**SANDIA NATIONAL LABORATORIES**
WASTE ISOLATION PILOT PLANT

# Analysis Plan for the Evaluation of Culebra Brine Compositions

**AP-125**

**Task Number 1.4.2.3**

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## Contents

# 1. Introduction

This Analysis Plan directs the investigation of the hydrochemical evolution of Culebra dolomite brines, and how the chemistry relates to the geologic factors related to Culebra transmissivity development and the conceptual flow model for the Culebra. If our conceptual understanding of flow in the Culebra is correct, the chemistry of the Culebra brines and systematics of the brine composition should provide an indirect validation of the Culebra flow model used in performance assessment calculations for the Waste Isolation Pilot Plant (WIPP).

The Culebra is the lower of two dolomite members of the Permian Rustler Formation. The other three members of the Rustler consist principally of beds of anhydrite and mudstone (or other fine-grained clastics). Figure 1 shows the stratigraphic subdivisions of the Rustler, including the informal stratigraphy of Holt and Powers (1988). Halite beds are found in association with the mudstones east of the WIPP site, and halite beds and/or cements are found over much of the WIPP site in the lower Los Medaños mudstone and clastics. The Rustler overlies the Salado Formation, which contains the WIPP transuranic and mixed-waste repository at a depth of 655 m below ground surface (Figure 2).

The Culebra is the most transmissive member of the Rustler and would accordingly provide the most significant groundwater pathway for radionuclides released from the WIPP repository by inadvertent human intrusion. Extensive characterization of the geologic, hydrologic, and hydrogeochemical properties of the Culebra has been performed to allow development of groundwater flow and transport models.

Under this Analysis Plan, we will evaluate the hydrochemical data from recently drilled wells and resampled wells to determine how they fit with the hydrochemical facies described by Siegel et al. (1991b). We will also assess the consistency of the solute concentrations and facies with the conceptualization of flow into and through the Culebra of Corbet (1998), and propose modifications of that conceptualization as appropriate. Finally, we will evaluate the consistency of the revised conceptual model for Culebra flow and hydrochemistry with the Culebra transmissivity (T) fields used for WIPP compliance calculations.

