluble per year (Waste Isolation Systems Panel, 1983).

Iron sulfide has also been recognized as an important redox buffer for several situations that are instructive for Cimarron. Pauwels and others (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

**DRAFT  
Work Plan – In Situ  
Bioremediation  
Treatment of  
Uranium in  
Groundwater in  
Burial Area #1**

Cimarron Corporation  
Crescent, Oklahoma

(half-life of reduction of two days in a sandy aquifer matrix), leading to the oxidation of pyrite to ferric iron and sulfate minerals, which deposited as jarosite and natroalunite. Tesoriero and others (2000) showed that in aquifers receiving agricultural runoff, that oxygen and nitrate in the runoff were reduced by iron sulfide when infiltrated runoff reached the deeper aquifer. Hartog and others (2001) showed that iron sulfide, reduced iron compounds in addition to iron sulfides (including siderite), and bulk organic matter can all provide redox buffering in aquifers receiving agricultural runoff. ARCADIS cites these examples as being relevant for the “resident farmer” scenario, indicating that even under agricultural runoff scenarios the uranium can be maintained insoluble by iron sulfide.

An additional factor to maintain 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. Lack and others (2002) showed that ferric iron oxides sorb uranium with strong binding energy (bidentate and tridentate inner-sphere complexes). Ferris and others (2000) showed that these iron oxides could maintain very low dissolved uranium concentrations (less than 30 pCi/L). Martin and Kempton (2000) have shown continued reactivity of hydrous ferric oxides formed in this way for more than 30 pore volumes. This means that for the Cimarron plume, the iron oxides that will form as oxygen enters the plume area (transported by diffusion, in rainwater and in groundwater) will prevent uranium from ever remobilizing at concentrations even approaching 180 pCi/L.

#### *2.4.2.3 Uranium Stability Summary*

The papers referenced above provide the information needed to identify the necessary characteristics of a stable, fully reduced 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 several orders of magnitude greater than the concentration of uranium in the reducing zone,
- Elemental sulfur,
- Residual reduced organic carbon either incorporated in cellular biomass or stored by microorganisms,
- Reduced uranium compounds (UO<sub>2</sub> and potentially US<sub>2</sub>), and

**DRAFT  
Work Plan – In Situ  
Bioremediation  
Treatment of  
Uranium in  
Groundwater in  
Burial Area #1**

Cimarron Corporation  
Crescent, Oklahoma

- Potentially a variety of other reduced sulfur, manganese, iron, and trace mineral compounds.

In this zone, the reoxidation and remobilization of uranium will be limited by the oxygen available to react with the precipitated uranium. The available oxygen will 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 all of the other reduced compounds stored in the aquifer, the potential oxidation of uranium will be very low compared to the potential oxidation of iron, sulfur and other reduced species. Utilizing FeS compounds alone, more than  $10^4$  moles of FeS will be present to every mole of  $UO_2$ . The proposed remediation plan anticipated the introduction of oxygen via natural pathways, and provides for sufficient reduced compounds to exhaust these sources of oxygen. As the aquifer materials are exposed to oxygen, FeS would oxidize at least as rapidly as the precipitated  $UO_2$  and consume the oxygen. Because the ratio of iron sulfide to uranium is so large, a very limited amount of oxygen will be available to react with uranium. Because  $UO_2$  will be precipitated first during treatment, the FeS precipitate would be laid down over the top of the  $UO_2$  as a FeS coating. FeS will therefore be exposed to the oxygen in the groundwater before uranium-containing precipitates would be exposed. 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, the uranium will only mobilize at concentrations substantially less than 180 pCi/L.

#### *2.4.2.4 Remobilization Calculations*

NRC requires assurance that uranium will not remobilize at concentrations exceeding 180 pCi/L over a period of 1,000 years. To ensure that uranium will not remobilize, it is necessary to project the potential delivery of oxygen to the aquifer over that time period. There are three significant sources of dissolved oxygen: groundwater entering the aquifer from upgradient, precipitation infiltrating from the surface, and diffusion of atmospheric oxygen through the vadose zone. ARCADIS has overestimated the quantity of oxygen delivered by these three pathways to ensure that more than enough iron sulfides remain in the aquifer to consume this quantity of oxygen.

ARCADIS measured the dissolved oxygen concentration in groundwater in BA#1 at several locations and determined an average concentration of approximately 0.62 mg/l, with a maximum measured value of 0.84 mg/l. Based on the width of the plume (maximum 300 ft), the depth of the plume (maximum 20 feet) the hydraulic gradient

**DRAFT  
Work Plan – In Situ  
Bioremediation  
Treatment of  
Uranium in  
Groundwater in  
Burial Area #1**

Cimarron Corporation  
Crescent, Oklahoma

(0.006 ft./ft), and the permeability of Sandstone A ( $5 \times 10^{-3}$  cm/sec), a total of 5.1 million liters of groundwater will enter the plume area per year. At a dissolved oxygen concentration of 0.8 mg/l, no more than 9 pounds of oxygen will be delivered to the plume via this pathway.

Assuming that rainfall is saturated with oxygen (8.0 mg/L), that annual precipitation averages 36 inches per year, that 100% of that water enters the aquifer without reduction in oxygen content, and that the plume and additional treatment area covers 4 acres, a total of approximately 260 pounds of oxygen will be delivered to the plume by this pathway.

Complete removal of oxygen in the groundwater will cause some increase in the oxygen transfer into the groundwater because the diffusional gradient will be increased. Based on a maximum measured oxygen concentration in the groundwater of 0.8 mg/L, calculations based on Henry's Law indicate that the oxygen content in the soil above the groundwater is now 0.0189 atmospheres, or 9% of the oxygen content in the atmosphere. Depletion of the groundwater oxygen will increase the gradient by that same percentage. The existing flux that is maintaining groundwater at the 0.8 mg/L concentration is 1,060 pounds per year over 4 acres. (This is based on Fick's Law, assuming a depth to groundwater of 10 feet, initial oxygen in the atmosphere is  $0.2352 \text{ kg/m}^3$ , a oxygen gradient of 0.21 to 0.02 atmospheres, a  $D_{\text{eff}}$  of  $4 \times 10^{-9} \text{ m}^2/\text{sec}$  limited by the nearly saturated conditions at the soil-groundwater interface, and an area of 4 acres). The increase of oxygen transmission when the gradient is increased by 9% is about 96 pounds per year over 4 acres.

