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May 23, 2000

U.S. Nuclear Regulatory Commission ATTN: John J. Surmeier, Chief Uranium Recovery and Low-Level Waste Branch Division of Waste Management, MS-T-7J9 Office of Nuclear Materials Safety and Safeguards 11545 Rockville Pike Rockville, MD 20850

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**NMSSaPublic** 

Subject: Zone 1 Groundwater Geochemistry Report United Nuclear Corporation Church Rock Site, Gallup, New Mexico

Dear Messrs. Surmeier and Lyssy:

Enclosed is a copy of the above-referenced report, which provides documentation of the March 3, 2000, technical presentation about Zone 1 geochemical processes. The report is contained in two volumes: Volume I consists of the text, tables and figures, and Volume II consists of Appendices A and B, which contain the calculation files and printouts of the model runs. A CD with an electronic copy of the calculation files and model runs is also provided.

Please contact me at (303) 804-2367 or suzie dupont@earthtech.com if you need additional information or copies.

Respectfully,

Earth Tech, Inc.

Suzie du Pont Project Manager

Enclosures

cc: Roy Blickwedel, General Electric Corporation (CD only) Larry Bush, United Nuclear Corporation (CD only) Ken Hooks, NRC Project Manager (CD only) Beiling Liu, NMED (hard copy and CD) George Padilla, Navajo Superfund (hard copy and CD)

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Project No. 32114 May 2000

### **ZONE 1** GROUNDWATER GEOCHEMISTRY **VOLUME I** OF **II**  TEXT, **TABLES, AND FIGURES**

Church Rock Site, Gallup, New Mexico

*Prepared for: Prepared by:*

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#### **1.0 INTRODUCTION**

Earth Tech, Inc. (Earth Tech), on behalf of United Nuclear Corporation (United Nuclear), is providing this technical documentation of the March 3, 2000, presentation on Zone 1 geochemical processes. The principal finding of that presentation was that natural geochemical processes, irrespective of the groundwater corrective action program, are responsible for the observed concentrations and attenuation of the remaining constituents of concern. As requested in the March 3rd meeting, this technical summary provides the detailed calculations and model runs that support the findings and conclusions of the presentation.

#### **1.1** CURRENT **STATUS**

Accomplishments for Zone 1 include:

- United Nuclear completed 17 years of active remediation, including the neutralization and removal of the source of seepage-impacted groundwater (tailings liquid in Borrow Pit No. 2).
- **0** The U.S. Environmental Protection Agency (EPA) issued the *Five-Year Review Report* in September 1998 which recognized that the groundwater recovery wells meet the decommissioning criteria specified in the Record of Decision (ROD).
- The Zone 1 pumping wells were turned off in July 1999 with agency approval.
- The alternate concentration limit (ACL) and Technical Impracticability (TI) waiver process was initiated to complete the remedial action process under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and in accordance with the *Five-Year Review Report.*

The ACL or TI process is considered to be the acceptable route for attaining closure of the Zone 1 remedial action. However, because of the hydrogeological and geochemical conditions in Zone 1, United Nuclear cannot implement the standard ACL process outlined in the ACL guidance documents. Therefore, United Nuclear prepared the March **3rd** presentation to document the hydrogeological and geochemical conditions that prevent use of the standard ACL process and to propose a hybrid remedy that can attain compliance with the CERCLA ROD. The hybrid remedy is a combination of:

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- Monitored natural attenuation (MNA) for neutralization and constituent removal;
- TI for the low formation yield and natural geochemical conditions that prevent manganese, sulfate and total dissolved solids (TDS) concentrations from meeting the water quality standards;
- Institutional Controls (IC) for supporting MNA and the TI waiver process and providing an added measure of protection of human health and the environment.

#### 1.2 **SITE** OVERVIEW

The March 3, 2000, presentation was based on Zone 1 water quality data collected since 1989 as part of the approved performance monitoring program (United Nuclear, 1989a and 1989b). Figure 1 (Slide 24 of the March 3 presentation) shows the locations of monitoring wells that are sampled quarterly as part of this program. These groundwater data have been provided to the regulatory agencies on a regular basis in annual reports (Canonie Environmental Services Corp. 1989 through 1993, 1995; Smith Technology Corporation 1995 and 1996; Rust Environment & Infrastructure 1997; and Earth Tech 1998 and 1999) and in electronic database format.