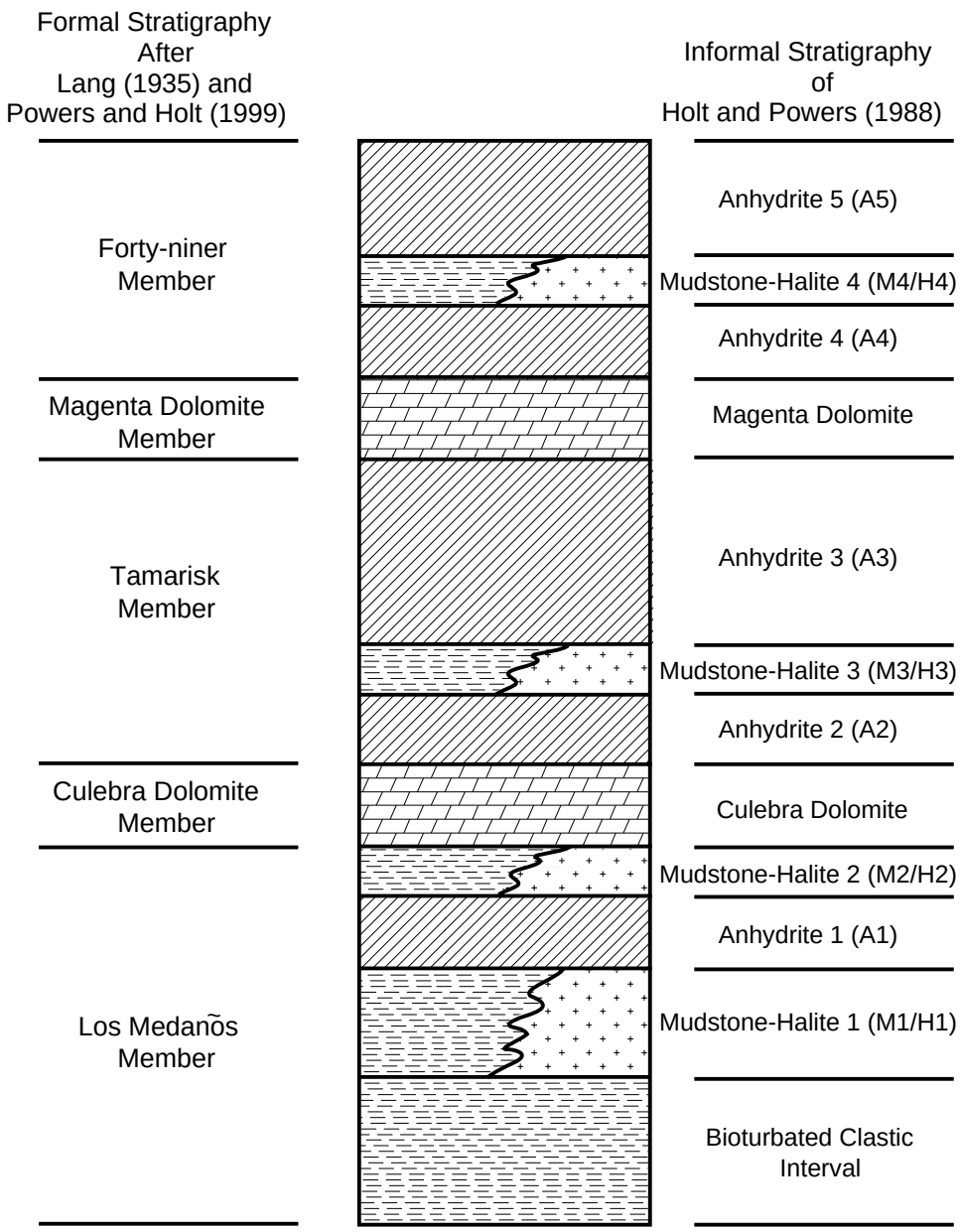


**Figure 1. Stratigraphic subdivisions of the Rustler Formation.**

If the revised conceptual model for the Culebra implies, or relies upon, specific geochemical conditions in the Magenta or other members of the Rustler, this investigation may also extend to the characterization of those brines, using the same techniques as are applied to the Culebra brines.