Combining the three pathways above, a total of 365 pounds of oxygen would be delivered to the plume area in one year. Assuming this remains constant for 1,000 years, a total of 365,000 pounds of oxygen will be delivered to the plume area over 1,000 years. Based on the equation:  $\text{FeS}_2 + 3.5\text{H}_2\text{O} + 3.75\text{O}_2 \rightarrow \text{Fe}(\text{OH})_3 + 2\text{SO}_4^{2-} + 4\text{H}^+$ , 357,550 pounds of iron sulfide would be needed to deplete this mass of oxygen from the water. ARCADIS proposes to place sufficient excess iron sulfides so that less than half of the iron sulfide is reacted by the end of 1,000 years.

The presence of other reduced compounds besides iron sulfide makes this calculation conservative. In groundwater saturated with dissolved oxygen, approximately 8 mg/L  $\text{O}_2$  would be available to react with the precipitated uranium and the iron sulfide that coats it. Since the molar ratio of iron sulfide to uranium will be at least  $10^4$ , only 0.0008 mg/L dissolved oxygen would be available to react with the uranium. The rest would react with the overwhelming available iron sulfide. This concentration is equivalent to  $2.5 \times 10^{-8}$  mol per liter  $\text{O}_2$ . This is all the oxygen that would be available

for uranium oxidation, yielding a maximum dissolved uranium activity of 4 pCi/L that would be in the groundwater at any given point in the plume.

## **2.5 Ecological and Human Health Impacts**

The proposed process will cause no negative impacts to the environment. The bacteria that reduce uranium and sulfate are nearly universally present in the environment, and are surely active on the Cimarron site (in the root zones of the plants, in the sediments of the reservoirs on site (Figure 1), and likely in the organic-rich clay zones). While ARCADIS will stimulate a natural process to remediate the groundwater, ARCADIS will only be relying on already existing, naturally occurring bacteria.

Sulfate reducing bacteria are not pathogenic bacteria. Soon after the injected organic carbon is oxidized, the abundance of SRB will return to background concentrations. While the aquifer is not a drinking water aquifer, due to the high chloride and TDS concentrations naturally present in the aquifer, this treatment process will not further degrade water quality in the aquifer.

Implementing this process poses no risk to the environment because:

- The bacteria are naturally occurring
- The bacterial population will increase and decrease as the “food supply” increases and decreases, just as in nature

The iron sulfides and other reduced compounds occur naturally in the environment and pose no risk to human health or the environment.

## **3.0 Work Plan**

### **3.1 Existing Geochemical Groundwater Data and Additional Baseline Data Collection**

In the Burial Area #1 Groundwater Assessment Report (Cimarron Corporation, 2003) existing uranium concentrations in the plume area were established. Figure 2 shows the uranium concentrations in the plume area as of October 2002. ARCADIS will select a subset of wells (listed in Section 3.4) to sample periodically to monitor treatment progress and demonstrate compliance with decommissioning criteria.

**DRAFT  
Work Plan – In Situ  
Bioremediation  
Treatment of  
Uranium in  
Groundwater in  
Burial Area #1**

Cimarron Corporation  
Crescent, Oklahoma

In addition to uranium concentrations obtained by Cimarron in previous groundwater characterization studies, ARCADIS has compiled groundwater and aquifer geochemical information and has used this information for the treatment design described in this workplan. In addition, ARCADIS has performed limited sampling of aquifer conditions in the BA #1 plume area. Groundwater was sampled in wells TMW-9, TMW-13, and TMW-24 to assess concentrations of dissolved oxygen (DO). The range of DO measured was from 0.31 to 0.84 mg/L, with an average of  $0.62 \pm 0.25$  mg/L. Iron was measured in aquifer materials and determined to be between 0.6% and 3.1% by weight in six samples obtained within 10 feet of those wells. Monitoring results obtained by Cimarron show nitrate concentrations of 2.88 and 0.12 mg/L in wells 1315 and TMW-13 in June 2002. Sulfate concentrations have been measured between 70 and 300 mg/L in the plume area.

ARCADIS will perform baseline groundwater and aquifer solids monitoring to establish geochemical conditions prior to field injection. These geochemical conditions will be used to determine the requirement for additional injection of iron, sulfate, and total organic carbon (TOC). Baseline monitoring will consist of the following:

1. Determine the concentration of iron, sulfate, nitrogen species (nitrate, ammonia, Total Kjeldahl Nitrogen - TKN) and TOC in groundwater in the plume area, in the FIRZ area, and in the sandstone. Representative wells in the plume area will be used to obtain this information.
2. Determine the concentration of iron, sulfur species (total and sulfate minerals), nitrogen species (nitrate, ammonia, TKN) and TOC in aquifer matrix material in the plume area, in the FIRZ area, and in the sandstone. These data will be obtained from cores or other samples obtained near the wells used to establish groundwater baseline data.
3. Determine the existing uranium dissolved phase vs. sorbed and mineralized phase to determine total uranium phase that will require reduction.

This information will be the basis for calculating the mass of organic carbon, iron, and sulfate that will be injected during the initial phase of remediation.

## **3.2 Treatment Injection/Application**

### **3.2.1 Development of a Forward IRZ**

An in situ fIRZ downgradient of the plume will be established prior to plume remediation. The location of the fIRZ is within the path of the natural plume movement (Figure 3). Monitoring the fIRZ will enable ARCADIS to refine its calculations of the mass of TOC, iron, sulfate, etc., needed to ensure both plume remediation and long-term stability. Additionally, the fIRZ will serve as a zone that will rapidly precipitate uranium should the migration of uranium be accelerated by subsequent upgradient remedial action.