Groundwater in Zone 1 in the vicinity of the Church Rock tailings impoundment was created by mine water that was discharged to Pipeline Arroyo. This mine water percolated into the alluvium and then into the underlying Zone 1 formation and created a temporary saturation in the vicinity of the tailings impoundment. The temporary saturation created by the mine water discharge is the recognized background water for Zone 1 (EPA 1988).

The background water in Zone 1 was later impacted by acidic seepage from Borrow Pit No. 2, shown on Figure 1, which is located on the eastern side of the tailings impoundment. The acidic seepage contained elevated concentrations of metals, radionuclides, and major ions such as sulfate and chloride. Source remediation (neutralization of and later dewatering the borrow pit) plus neutralization of the seepage by natural attenuation and mixing with the background water has reduced the concentrations of most of the constituents to below the cleanup standards established for the site. However, cleanup standards are still exceeded in parts of Zone 1, including off the property in Section 1.

Figure 1 shows the approximate extent of seepage impacts in blue. Currently, groundwater standards are exceeded outside United Nuclear's property boundary in Section 1 for cobalt (Co), nickel (Ni), combined radium-226 and 228 (combined Ra-226/228), manganese (Mn), sulfate (SO4), and TDS. The exceedances of cobalt and nickel are evident only at Well EPA 7. Figure 2 shows that the concentrations of cobalt and nickel in this well have decreased to near the standard. As discussed in Section 3.0, these concentrations are expected to decrease to below the standards in the future as a result of natural neutralization processes.

The remaining constituents are exceeded throughout Zone 1 both in wells that have been impacted by tailings seepage and those not impacted. Figures 3 and 4 are graphs of the remaining four constituents (combined radium-226/228, manganese, sulfate, and TDS) over time in the Zone 1 monitoring wells. Of these constituents, the current combined Ra-226/228 exceedances (Figure 3) are likely due to variability in analytical precision (see Section 3.1). The concentration trends for manganese, sulfate, and TDS indicate that these constituents will continue to exceed the standards in the future. Although these three constituents are nonhazardous and present in background water, they are considered constituents of concern for Zone 1 and are discussed further in Sections 3.2 and 3.3.

#### 2.0 **ZONE 1** GEOCHEMISTRY

This section presents an overview of the Zone 1 geochemistry that is the basis for predicting future concentrations of constituents of concern. The conceptual geochemical model developed to understand the evolution of the Zone 1 water chemistry is also discussed. The section on the evolution of the water chemistry includes a discussion of the extent of seepage impacts and the effectiveness of the active remediation system that was operated to control the seepage.

#### 2.1 GEOCHEMICAL **AREAS**

To better understand current groundwater quality and to predict future conditions, a conceptual geochemical model of constituents in the Zone 1 groundwater was developed. The model was built upon the observed evolution of groundwater geochemistry along flow paths from the center of seepage (former source area) to the leading edge of the seepage-impacted groundwater.

Four geochemical areas are defined on Figure 1 (Slide 24) based on the water types that are presented in Table 1 (Slide 25). They are:

- **0** Center of Seepage (shown in red)
- Transition 1 (shown in green)
- Transition 2 (shown in blue)
- Background (shown in white)

The Center of Seepage area is characterized by acidic pH (less than 5) and low (near nondetect) bicarbonate concentrations. It is the only area where the aluminum standard is exceeded. The Transition 1 area has less acidic pH, bicarbonate concentrations in a few hundred milligrams per liter (mg/L), and exceedances of the manganese standard. Transition 2 area has near neutral pH values, bicarbonate concentrations above 1,000 mg/L, and no manganese exceedances. The Background area is the water beyond the seepage-impacted area and has near neutral pH, bicarbonate concentrations in the hundreds of milligrams per liter and low concentrations of metals. Although not evident from the limited data presented in Table 1, manganese is also exceeded in some background wells, as shown on Figure 3. The sulfate standard is consistently

exceeded in all four areas, including background water that is unaffected by the plume that emanated from Borrow Pit No. 2.

The overall chemical evolution in this groundwater system is brought about by the successively greater neutralization of acidic seepage via reaction with carbonate minerals along the groundwater flow paths. Carbonate minerals, principally calcite and dolomite, are known to occur in the Gallup Formation (Kaharoeddin 1971). The increasing bicarbonate concentrations that accompany the increasing pH trend along groundwater flow paths are evidence that the acidic seepage water is reacting with the carbonate minerals.