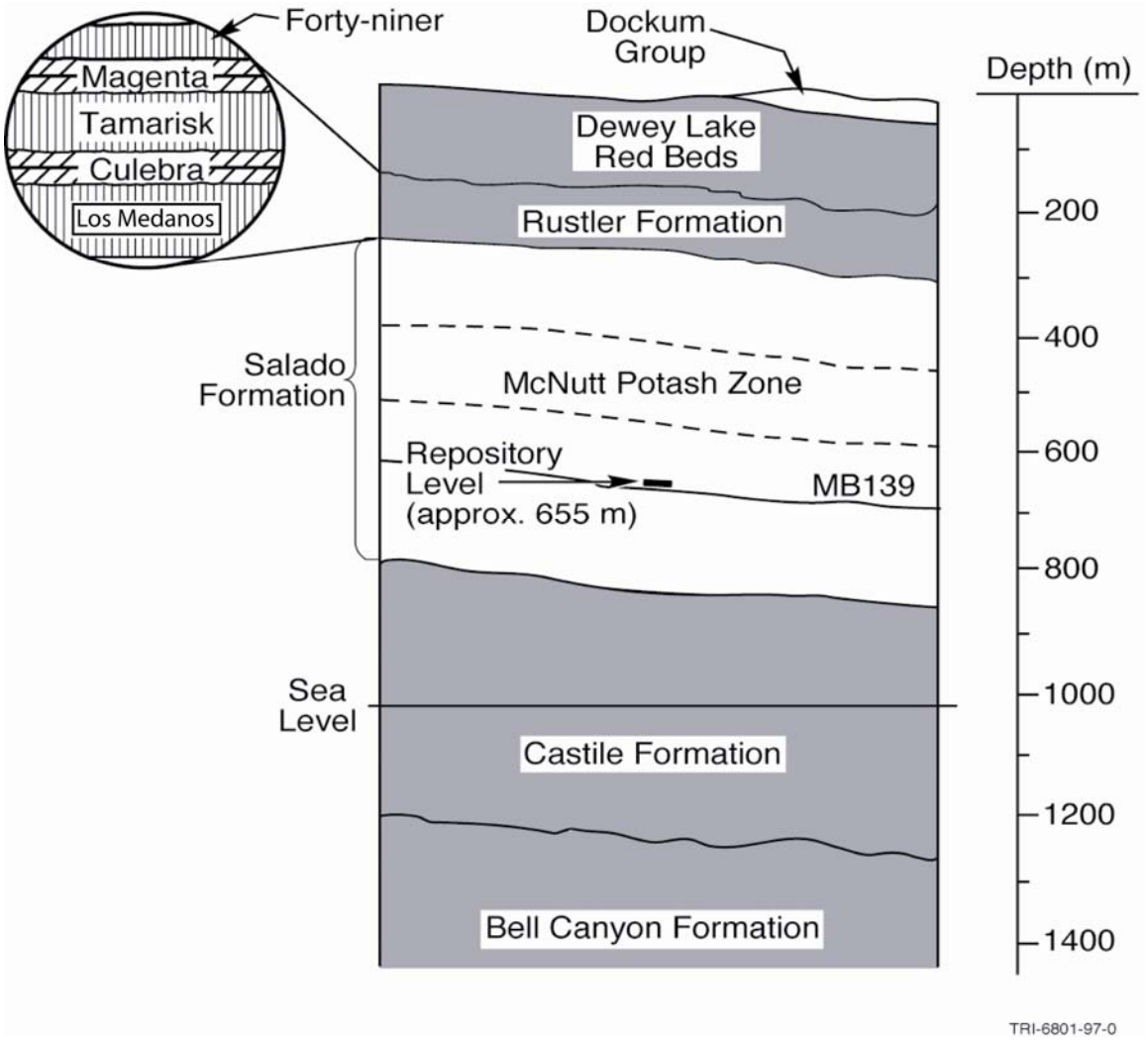


**Figure 2. General stratigraphy at the WIPP site.**

# 2. Motivation for Study

An examination of Culebra brine compositions and their relationship to flow in the Culebra has not been performed since Siegel et al. (1991a). During the interim period between 1989 (date of the latest analyses used in Siegel et al. (1991a)) and today, additional geochemical data have been collected by resampling of existing wells and sampling of newly installed wells (Figure 3), a new geologic model relating transmissivity to upper Salado dissolution and halite margins within the Rustler has been developed (Powers et al., 2003), and the flow model of the Culebra has been revised to reflect the geologic model better. Thus, the primary motivation for this analysis is to evaluate the new chemical data and examine the consistency between the compositions of Culebra brines and the current geologic and groundwater flow models of the Culebra.

## 2.1 Previous Work

Ramey (1985) recognized three hydrochemical facies within the Culebra and, based on the flow model in use at that time, concluded that flow was from regions of high total dissolved solids concentration to regions of lower concentration. Table 1 provides information on the hydrochemical facies identified by Ramey (1985). Subsequent studies sought to explain the compositional variations in the Culebra brines citing factors such as climatic change (Lambert, 1991; Lambert and Carter, 1987) and dilution and/or recharge (Chapman, 1988; Myers et al., 1991). Some of these later studies (Lambert, 1991; Lambert and Carter, 1987) supported the conceptual model of confined groundwater flow in the Culebra, and used several lines of argument against vertical flow into the Culebra. Among these were the prevalence of anhydrite over gypsum in the Rustler members above the Culebra (Siegel and Lambert, 1991), hydrogen and strontium isotope signatures of gypsum and sulfate and carbonate minerals (Lambert, 1991; Brookins and Lambert, 1988), and radiocarbon dates of Culebra waters (Lambert, 1987).

Siegel et al. (1991b) used statistical techniques to classify the brines and delineate four regions within the Culebra, each with its own hydrochemical signature (see Table 1 and Figure 4). Bodine and Jones' (1990) analyses supported the hydrochemical facies of Siegel et al. (1991b), and explained the complex chemistry of the Culebra brines as mixtures of connate brines with meteoric waters that had reacted with the overlying Rustler members.