The fIRZ will be established by injection of an organic carbon mixture. The organic carbon will consist of a mixture of sugars, alcohols, and organic acids such as: acetate, ethanol, formic acid, fructose, glucose, hemicellulose, lactate, and sucrose (collectively referred to as TOC). It should be noted that all of these compounds are agricultural products or microbiological nutrients commonly used in groundwater remediation. The fIRZ will be established by injecting water containing 0.5% to 3% TOC mixtures into the formation at approximate locations shown in Figure 3 using a geoprobe or similar apparatus. Approximately 40 injection points will be used to inject the material to establish the fIRZ. Each injection will be rapid (in the order of 8-12 hours) based on the properties of the receiving aquifer. Each injection will consist of between 10,000 and 20,000 gallons of TOC mixture, and this injection mixture will displace the aquifer water around the injection point an average radius of between 10 and 15 feet.

The fIRZ will be monitored for several months following the initial TOC injections by measuring redox potential in wells within the fIRZ area. After strongly reducing conditions are established in this area, a second injection series will be performed. This second injection series will consist of additional TOC, potentially iron, and potentially sulfate. The addition of iron and sulfate will depend on the data collected during baseline monitoring, and will be balanced to provide the stoichiometric requirement for iron sulfide formation.

Additional monitoring (Section 3.3) will be performed to show that sufficient iron sulfide is being formed. This will be accomplished by sampling groundwater and aquifer matrix material removed from within the fIRZ area where total reduced iron and sulfur are measured. Additional injections may be performed in the fIRZ area until the appropriate iron sulfide concentrations are achieved.

### **3.2.2 Surface Application of TOC**

An organic carbon mixture will be applied to the ground in shallow trenches (less than 2 feet in depth) on the surface above the plume and the additional stabilization area. These trenches will be located in the area identified on Figure 3. The trenches will be placed on contour, and a mixture of TOC will be applied in and around these trenches. To minimize surface disturbance, injection trenches will not be constructed by excavator or dozer, but will be cut by ripper teeth or agricultural equipment through which liquids can be injected into the soil. The TOC may be in a liquid or solid form, and will be designed to slowly infiltrate in to the vadose zone by surface recharge. It is hoped that meteoric precipitation will provide sufficient water for infiltration of the TOC mixture. However, if surface application occurs during the dry season, ARCADIS may irrigate the field to enhance the downward migration of these compounds. The organic carbon added in this manner will stabilize any uranium that might be present in the unsaturated zone, and will generate reduced material that will consume oxygen diffusing into the plume from the atmosphere.

### **3.2.3 Remediation of the Plume**

This is the first step of the process that actually reduces the concentration of uranium in groundwater that exceeds the decommissioning criteria; hence, this constitutes the beginning of groundwater remediation. The entire plume will be remediated in place by the in situ reduction of uranium and placement of iron sulfide in place to maintain uranium in an insoluble form. The process will be identical to that performed for the establishment of the pIRZ, but the location of the treatment will be throughout the plume area. The locations of the plume injections are shown in Figure 3. The purpose of the plume treatment is to create conditions in the plume that stabilize uranium in place for more than 1000 years. This will be accomplished by first reducing uranium concentrations by in situ microbial precipitation, and second by injecting the reagents that naturally occurring microbes transform to create an iron sulfide phase. As previously discussed (Section 2.4.2) this will lead to the consumption of oxygen and maintenance of reduced conditions in situ for over 1,000 years.

The pIRZ will be established by injection of an organic carbon mixture. The organic carbon will consist of a mixture of sugars, alcohols, and organic acids, and may contain any of the following materials: acetate, ethanol, formic acid, fructose, glucose, hemicellulose, lactate, and sucrose (collectively referred to as TOC). The pIRZ will be established by pushing 0.25% to 5% TOC mixtures into the formation in the pIRZ location (Figures 3 and 5) using a geoprobe or similar apparatus. Approximately 60 injection points will be used in to form the pIRZ. Each injection point will receive

**DRAFT  
Work Plan – In Situ  
Bioremediation  
Treatment of  
Uranium in  
Groundwater in  
Burial Area #1**

Cimarron Corporation  
Crescent, Oklahoma

between 10,000 and 20,000 gallons of TOC mixture, which will be injected over a period of 8-12 hours. The displacement around each injection point will be between 20 and 30 feet. The total volume of water injected in this way will be approximately 500,000 gallons of water for the first injection event. Injections will begin in the downgradient area near the firZ and at the edges of the plume, and work their way toward the center of the plume and into the upgradient area. This will minimize the movement of uranium, keeping as much as practical immobilized at its current location. Because the injections will occur within a period of only a few weeks, groundwater will not travel a significant distance. Groundwater movement will be controlled by the high permeability “channel” in which the plume resides, and will flow toward the firZ.

The pIRZ will be monitored for several months following the initial TOC injections by measuring redox potential in wells within the plume area (Section 3.3). After strongly reducing conditions are established in the pIRZ, a second series of injections will be performed. This second injection series will consist of additional TOC and may include iron and/or sulfate. The addition of iron and sulfate will depend on the data collected during baseline monitoring, and will be balanced to provide the stoichiometric requirement for iron sulfide formation. Depending on the pH of the aquifer solutions, a minor amount of buffer such as sodium bicarbonate or sodium phosphate to raise the pH to approximately 7 may also be added. Up to a total of four injections will occur, with successive injections more concentrated with respect to TOC, and somewhat lower injection volumes than the initial injection. As the monitoring information is received (Section 3.3), the injection mixtures will be refined to adjust the TOC concentrations, the necessary iron and sulfate ratios (to adjust to the potential iron and sulfate sources in the aquifer matrix), and the frequency of the injections will be timed to limit movement of injected materials out of the additional treatment area.