#### 2.2 **EXTENT** OF **SEEPAGE IMPACTS**

The extent of seepage impacts was determined using chloride. Chloride was used for two reasons:

- \* Chloride was present in Borrow Pit No. 2 water at concentrations 10 times greater than in the postmining-pretailings water.
- **0** Chloride is a non-reactive, conservative species that migrates coincident with groundwater.

Therefore, chloride is a good tracer of the extent that the seepage has migrated from Borrow Pit No. 2. The relative mobility of the remaining constituents of concern may be measured against the extent of seepage water migration as defined by chloride migration.

The chloride concentration delineating seepage impacts was determined based on a review of the chloride concentrations in the monitoring wells over time. Figure 5 presents the range of chloride concentrations for Borrow Pit No. 2 and the monitoring wells in the performance monitoring program. All the data available for each well were used in developing the figure, including data collected prior to 1989. Figure 5 shows that the wells on the left side of the graph (Wells 516 A, 614, EPA *5, 515* A, and EPA 7) exhibit higher and a greater range of concentrations than the wells on the right side of the graph (Wells 604, 619, EPA 2, EPA 4, and EPA 8). The wells on the right side exhibit a much smaller range of chloride concentrations and the maximum concentration is typically near 50 mg/L. Based on the chloride and other constituent data, these wells have not yet been impacted by the seepage from Borrow Pit No. 2. Well 604 is the only exception as the water from this well is currently acidic and is clearly seepage impacted. This well has always had anomalously low chloride concentrations compared to the other seepage-impacted Zone 1 wells.

Changes in chloride and other constituent concentrations over time in Wells 515 A, 516 A and EPA 5 were used to verify the minimum chloride concentration that indicates seepage impacts from Borrow Pit No. 2. The data used include chloride, field pH, bicarbonate and aluminum and are plotted on Figure 6. The scale for the Y-axis does not account for bicarbonate concentrations greater than 400 mg/L because it was scaled to the lower concentrations of chloride and aluminum to highlight the early changes in concentration. The blue shading on the left side of the graphs on Figure 6 identifies the time period when Wells 515 A, 516 A and EPA 5 had much lower chloride concentrations (near 50 mg/L). These concentrations increased several fold when the borrow pit seepage migrated into these locations.

Changes in the other constituent concentrations in water from these wells correspond with the increases in chloride concentrations. The clearest example of this corresponding change in constituent concentrations is the data for Well EPA 5, which are presented on the bottom graph on Figure 6 and also in Table 2. The initial six quarters of data show chloride at stable levels averaging 67 mg/L (Table 2). The pH during this time period averaged 7.0, bicarbonate averaged 234 mg/L, and aluminum was not detected in the one sample that was analyzed for aluminum. The water quality began to change after April 1989 when chloride began increasing, pH began decreasing, bicarbonate increased and aluminum was detected. The changes in these other constituent concentrations provide additional evidence that the increases in chloride concentrations indicate migration of seepage into these areas. Therefore, chloride concentrations of 50 mg/L and greater were selected as a conservative indicator of seepage impacts.

The current extent of the chloride plume (chloride greater than 50 mg/L) was estimated based on concentrations at the individual wells through time as well as by projecting a travel distance for groundwater based on the hydraulic gradients between wells for those areas with limited data. Chloride concentrations for all wells with chloride data, including wells not used in the current monitoring program, were plotted on an annual basis beginning in 1980. These plots were included as a slide animation (Slide 19) in the March  $3<sup>rd</sup>$  presentation. Figure 1 (Slide 24) shows the final map that was prepared from the 1999 data and represents the current estimated extent of seepage impacts.

#### 2.3 REMEDIAL **ACTION** SYSTEM

United Nuclear began operating a corrective action pumping system in 1984 to contain and remove the acidic seepage originating from Borrow Pit No. 2. This system consisted of extraction wells located along the downgradient (east and north) sides of the borrow pit. However, review of the water quality and pumping data indicates that, although this system extracted some of the hazardous constituent mass present in the seepage, it was ineffective in containing and removing the acidic seepage. Rather, source treatment and removal (i.e., neutralizing and then dewatering the borrow pit) and natural processes (i.e., neutralization by the Zone 1 formation and mixing with the background water) were effective in containing the seepage and reducing constituent concentrations.