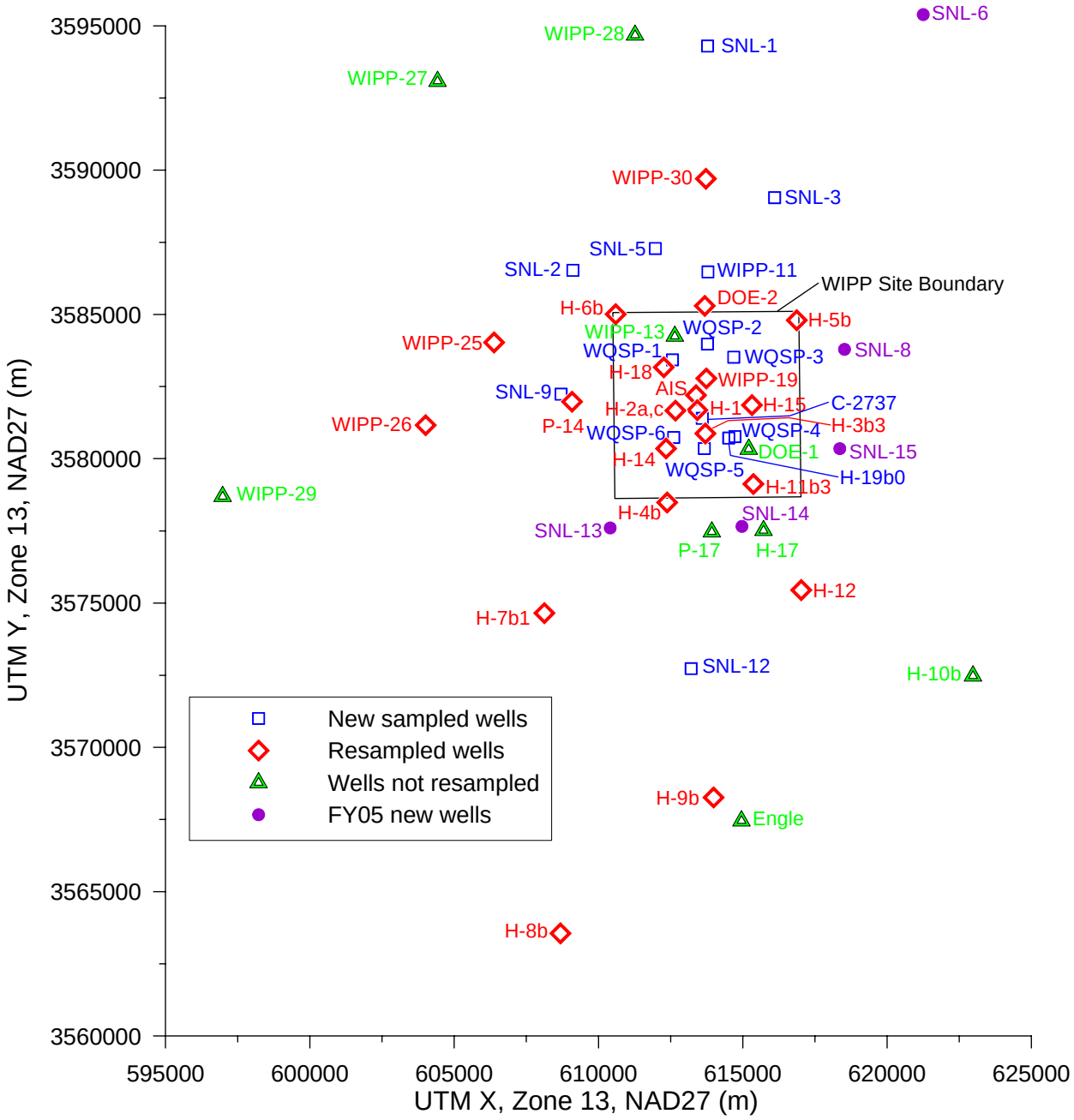


**Figure 3. Locations of Culebra wells providing new water-quality information since Siegel et al. (1991a).**

**Table 1. Previously Identified Culebra Hydrochemical Facies.**

| Author | Facies | Location (relative to the WIPP site) | Predominant Ions | TDS/Ionic Strength Range | Culebra Transmissivity Condition |
|---|---|---|---|---|---|
| Ramey (1985) | A | East | Na – Cl (high K & Mg) | >60,000 mg/L | low |
| | B | South | Ca – $SO_4$ | Typically <9000 mg/L | high |
| | C | North and west | Na – Cl (low K & Mg) | 9000–239,000 mg/L (increases W to E) | variable |
| Siegel et al. (1991b) | A | East | Na – Cl Mg:Ca molar ratios 1.2 - 2 | 2 – 3 molal | low |
| | B | South | Ca - $SO_4$ | <0.1 molal | high |
| | C | West, east side of Nash Draw | Variable | 0.3 – 1.6 molal | generally high |
| | D | North and west, west side of Nash Draw | Possible contamination from potash mining | 3 – 7 molal | high |

Later groundwater modeling studies (Corbet and Knupp, 1996; Kröhn and Schelkes, 1996; Corbet, 1998) sought to develop alternate conceptual models of flow in the Culebra that included vertical flow (leakage) from other Rustler members. From 3D basin-scale modeling, Corbet (1998) concluded that vertical leakage through the halite-free members of the Rustler overlying the Culebra south and southwest of the WIPP site has created the facies B water defined by Siegel et al. (1991b) (Figure 4), while the facies C water was created by slower leakage of Dewey Lake water, recharged northeast of the WIPP site, through anhydrite, and locally halite, in the Rustler. Kröhn and Schelkes (1996) constructed a vertical cross-section model from east to west across the southern WIPP site with density-dependent flow. Starting from initial conditions of fresh water everywhere in the modeling domain except for fixed saturated brine conditions at the top of the Salado and in the Rustler halite beds, they were able to simulate the present-day distribution of Na-Cl in Culebra and Magenta waters by allowing decreasing amounts of leakage from west to east. They concluded that flow and groundwater compositional variations in the Culebra are determined by a combination of large-scale heterogeneities in Culebra permeability and the contribution of vertical leakage (primarily in Nash Draw) to the Culebra.