Additional monitoring (Section 3.3) will be performed to demonstrate that the uranium is being converted to the solid phase, and that an iron sulfide phase is being formed. This will include both groundwater sampling for uranium, iron and sulfate, as well as aquifer matrix sampling within the plume area for total reduced iron and sulfur.

### **3.2.4 Upgradient Sandstone Injection**

Similar to the firZ and pIRZ remedial activities, the sandstone aquifer upgradient from the plume will be treated to create reducing conditions, and an iron sulfide phase will be deposited in the aquifer. The purpose of this upgradient treatment is to deplete dissolved oxygen so that upgradient groundwater will be de-oxygenated prior to

migration into the plume area. Approximately 12 injection wells will be created, some of which may be existing wells (Figure 3). These wells will be screened in the B Sandstone (Figure 5).

A TOC mixture approximately 3% TOC will first be injected into the B sandstone wells, (the only sandstone impacted by uranium from the former burial trenches). A total volume of between 20,000 and 40,000 gallons will be injected over several days, after which a small volume of freshwater will be injected to push the TOC away from the well. After reducing conditions have been formed, additional TOC mixtures with iron and sulfate will be injected to create iron sulfide-forming conditions. Depending on the pH of the aquifer solutions, a minor amount of sodium bicarbonate or sodium phosphate buffer to raise the pH to approximately 7 may also be added. Multiple injections (a total of 4 are planned, with additional injections possible depending on field monitoring results) may be used to obtain sufficient iron sulfide deposition to achieve more than 1000 years of uranium stabilization as outlined in Section 2.4.

### **3.2.5 Surface Ecosystem Creation**

After remedial activities are complete, including the plugging and abandonment of unnecessary monitoring wells in the area, the area above the plume will be graded to provide positive drainage, and native vegetation will be planted. These two steps will decrease infiltration of precipitation into the plume area. This will further reduce the potential delivery of oxygen to the plume area.

### **3.3 ARCADIS Treatment Monitoring and QA/QC During Remedial Activities**

ARCADIS will perform several monitoring activities that will ensure that treatment reagents have been successfully applied in the treatment area, and that the biogeochemical reactions of uranium reduction, sulfate reduction, and iron sulfide formation are occurring as expected. This section addresses these monitoring activities. Section 3.4 addresses the compliance monitoring and additional monitoring that ARCADIS will perform to demonstrate that uranium has been successfully immobilized and will remain immobilized for at least 1000 years.

Treatment of affected groundwater will be accomplished with a series of closely spaced injection points located throughout the plume area. The object is to create treatment zones surrounding each injection point that will overlap with the treatment zones created by adjacent injection points (Figures 3 and 5). This will assure treatment coverage throughout the plume area. Based on the physical properties of the alluvial

**DRAFT  
Work Plan – In Situ  
Bioremediation  
Treatment of  
Uranium in  
Groundwater in  
Burial Area #1**

Cimarron Corporation  
Crescent, Oklahoma

material, it is estimated that each injection point will affect treatment for an area of approximately 700 ft<sup>2</sup>. (This estimate is based on 20,000 gallons injected in a 15-foot thick saturated zone, with a 25% effective porosity creating a 15-foot radius per treatment injection.) The initial distribution of TOC, iron, and sulfate will be in the areas of highest permeability, and hence it is not likely that a “circular” zone of influence will actually be achieved. However, as diffusion and advection of the treatment reagents moves the individual treatment zone from each injection point downgradient, overlap of treated areas are expected. The multiple monitoring points we will utilize for this injection will be normally spaced from the injection points, and will thus provide a range of distances from injection to monitoring to provide adequate evaluation of treatment progress.

In addition to monitoring treatment injection rates and volumes, two methodologies will be employed to verify the adequacy of injection point spacing. ARCADIS will co-inject a conservative tracer (*i.e.* potassium bromide) at select injection points within the plume. Monitoring for the tracer will then be conducted in adjacent monitoring wells in the area of the injections to confirm that groundwater is sufficiently dispersing treatment reagents throughout the plume. Secondly, periodic screening samples will be collected from select monitoring wells near the injection points and analyzed for TOC, iron, and sulfate to document the distribution of expected geochemical conditions within the plume.

ARCADIS will monitor groundwater, aquifer solids, and the vadose zone for biogeochemical parameters that indicate treatment progress. This will allow ARCADIS to adjust the concentration and/or quantity of injected materials during subsequent applications. This will be an iterative process until the groundwater standard for uranium is achieved and sufficient iron sulfide and other reduced compounds have been deposited to ensure uranium stability.

Figure 6 shows the locations of the groundwater wells ARCADIS will utilize for compliance monitoring (Section 3.4). These will be monitored for concentrations of injected compounds, for uranium concentrations during the first few months of treatment, and for microbiology parameters. In addition to compliance monitoring wells, other monitoring wells may be periodically sampled to monitor treatment progress as desired by ARCADIS.

ARCADIS will remove soil cores from locations adjacent to the cores removed in the pretreatment baseline geochemical monitoring described in Section 3.1. These cores will be analyzed for a variety of parameters, including total mass of organic carbon, reduced iron, and reduced sulfur (elemental sulfur and sulfide), and microbial

abundance and distribution. By comparing dissolved iron and sulfur species with solid phase iron and sulfur mineral phases, ARCADIS will determine if sufficient treatment reagents are present to terminate treatment.

### **3.4 Groundwater Uranium Compliance Monitoring and Stability Demonstration Monitoring**

License condition 27(b) requires eight quarters of monitoring demonstrating that the 180 pCi/L limit is not exceeded in any wells. ARCADIS proposes to demonstrate this by sampling the compliance monitoring wells. For each quarterly monitoring event groundwater samples will be collected from compliance monitoring wells and analyzed for uranium to demonstrate that uranium levels in groundwater remain below 180 pCi/L.