Figure 7 (Slide 20) illustrates the lack of effectiveness of the corrective action system. This graph is a plot of the cumulative volume of water pumped by the corrective action system wells versus the volume of the acidic pH and chloride plumes. The pumping is shown as the green line, the pH plume as the red line and the chloride plume as the blue line. The volumes of the chloride and pH plumes plotted on Figure 7 (Slide 20) were determined from the area of the plumes estimated annually for the animation (Slide 19). These areas were then multiplied by the average saturated thickness at the monitoring wells for each year and an effective porosity of 10 percent.

Figure 7 (Slide 20) shows that initially the chloride and pH plumes were expanding rapidly as the seepage from Borrow Pit No. 2 migrated into Zone 1. Migration occurred because the one-foot thick compacted clay liner in the borrow pit was insufficient to prevent leakage of the tailings liquor, which was as much as 40 feet deep. As a result, the driving head of the water in the borrow pit overwhelmed the containment capacity of the liner and the pH and chloride plumes developed and expanded. The expansion of the pH plume slowed beginning in 1982 because United Nuclear began neutralizing the water in the borrow pit. The neutralization had little effect on the chloride plume, which continued to expand.

In 1984, United Nuclear began pumping from the corrective action system wells in an attempt to capture and control the acidic seepage. Figure 7 (Slide 20) shows that the pumping had little or no effect on the migration of the seepage-impacted water. If pumping had an effect, it would be evident as a deflection (reduction in the slope) of the pH and chloride plume lines. However, the pH line continued to show the same slope that was evident after the borrow pit was neutralized and before the pumps were turned on. Similarly, the increasing trend of the chloride plume line showed little change after the pumps were turned on.

A deflection in the slope of both the pH and chloride plume lines does occur in 1989 in response to dewatering the borrow pit. This deflection occurred even though the 17 extraction wells were still pumping. The slope of the pH plume line reversed after this time indicating that the pH plume was reducing in size. In fact, the volume of the pH plume decreased so much that by about 1997 the acidic pH plume was contained within the property boundary. The lesser slope of the chloride plume line indicates that the expansion rate of the chloride plume slowed.

The reduction in the pH plume volume and slower expansion of the chloride plume volume occurred primarily because groundwater flow rates slowed in response to reduced hydraulic gradients. An artificially steep gradient was created by the water in the borrow pit. Once this water was removed, the hydraulic gradients decreased and groundwater flow velocity slowed. The slower flow velocity slowed the chloride plume expansion. Also, the slower flow rates allowed the natural neutralization process to be more effective, which resulted in the contraction of the acidic pH plume. As is evident from Figure 7 (Slide 20), these changes in the chloride and pH plumes occurred independent of the corrective action pumping.

#### **3.0 FATE** OF **CONSTITUENTS** OF **CONCERN**

This section presents a discussion of the fate of the constituents of concern that exceed the standards outside the property boundary in Section 1. These are the metals cobalt, nickel and manganese, combined radium-226/228, sulfate and TDS. The discussion focuses on assessing the dominant geochemical mechanisms controlling the migration of the constituents. Both empirical and modeled data were used to identify the mechanisms and illustrate how they function in the different geochemical areas in the Zone 1 water.

#### **3.1 METALS AND RADIONUCLIDES**

The dominant geochemical mechanism for removing metals and radionuclides from water is acid neutralization accompanied by the precipitation of stable solids and an increased affinity for adsorption in the less acidic water. Metals concentrations decrease when the acidic seepage from Borrow Pit No. 2 is neutralized. Figures 8 and 9 show temporal concentration trends for cobalt, nickel, and combined radium-226/228 at Wells 515 A, 516 A and EPA 7. All three wells were impacted by borrow pit seepage and had acidic pH values and bicarbonate concentrations near 0.0 mg/L. These wells are now Transition area wells because the acidic seepage from the borrow pit has been neutralized as indicated by the trend of increasing pH shown on the graphs. Currently all three wells have water with pH near or above 6.0.