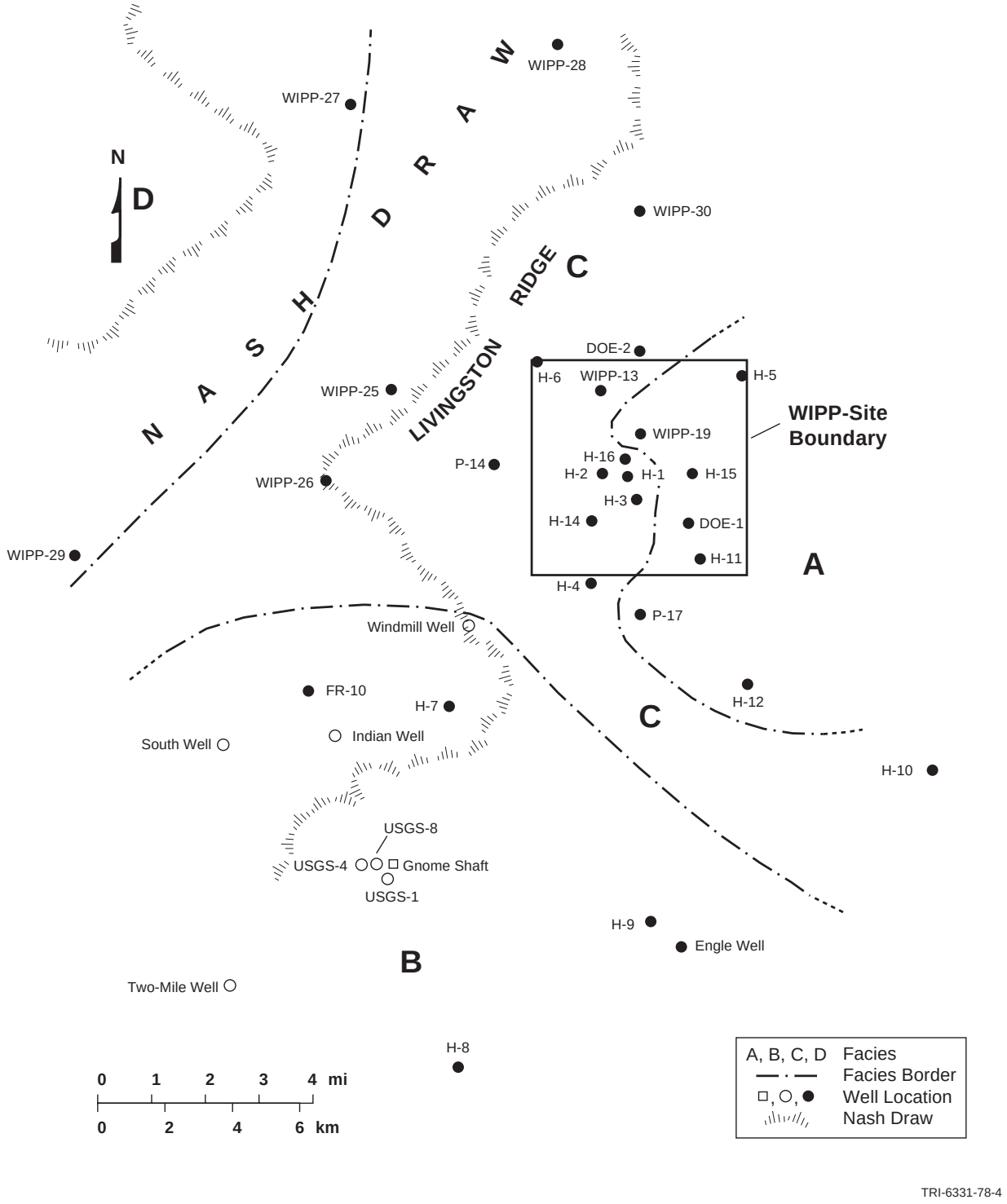


**Figure 4. Locations of Culebra hydrochemical facies of Siegel et al. (1991b).**

## 2.2 Additional Brine Chemistry Data

The most recent water analyses included by Siegel et al. (1991a) were collected in 1989. In the interim 16 years, 14 new wells (Figure 3) have been drilled and sampled (with more planned), and numerous old Culebra wells have been resampled. Thus, a significant amount of additional Culebra brine chemistry data is currently available. These data will be subject to a preliminary geochemical evaluation to determine hydrochemical facies, normative salt assemblages, and mineral saturation indices. Anomalous compositions, i.e., those which appear not to fit into the hydrochemical facies of Siegel et al. (1991b), or wells that display temporal variations in chemistry will be further evaluated with the goal of determining the geologic, hydrologic, or geochemical process(es) responsible for their anomalous composition(s) or variations.

Depending on the results of the preliminary geochemical evaluation, additional geochemical modeling could be warranted. This modeling could take the form of mixing calculations, ion exchange calculations, or mineral equilibrium/reaction-path calculations. The purpose of the secondary modeling would be to simulate the observed geochemical trends in the measured data to aid in identifying possible geologic or hydrologic causes for the observed phenomena. For example, geochemical mixing calculations could be used to evaluate the magnitude of vertical leakage to Culebra—a potentially important process to include when calibrating T fields. Furthermore, hydrochemical facies patterns and temporal variations may provide insight into changes occurring in the Culebra in less than the 10,000-yr period of regulatory concern.

## 2.3 Installation of New Wells and Performance of Hydraulic Tests

Hydraulic tests have been performed following the installation of new wells in the Culebra over a wide area around the WIPP site (see Figure 3). Hydraulic tests provide information on the hydraulic properties of the formation and on the nature of flow (e.g., through fractures or pores) in the localized area around the well and between wells. Thus, by comparing the hydraulic test results, the borehole geologic data, and the brine composition information, we may be able to draw inferences about the development of the chemical and physical environment in localized regions of the Culebra.

Holt et al. (2005) concluded that upper Salado Formation dissolution increased the probability of Culebra fracturing and high T, and that high-T zones were also associated with areas where halite is absent in adjacent members of the Rustler. Figure 5 shows the pertinent halite margins (see Figure 1 for stratigraphy and nomenclature) related to Culebra transmissivity in the area of the WIPP. The zones of high T should form preferred pathways for flow which should yield variations in the brine composition compared to low-T locations and should have unique geochemical signatures.