The proposed compliance monitoring well network will include TMW-09, TMW-13, 02W-04, 02W-43, 02W-62, TMW-24, and 1315R (Figure 6). No wells that will be used for treatment reagent injection will be used for compliance monitoring. This ensures that compliance monitoring data is not generated from wells in which treatment reagents have been injected. The first quarterly monitoring event will take place soon after the final injection.

At some point during the 8 quarters of stability monitoring, verification monitoring will be performed to document additional parameters beyond groundwater uranium concentrations. ARCADIS will use these data to show that the uranium plume will remain immobilized for at least 1000 years. This will include assessment of saturated and unsaturated biogeochemical parameters. Mass concentrations of reduced materials in the aquifer, including iron sulfides, elemental sulfur, total organic carbon, and of other reduced sulfur, manganese, iron, and trace elements will be assayed. These concentrations will be compared with the mass of solid phase uranium that has been deposited as a result of treatment. Utilizing calculations similar to what was presented in Sections 2.4.2.3 and 2.4.2.4, ARCADIS will demonstrate that the maximum uranium concentrations under worst-case conditions will not exceed 180 pCi/L for at least 1000 years. The key to this demonstration is the presence of sufficient iron sulfides (along with other reduced compounds) to consume all projected oxygen introduced into the plume over this time period, and sufficient iron sulfides to limit uranium concentrations to less than 180 pCi/L even if substantially more oxygen were introduced into the plume than is projected.

### **3.5 Timeline**

The planned timeline for groundwater decommissioning and license termination activities is outlined on Figure 7. This figure presents a timeline based on two key premises. First is NRC's concurrence that establishment of a forward in situ reactive zone does not constitute remediation, and can be performed without regulatory approval of a decommissioning plan. Second is the assumption that NRC amends the license to provide for remediation by immobilization by the end of July 2004. ARCADIS will mobilize to install the pIRZ within 30 days of license amendment. Active remediation will then continue for approximately another 18 months. The eight quarters of compliance monitoring will begin after the final injection.

### **3.6 Well Abandonment**

There are over 70 monitoring wells within BA#1 (Figure 4). Many of these wells will be utilized during the active remediation period to evaluate injection treatment coverage and remedial progress. Seven representative wells have been proposed for post-remediation monitoring (See Section 3.5). The remaining wells will be plugged and abandoned within six months of the final injection, when their use is no longer required.

Monitoring well plugging and abandonment will take place in phases and may extend over a period of greater than one year. Wells will be plugged and abandoned in accordance with guidelines specified by the Oklahoma Water Resources Board and those requirements provided in the site-specific Sampling and Analysis Plan.

#### **4.0 Sampling and Analysis Plan**

The current Sampling and Analysis Plan (SAP) developed for the Cimarron Site will be followed for the work conducted in BA#1. The SAP governs activities being performed at the Cimarron Site. It specifies sample collection requirements for environmental media, and includes sampling requirements for quality assurance (QA)/quality control (QC) programs. It also specifies required laboratory analytical methods, sampling equipment decontamination, documentation, and sample preparation and shipment. Finally, it specifies requirements for groundwater monitor well installation and abandonment.

Departures from the SAP may become necessary if activity requirements make the provisions of the SAP impractical or inappropriate. Any deviations to the SAP that may become necessary will be documented in accordance with the Cimarron Quality System. For any sampling and analysis performed during the work that may not be addressed in the current SAP, the process or specific methodology will be documented in writing in accordance with the Cimarron Quality System. All such documentation will be retained in the project files.

## **5.0 Health and Safety Plan**

The work will be conducted in compliance with the current Site Health and Safety Plan (HASP) developed for the Cimarron Site. The HASP will be utilized and modified as necessary in order to minimize and prevent exposures to hazardous substances and conditions related to the Cimarron Facility Decommissioning Project.

All personnel on site, contractors, subcontractors and unescorted visitors included, shall be informed of the site emergency response procedures and any potential fire, explosion, health, or safety hazards of the operation. The HASP summarizes those hazards and defines protective measures planned for the site.

The Facility Radiation Protection Plan and associated Procedures, in conjunction with the HASP, will govern all radiological hazards that could be encountered at the Cimarron Facility. This will include the “Declaration of Pregnancy” aspects for Female Employees and visitors who enter radioactive materials areas.

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**DRAFT  
Work Plan – In Situ  
Bioremediation  
Treatment of  
Uranium in  
Groundwater in  
Burial Area #1**