Figure 8 shows that concentrations of cobalt and nickel have been decreasing with time as pH increases. Cobalt and nickel are removed from groundwater at sub-neutral or near-neutral pH values by adsorption. Cobalt is adsorbed strongly by manganese oxides (Murray and others 1968). Nickel and barium (and probably radium) are also adsorbed, but have lesser affinities for manganese oxides (Murray 1975). Cobalt and nickel are also adsorbed, by ferric oxyhydroxides (Dzombak 1986). Adsorption by ferric oxyhydroxides occurs most effectively between pHs of approximately 5.5 to 8 for cobalt and 5 to 7 for nickel, depending on conditions (Dzombak 1986). Figure 8 shows that in Zone 1, pH values consistently greater than 6.0, as are encountered in the Transition 2 area (Well 516 A), are needed for removal of these metals to below standard concentrations. The water from EPA 7, the only well in Section 1 with exceedances of these two metals, is expected to continue its trend of increasing pH and decreasing nickel and cobalt so that the standards will not be exceeded in the future.

Figure 9 shows that combined radium-226/228 exhibits similar trends of decreasing concentration over time as the pH increases. A pH of about 6.0, as is encountered at Wells 516 A and EPA 7, is needed for the combined radium to be reduced below the standard concentration. Unlike cobalt and nickel, radium adsorption by ferric oxyhydroxides may be minor because of the presence of large concentrations of calcium and magnesium in Zone 1 water (Ames and others 1983a). Radium may be removed by adsorption onto clay minerals (Ames and others 1983b) and by precipitation. Precipitation of radium may be a more important mechanism in Zone 1 as radium behaves chemically somewhat like barium and precipitates as a sulfate (Hem 1989; Jim Otton, personal communication 2000). The slow groundwater flow velocities in Zone 1 would allow the precipitation to occur, as this process is documented to be slow (Moffett and others 1981).

Radionuclides and metals (except manganese) are not predicted to exceed standards in Section 1 in the future. Neutralization of water in the plume has been occurring as a result of source removal (dewatering of Borrow Pit 2) and reactions with carbonate minerals in the formation. The lower groundwater flow rates brought about by significant decrease in the hydraulic gradient have increased the contact time between impacted Zone 1 water and the formation. Dissolution of carbonates in the sandstone will further increase pH and will result in additional removal of metals and radionuclides.

#### 3.2 MANGANESE

Like the other metals, manganese exhibits decreasing concentrations as the acidic seepage from Borrow Pit No. 2 is neutralized. However, the concentrations do not always decrease to the current standard. Table 3 and Figures 10 and 11 (Slides 32 and 33) show temporal manganese concentration trends for wells from the four geochemical areas. As indicated, the manganese standard is exceeded in the Center of Seepage and Transition 1 area, and in Background area Well EPA 8.

Data for Transition 2 area Wells 516 A and EPA 5 show manganese concentrations have decreased to below the standard. An important mechanism for decreasing manganese concentrations in near-neutral pH water is precipitation of manganese as a carbonate. Carbonate is added to water by dissolution of calcite or dolomite. These minerals have been documented in the Gallup Sandstone (Kaharoeddin 1971). The reaction is depicted as:

$$
CaCO3 + H+ ---- > Ca2+ + HCO3
$$
 (1)

The increase in bicarbonate allows reaction (2) to occur:

$$
Mn^{2+} + HCO_3 + OH \quad \text{---} > MnCO_3 + H_2O \tag{2}
$$

Thus, manganese concentrations are decreased by reaction (2).

Figure 12 (Slide 35) shows that manganese concentrations decrease as bicarbonate concentrations increase in Transition area wells. This inverse relationship provides empirical evidence that manganese carbonate precipitation is occurring. To evaluate the extent of carbonate precipitation as a mechanism for removal of manganese, analytical data were evaluated using MINTEQA2 (Allison and others 1991). MINTEQA2 is a widely accepted aqueous speciation model distributed by the EPA. Analytical data and water quality parameters are input into the model, which calculates the distribution of the aqueous species as dissolved, adsorbed, and precipitated species at equilibrium conditions. The assumption of equilibrium conditions is a reasonable approximation for Zone 1 groundwater. Evidence for geochemical equilibrium is provided on Figures 3, 4, 10, and 11, which show that constituent concentrations are stabilizing in the wells. Also, as discussed in Section 3.3, Zone 1 groundwater is near equilibrium with gypsum.