## 2.4 Changes to the Culebra Flow Model

Based on the concepts explained in Powers et al. (2003) and Holt et al. (2005), new Culebra T fields were developed for compliance modeling (McKenna and Hart, 2003). Comparison of the flow directions predicted by the new T fields with the Culebra brine composition data provides an indirect check of the flow model's validity. The geochemistry of the Culebra brines will be used as a tool to make an evaluation of the representation of the Culebra as a confined, two-dimensional system, and whether this representation is a realistic and/or conservative approach for compliance calculations on a 10,000-yr time frame.

Corbet and Knupp's (1996) and Corbet's (1998) 3D basin-scale model included a coarse and somewhat crude version of the geologically based model of Culebra transmissivity used by McKenna and Hart (2003). This basin-scale model included vertical flow between Rustler members. This model provided information on possible rates and spatial distribution of vertical leakage to the Culebra. An updated understanding of the brine geochemistry will provide more information as to the plausibility of the occurrence and magnitude of vertical flow in the Rustler Formation.

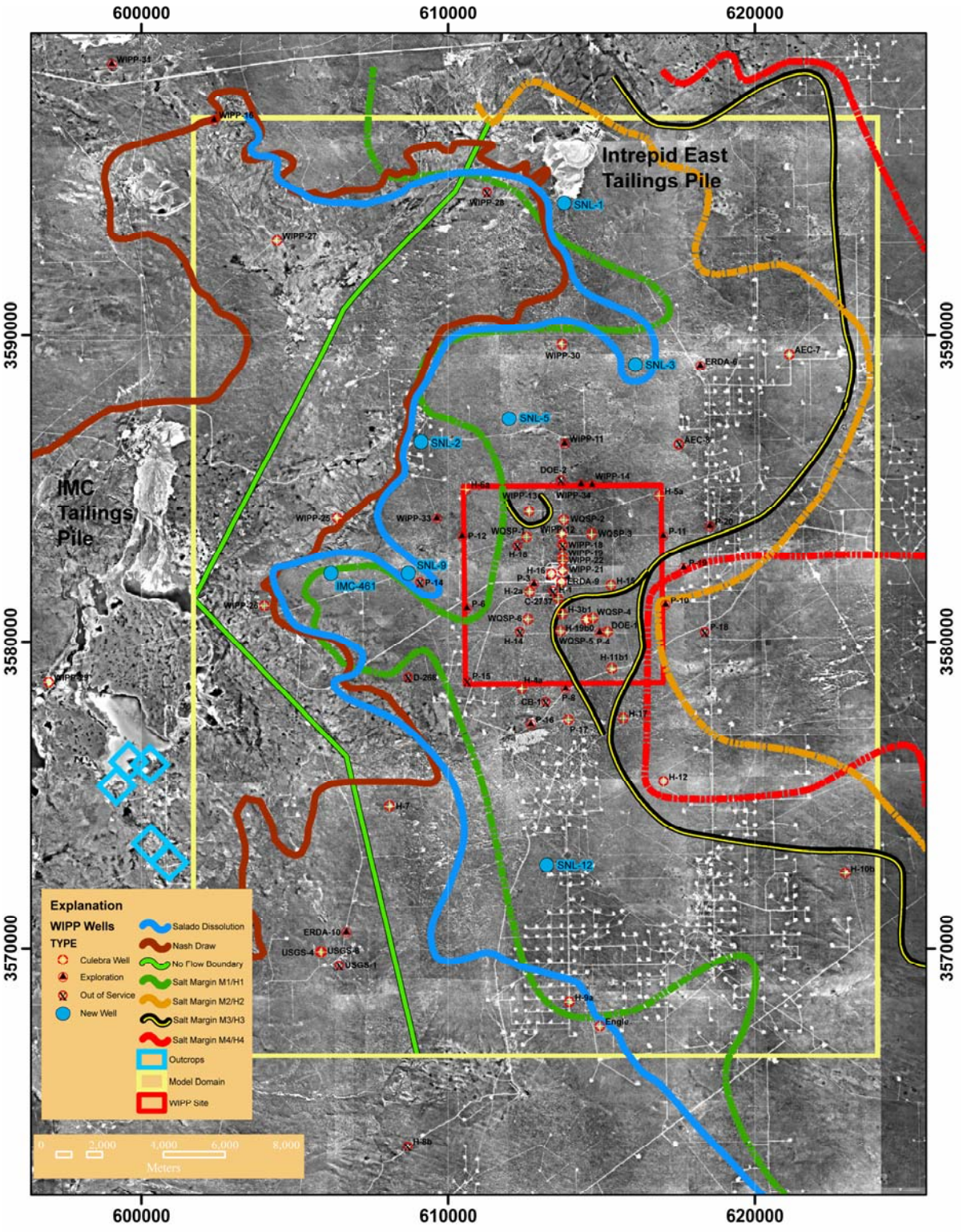


**Figure 5. Air-photo map of WIPP area showing halite and dissolution margins and tailings piles.**

## 3. Information Sources

The data required to perform the analysis described in the previous section include chemical analyses of the brines, mineralogic and geologic information, borehole location information, and output from the Culebra flow model.