Cimarron Corporation  
Crescent, Oklahoma

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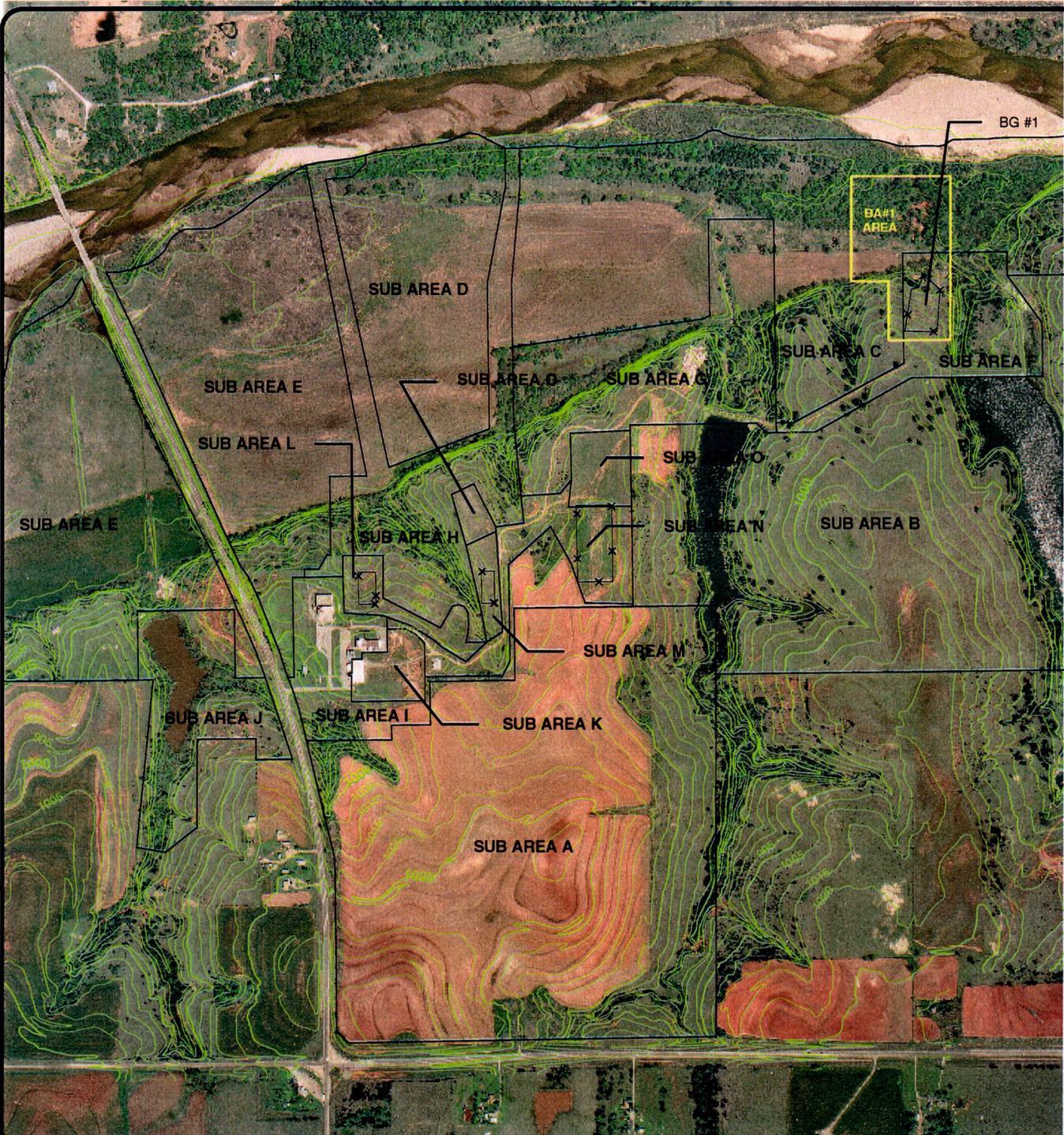
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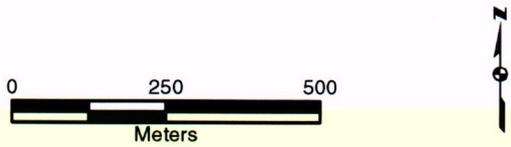
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DWG DATE: 5/21/2003 | PRJCT NO.: OK001376.0001 | DRAWING: CIMARRON SITE MAP | CHECKED: CHECKED | APPROVED: APPROVED | DRAFTER: JKC



LEGEND	
AREAS	CONTOUR ELEVATION
 Burial Grounds	 25 FOOT
 Subareas	 5 FOOT



## Cimarron Site Map

Cimarron Facility  
Burial Area #1

FIGURE

1

COI

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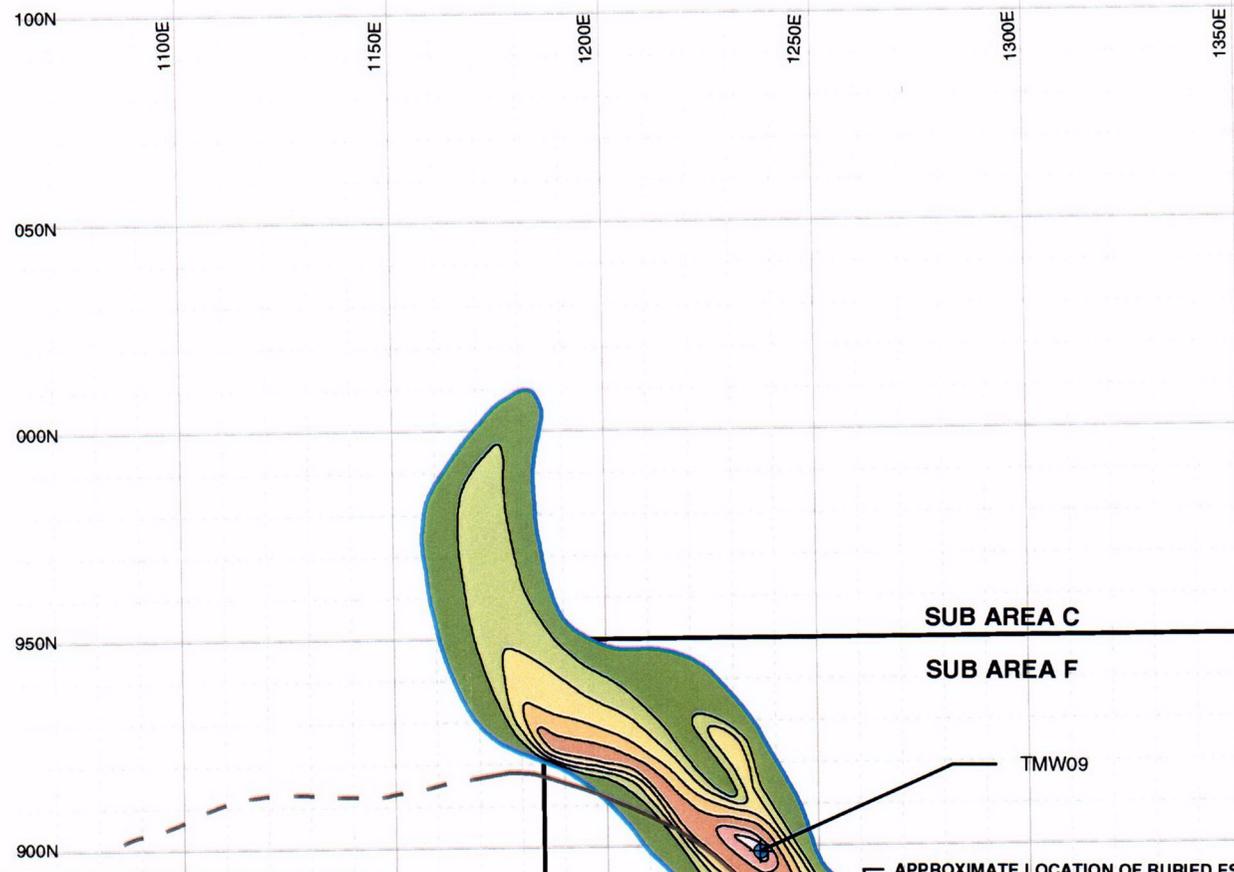
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DWG DATE: 6/17/2003