To model whether carbonate precipitation could be responsible for the observed decrease in manganese in the Transition 2 area, Well EPA 5 water quality data from sampling events with the highest manganese concentrations were used. Bicarbonate concentrations were increased incrementally to determine at what concentration the manganese standard would be met. As shown on Figure 13 (Slide 37), model results indicate that when the solution bicarbonate is approximately 710 mg/L, manganese concentrations are below the standard of 2.6 mg/L. Bicarbonate concentrations in the Transition 2 area are over 1,000 mg/L, which is higher than the 710 mg/L needed to reduce manganese concentrations to the standard. Therefore, manganese removal by precipitation as a carbonate is a likely mechanism for the decrease in manganese concentrations.

Calculation file 1 in Appendix A provides details of the modeling using data from Wells EPA 5 and 516 A, including input parameters, model runs, and results. Results for Well 516 A data were similar to those for Well EPA 5.

Based on the manganese modeling results, Zone 1 waters with bicarbonate concentrations less than 710 mg/L and manganese concentrations exceeding the standards are expected to continue exceeding the manganese standards. An example is Well 515 A, which is a Transition 1 area well. As shown on Figure 14 (Slide 38), bicarbonate concentrations at Well 515 A are below 600 mg/L and observed manganese concentrations are greater than the water quality standard as the model predicts. These manganese concentrations will continue to exceed the standard unless bicarbonate concentrations increase. However, as the water reaches neutral pH conditions, as is the case at Well 515 A, carbonate dissolution ceases and additional bicarbonate will not enter solution. The result is that the manganese standard will not be attained. This applies to the background water as well where the pH is neutral and, as shown on Figure 3, manganese concentrations are exceeded at Wells EPA 8 and EPA 4.

#### **3.3 SULFATE**

Table 3 lists concentration data for sulfate and Figure 15 (Slide 43) shows temporal sulfate concentration trends for wells from the four geochemical areas. The figure illustrates that the groundwater standard for sulfate is exceeded in wells in all parts of the seepage-impacted area and in background wells. The figure also shows that sulfate concentrations appear to be stabilizing in individual wells.

The occurrence of sulfate above the groundwater standard in background wells indicates a post mining pre-tailings source of sulfate, such as dissolution of a naturally occurring mineral. Gypsum (CaSO<sub>4</sub> • 2H<sub>2</sub>O) is ubiquitous in arid environments such as the site. As the background mine water infiltrated through the alluvium and into the Zone 1 formation, gypsum dissolved, resulting in calcium-sulfate rich water. This is the source of sulfate in the postmining-pretailings background water. A second source of sulfate in the impacted part of Zone 1 was the acidic plume. Sulfate in the plume originated primarily from sulfuric acid used in the milling process.

To evaluate the controls on sulfate concentration in Zone 1, water quality data were evaluated using the geochemical model, MINTEQA2 (Allison and others 1991). Median concentrations for 1998-1999 at each well were used as input to the model. Calculation file 2 in Appendix B provides details of the modeling, including input parameters, model runs, and results.

Figure 16 (Slide 47) illustrates the model results. This figure shows the modeled gypsum saturation indices for water at each well location. The indices (indicated by red diamonds) are all slightly above and very close to the zero line within the zone where gypsum saturation occurs. The indices demonstrate that water in Zone **I** is near equilibrium with gypsum. The fact that the indices are close to the zero line shows that gypsum precipitation and/or dissolution are important controls on Zone 1 sulfate concentrations. If this were not the case, the saturation indices would be scattered rather than nearly parallel to the zero saturation index line.

The saturation indices for the Background area wells (EPA 2, EPA 4 and EPA 8) are above the zero line, indicating that gypsum dissolution has occurred. This confirms dissolution of gypsum as the likely mechanism for the presence of sulfate in background groundwater at concentrations above the standard.

Reaction 3 shows the equation for the formation (or dissolution) of gypsum (CaSO<sub>4</sub>  $\cdot$  2H<sub>2</sub>O):

$$
Ca^{2+} + SO_4^{2+} + 2H_2O \quad \leftarrow \quad \text{Cas} O_4 \cdot 2H_2O \tag{3}
$$

The reaction shows that sulfate concentrations can decrease if calcium concentrations increase, resulting in gypsum precipitation. Only two wells, 515 A and 516 A, have water quality data indicating a decrease in sulfate concentrations. Figure 17 (Slide 45) shows that sulfate concentrations in Well 515 A have decreased, but a corresponding increase in calcium concentrations is not evident. Rather, calcium concentrations remain stable. Figure 18 shows that calcium concentrations are also stable in other Zone 1 wells, including Well 516 A.