- Brine chemistry data: From 1989 until 1995, Culebra water samples were collected and analyzed by Westinghouse Electric Corporation (WEC; now known as Washington Regulatory and Environmental Services (WRES)) under the WIPP Water Quality Sampling Program (WQSP) from most of the wells designated as "Resampled wells" in Figure 3 (WEC, 1991; 1992; 1993; 1994; 1995; 1996). A smaller number of Magenta and Dewey Lake wells were also sampled. Beginning in 1995, WEC began sampling only seven newly installed, fiberglass-cased wells designated WQSP-1 through WQSP-6 (Culebra wells) and WQSP-6A (a Dewey Lake well). Two rounds of sampling are performed in the WQSP wells each year, with 20 rounds being completed through June 2005 (Kehrman, 2002; WRES, 2003; WIPP MOC, 2004). All of the samples collected under the WQSP have been analyzed for an extensive list of anions, cations, trace metals, and organic compounds.

  Since 2003, water samples have also been collected by Sandia National Laboratories under Test Plan TP 03-01 (Chace, 2003) in the non-WQSP wells designated as "New sampled wells" on Figure 3 and in a few of the "Resampled wells". These samples have been analyzed by Hall Environmental Analysis Laboratory (HEAL; Albuquerque, NM) for major ions ($Ca^{2+}$, $Mg^{2+}$, $K^{+}$, $Na^{+}$, $Cl^{-}$, $SO_4^{2-}$, $HCO_3^{-}$) as well as $Fe^{3+}$, $Br^{-}$,$F^{-}$, and $NO_3^{-}$. The laboratory reports are compiled in WIPP Records Package ERMS# 536041.

  For both the WQSP and Sandia samples, field measurements of pH, specific conductance, temperature, and specific gravity are also available.

- Mineralogic data and geologic logs: The Culebra mineralogy has been documented most thoroughly by Sewards et al. (1991), and additional information has been provided by Holt (1997). Limited information on the readily apparent presence or absence of clays,

sulfates, and halite in Culebra core at specific boreholes is given in the geologic logs provided in borehole basic data reports (e.g., Powers and Richardson, 2004) available in the Sandia National Laboratories library.

- Borehole location data: This information is typically documented in the basic data reports mentioned above. Location information on WIPP boreholes drilled through 1988 is also summarized in Gonzales (1989).

- Transmissivity fields: Culebra transmissivity (T) fields were developed and calibrated by McKenna and Hart (2003) using MODFLOW-2000 (Harbaugh et al., 2000). New T fields will also be calibrated under Analysis Plan 114 (Beauheim, 2004) that may be completed in time to be used for this study. The T fields and associated MODFLOW files will require transmittal via the appropriate QA procedure.

# 4. Analysis Tasks

## 4.1 Task 1—Data Assembly

### 4.1.1 Geochemical and Well-Location Data

All of the chemical analyses of the Culebra brines described in Section 3 have been compiled into an Excel spreadsheet, *WIPP gwgeochem######.xls*, where ###### is the date the spreadsheet was last updated (e.g., 033005). This spreadsheet also contains the water-quality information previously evaluated by Siegel et al. (1991b). This spreadsheet will be reviewed as a routine calculation under NP 9-1 and submitted to the WIPP Records Center. The spreadsheet will be updated as additional data become available, and the data added to the spreadsheet will be checked against the information provided by the analytical laboratories to ensure correctness, again following the procedures for routine calculations under NP 9-1. The final version of the spreadsheet used for this AP will be identified in the final Analysis Report.

Well-location data will be added to the spreadsheet to facilitate map-view plotting and contouring of data.

### 4.1.2 Culebra Mineralogical Data and Geologic Logs

Mineralogy and borehole-specific geologic data will be assembled that may be used in the geochemical modeling and as interpretive information. The presence or absence of minerals such as halite, anhydrite, or gypsum in a core log provides information that, when combined with the results of the hydrochemical analysis, may be interpreted to increase our understanding of the hydraulics at a particular location. Additionally, if EQ6 simulations are deemed necessary at a later stage of the analyses, then the mineralogy obtained from the core logs of the Culebra may be used in generating the input files for EQ6.

## 4.2 Task 2—Primary Geochemical Assessment

The purpose of this task is to characterize the recharge waters, anomalous chemistries, and trends in chemistry using speciation/saturation calculations and salt norm calculations, and assign the

Culebra brine compositions to hydrochemical facies. No calculations of the reduction-oxidation (redox) potential of the brines will be performed because analyses of redox couples (oxidized and reduced species of a single element) have not been performed.