SUB AREA C  
SUB AREA F

TMW09

APPROXIMATE LOCATION OF BURIED ESCARPMENT

FORMER BURIAL TRENCHES

**LEGEND**

- TMW09
- Section Areas
- Former Burial Trenches
- Escarpment line
- Uranium Plume (October 2002)

**Alpha Spec (pCi/l)**

- 180 - 500
- 500 - 1000
- 1000 - 2000
- 2000 - 3000
- 3000 - 4000
- 4000 - 5000
- >5000 color swatch"/> > 5000

0 25 50  
Meters



# Uranium Plume

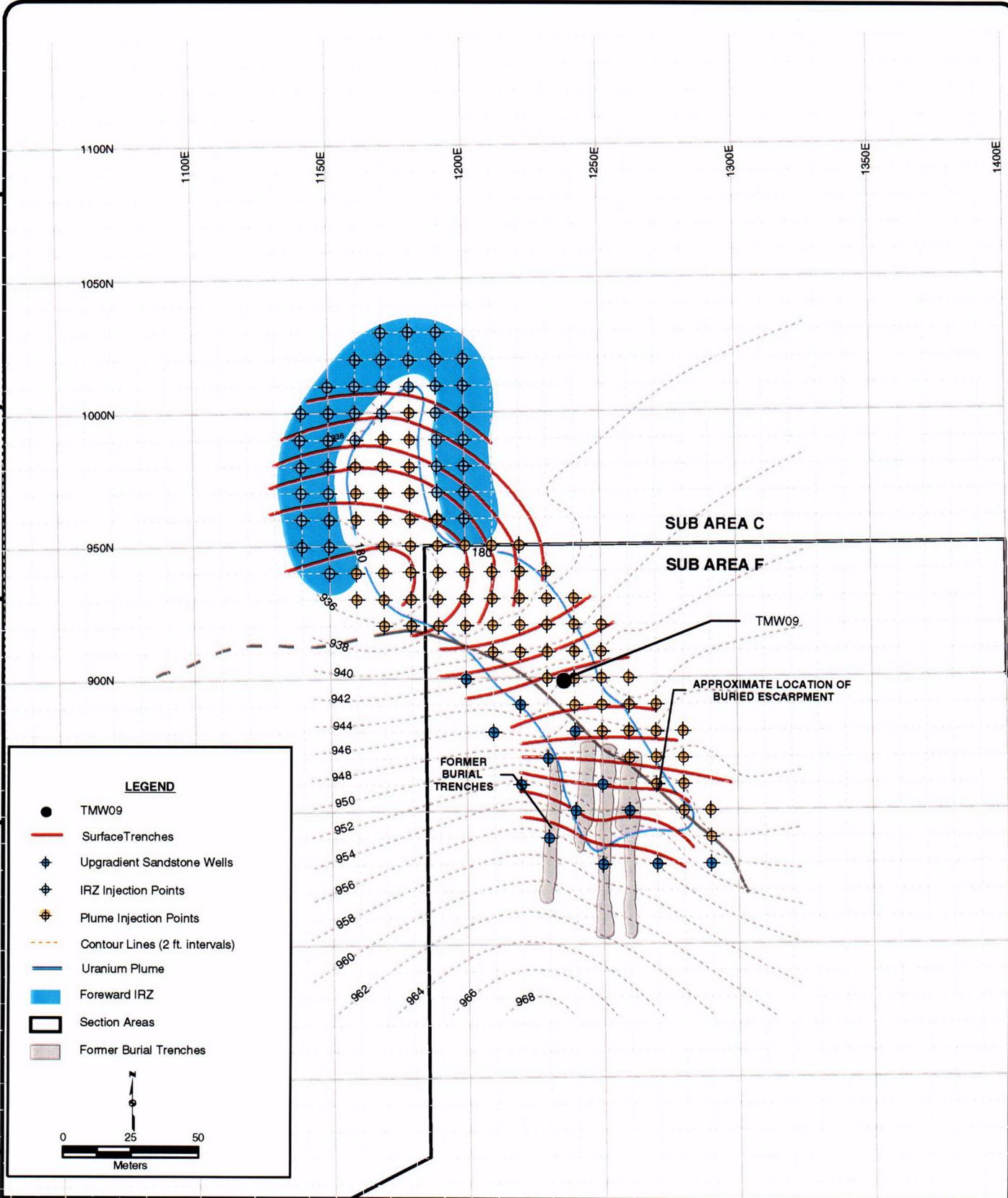
Cimarron Facility  
Burial Area #1

FIGURE

2

CO2

DWG DATE: 6/17/2003    PROJ NO:    DRAWING: DRAWING    CHECKED: CHECKED    APPROVED: APPROVED    DRAFTER: DRAFTER



**Remedial Elements Location**  
 (IRZ, plume injection, sandstone injection, and surface trenches)  
 Cimarron Facility  
 Burial Area #1