As dictated by the Phase Rule, calcium concentrations are essentially fixed by the presence of two calcium-bearing minerals, gypsum and calcite, in the Zone 1 formation. This observation is perhaps the best indication of the validity of the reaction mechanisms used to explain the evolution of water quality in Zone 1. Because of the Phase Rule, calcium concentrations cannot increase and, therefore, sulfate concentrations are stabilizing.

Despite the geochemical control on Zone 1 water chemistry by gypsum, sulfate concentrations range from approximately 2,000 mg/L at Well EPA 2 to 7,000 mg/L at Well 516 A. This range of sulfate, along with the nearly stable calcium concentrations (Figures 17 and 18), indicates that calcium limits the occurrence of gypsum precipitation and therefore limits the decrease in sulfate concentrations. Sulfate decline due to mixing with background water is also limited, as indicated by the leveling of sulfate concentrations on Figure 15. As a result, it is not possible for sulfate concentrations to change much from what they are or to meet the sulfate standard outside the property boundary in Section 1.

#### 3.4 TOTAL **DISSOLVED SOLIDS**

TDS concentrations are also exceeded in several of the Zone 1 wells including Background area Well EPA 8. These exceedances are related to the presence of elevated concentrations of sulfate in the water. Figure 19 (Slide 42) illustrates the contribution of major ions to TDS and shows that sulfate contributes more than 50 percent of the TDS. Because sulfate contributes more to TDS than all other ions combined, TDS concentrations are determined primarily by the concentrations of sulfate in the water. As discussed above, sulfate is expected to remain at concentrations that will cause TDS to exceed the standards both within the seepage-impacted area and in the unimpacted water.

#### 4.0 **SUMMARY AND RECOMMENDATIONS**

The evaluation of Zone 1 water geochemistry demonstrates the following:

- Metals and radionuclides are naturally attenuated in Zone 1 water as pH increases toward neutral.
- Manganese is the exception for the metals because concentrations continue to exceed the standard in wells where there is insufficient bicarbonate for manganese carbonate precipitation.
- Manganese exceeds the standards in the postmining-pretailings (background) water.
- Sulfate control by gypsum precipitation is limited by calcium availability.
- Sulfate will continue to exceed the water quality standards both in the seepage-impacted area and in the Background area.
- The majority of TDS is composed of sulfate, therefore TDS concentrations mimic sulfate.

Considering the Zone 1 geochemical conditions documented in this report, United Nuclear believes that the solution for closure of Zone 1 is a combination of three different approaches:

#### 1. Monitored Natural Attenuation

- **0** To account for source treatment and removal (Borrow Pit No. 2 was neutralized in 1982 and dewatered in 1989), and
- To account for natural attenuation which:
	- Contracts the plume acidic pH is neutralized, causing metals and radionuclide precipitation, and
	- Stabilizes the plume equilibrium conditions and mixing with the background water maintain sulfate and manganese at their current or lower concentrations.

#### 2. Technical Impracticability Waiver

- To account for the natural hydraulic conditions which:
	- Limit well yields to very low rates, and
	- Prevent pumping wells from achieving hydraulic control.
- **0** To account for the natural geochemical conditions which:
	- Prevent attaining standards for manganese (bicarbonate availability), and
	- Prevent attaining standards for sulfate and TDS (gypsum equilibrium).

#### 3. Institutional Controls

- To support MNA and TI,
- **0** To provide an added level of protection of human health and the environment, and
- To meet administrative needs.

The administrative process for implementing this combined approach includes input from all four agencies involved at this site. To handle the MNA and TI processes, United Nuclear would submit a TI Waiver to the EPA and an ACL application to the Nuclear Regulatory Commission (NRC). The ACL application is addressed in Appendix A to 10 Code of Federal Regulations Part 40. The Navajo Superfund would provide concurrence on IC and the submittals provided to EPA and NRC. New Mexico Environment Department would provide concurrence on the overall approach as well as the submittals provided to EPA and NRC. Final concurrence for the combined approach would be obtained from the Department of Energy prior to site transfer for long-term care.

#### **5.0 REFERENCES**

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#### **TABLES**

## $\sim$   $\sim$  $\ddot{\phantom{a}}$

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#### **TABLE 1** THIRD QUARTER 1999 ZONE 1 GEOCHEMICAL AREA CHEMISTRY



#### Notes:

 $SU =$  standard units

 $mg/L =$  milligrams per liter

 $NA = not applicable$ 

"\*" = NRC designated point of compliance well.

or blue lettering = Wells that formerly had acidic pH less than 5.0 and have been neutralized.

= Constituent exceeding the NRC or EPA standard.



#### WELL **EPA** 5 **CHANGES IN CONSTITUENT CONCENTRATIONS INDICATING SEEPAGE** IMPACTS  $\bar{\mathcal{A}}$

Notes:

 $mg/L =$  milligrams per liter

 $SU =$  standard units

Blank **=** no data available

**"-"** (minus sign) indicates that the concentration is less than the laboratory reporting limit.



#### TABLE 3 SELECTED WATER QUALITY DATA FOR EVALUATING FUTURE MANGANESE AND SULFATE CONCENTRATIONS IN ZONE 1 WATER

\_\_\_\_\_\_\_\_\_\_\_ **L** \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_

II

#### SELECTED WATER QUALITY DATA FOR EVALUATING FUTURE MANGANESE AND SULFATE CONCENTRATIONS IN ZONE 1 WATER



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#### SELECTED WATER QUALITY DATA FOR EVALUATING FUTURE MANGANESE AND SULFATE CONCENTRATIONS IN ZONE 1 WATER



## SELECTED WATER QUALITY DATA FOR EVALUATING<br>FUTURE MANGANESE AND SULFATE CONCENTRATIONS IN ZONE 1 WATER



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#### TABLE **3 SELECTED** WATER QUALITY **DATA** FOR **EVALUATING**  FUTURE MANGANESE AND SULFATE CONCENTRATIONS IN ZONE 1 WATER

Notes:

SU = standard units

mg/L **=** milligrams per liter

 $NA = not applicable.$ 

Shading indicates that the constituent concentration exceeds the NRC or EPA water quality standard.  $Blank = no data available.$ 

FIGURES

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# **Location of Geochemical Areas**

(Zone 1 Geochemical Processes)



**Cobalt and Nickel Exceedances in Section 1** 



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**Combined Radium 226/228 and Manganese Exceedances in Section 1** 

L:Work\32114\Work\Product\ZI GW Geochem\Figures\Z1 Excel Figures\Figure 3 - Mn & Ra

**FIGURE 3** 







**Sulfate and TDS Exceedances in Section 1** 

**FIGURE 4** 

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### Range of Chloride Concentrations



**FIGURE 5**

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**Changes in Concentrations Indicating Seepage** 

**FIGURE 6** 

# **Effect of Pumping on Plume Volume**

(Evolution of Zone 1 Water)



 $($   $)$ 



### **Reduction in Metals Concentrations**

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**Reduction in Radionuclide Concentrations** 

**FIGURE 9** 

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## **Manganese Concentrations**

(Zone 1 Geochemical Processes)

## **Center of Seepage and Transition 1**





 $C-11$ 



## **Manganese vs Bicarbonate**

(Zone 1 Geochemical Processes)



**FIGURE 12** 

 $c - 12$ 

## Modeled Manganese Concentrations

 $\big(\!\! \begin{array}{c} \end{array} \!\!\big)$ 

(Zone **1** Geochemical Processes)



**FIGURE 13**

 $\Big(\Big)$ 

## **Bicarbonate Limiting Manganese Precipitation**

(Zone 1 Geochemical Processes)

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### **Well 515 A**



 $C-13$ 

# Sulfate Concentrations

**0**

(Zone **I** Geochemical Processes)



**FIGURE 15**   $c - 14$ 

**0**

# Gypsum Saturation Indices

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k **(**

(Zone **1** Geochemical Processes)



# **Sulfate and Calcium**

(Zone 1 Geochemical Processes)





L:\Work\32114\Work\Engineering\ACLs Background\NMED PRESENTATION\Zone 1\Figure 18 - Calcium Grph Chart 2\Figure 18 - Calcium Grph Chart 2

**FIGURE 18** 



**FIGURE 19**

### Geochemical Area

#### Note:

Figure based on the median 1999 ion concentrations (first three quarters) for the wells in each geochemical area.