FIGURE  
**3**

C03



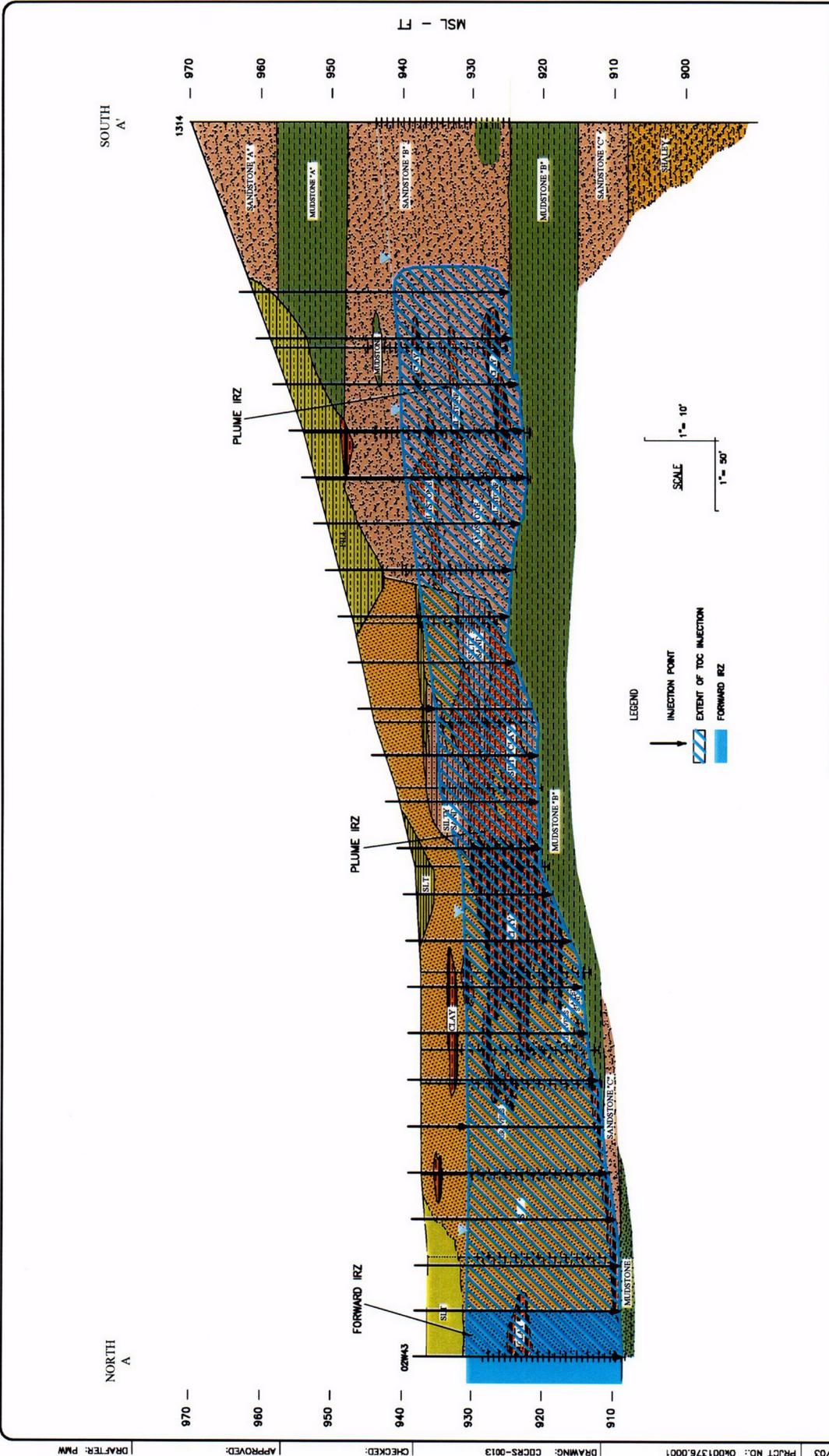


FIGURE 5  
 Geomarron Facility  
 Burial Area #1



05

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CHECKED: CHECKED

DRAWING: Monitoring Wells

PRJCT NO.: OK001376.0001

DWG DATE: 6/17/2003

1100E 1150E 1200E 1250E 1300E 1350E 1400E

1100N

1050N

1000N

950N

900N

TMW24

02W43

02W62

SUB AREA C

SUB AREA F

180

TMW13

02W04

TMW09

1315R

APPROXIMATE LOCATION OF BURIED ESCARPMENT

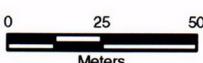
FORMER BURIAL TRENCHES

**LEGEND**

- Section Areas
- Former Burial Trenches
- Escarpment line
- Uranium Plume

MONITORING WELL WITH ID

- ALLUVIAL
- SANDSTONE B

# Proposed Compliance Monitoring Wells

Cimarron Facility  
Burial Area #1

FIGURE

6



C06

TASK	2004				2005				2006				2007				2008					
	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	
Workplan Submission	█																					
NRC Meeting	Nov-03			█		█		█			█				█					█**		
Application for License Termination																				█		
Field Injection TOC (fIRZ)	█	█		█																		
Field Injection Fe/S (fIRZ)		█		█		█		█		█												
Field Injection TOC (pIRZ)				█		█		█		█												
Field Injection Fe/S (pIRZ)				█		█		█		█												
Surface Application TOC				█		█		█														
NAOH / NaHCO <sub>3</sub> injections - precip FeS								█		█												
GW Treatment Monitoring		█	█	█	█	█	█	█	█	█	█											
Solids Monitoring	█		█					█			█											
Well Closure/Surface Regrading											█	█	█									
GW Compliance Monitoring											█	█	█	█	█	█	█	█	█	█	█	█

\*\* License Termination Q3 2008

C07