### 4.2.1 Data Plotting

The brine compositional data will be plotted using AquaChem. AquaChem is a hydrochemical database program that was designed to manage large quantities of water-quality data, with facilities to generate user-defined reports and a multitude of plots from simple X-Y plots to Piper, Stiff, and Durov plots. All of these hydrochemical plots have strengths and weaknesses, but their main purpose is to aid in the classification of hydrochemical facies and to display trends in water chemistry not readily apparent by simple inspection of tabulated data.

### 4.2.2 Speciation–Mineral Saturation Calculations

Chemical data will be evaluated using the soon-to-be-released EQ3NR Version 8.1 module of the EQ3/6 code package (see Wolery (1992a,b) for documentation of version 7 of this code package). EQ3NR will be used to evaluate the mineral saturation state of the Culebra brines. If warranted, the results of the EQ3 calculations, e.g., the saturation indices, may be geospatially plotted and contoured in Task 3 to identify areas that may share common genetic origins.

The Pitzer thermodynamic database will be used for high-ionic-strength (>1 molal) brines. For waters with low to moderate ionic strength (<1 molal), the B-dot equation (Helgeson, 1969) for calculating activity coefficients will be used because it is more appropriate than the Pitzer database in this range of ionic strength. The Pitzer thermodynamic database suitable for use with high-ionic-strength solutions, such as the Culebra brines, has been expanded for EQ3NR v. 8.1 to include a wide range of elements such as Al, Si, and Fe that may be important for this analysis.

### 4.2.3 Salt Norm Calculations

Normative salt calculations will be performed using the computer code SNORM (Bodine and Jones, 1986). The salt norm is a diagnostic tool which lends insight to the specific origins of a water sample's solute makeup. The SNORM software recasts the chemical analysis of a water sample as

an idealized equilibrium assemblage of mineral salts resulting from a single-step evaporation at 25°C and atmospheric carbon dioxide partial pressure. Bodine and Jones (1986) have cataloged the normative salt assemblages for waters of known origin, and identified the three primary salt norms: meteoric, marine, and diagenetic. Further, Bodine and Jones (1986) state:

*"The normative assemblage yields a diagnostic chemical-mineralogical characterization of the water, aids in the interpretation of the origin of the water's solutes, is indicative of the character of water-rock interaction in subsurface environments, and may contribute to determining the evolutionary path of the water chemistry."*

Aside from the diagnostic strengths of the salt norm approach is the legacy of the approach with regard to the WIPP project and, in particular, the characterization of the Culebra brines (Bodine and Jones, 1990). Thus, applying the salt norm to the recent chemical data provides a transparent means of comparison to the historical data.

### 4.2.4 Classify Brine Compositions

Each brine composition will be assigned to a hydrochemical facies after Siegel et al. (1991b). The spatial distribution of the hydrochemical facies will be checked with respect to those defined by Siegel et al. (1991b) and discrepancies noted.

## 4.3 Task 3—Flow Path Modeling

The MODPATH option of MODFLOW-2000 will be used in backward particle tracking mode to define the flow paths that brought brines to the sampled wells. For each available T field, a circle of particles will be placed at the location of each sampled well, and their movement tracked backwards to the boundary of the model domain. This flow path information will be used in Tasks 4 and 5 to evaluate the processes (including, potentially, vertical leakage) that must be active to explain how groundwater chemistry evolves along various flow paths.

## 4.4 Task 4—Secondary Geochemical Assessment

### 4.4.1 Evaluation

The output of Tasks 2 and 3 will be evaluated to identify geologic, geochemical, or hydrologic processes and/or anomalous compositions and trends in the data. Possible results from Task 2 could include the presence of a low-TDS water in an otherwise high-TDS area which could suggest the presence of vertically introduced fresh water through a previously unidentified geologic feature. Evaluation of the Task 2 results will be facilitated by plotting the results using the well-location data and possibly plotting the results using a contouring/visualization software package such as mView. Additionally, plotting the EQ3 output, such as the mineral saturation indices, will be used as a means to assess the geochemical processes and controls on the brine compositions.

### 4.4.2 Geochemical Modeling

Based on the results of the evaluation described in Section 4.4.1, EQ6 input files will be designed to simulate the processes that were identified. The simulations may take the form of one-dimensional column-type experiments where the solid-centered flow-through (SCFT) mode of EQ6 would be used. The SCFT model is a 1-dimensional batch reactor with plug flow that assumes complete mixing. Thus, it is an idealized conceptualization of advective transport with chemical reactions, as dispersion is not modeled. The reactants, including the reacting groundwater compositions, will be set up with kinetic rate laws which permit modeling in the time domain. In this example, the mixing of two fluids, set up as special reactants, simultaneously reacting with the porous medium would be simulated. The rates of water addition to the modeled system would be varied until the resultant water composition matched the observed field composition as closely as possible. Of course, a simplified and idealized model system may only capture the broad features of the real system, but nonetheless the modeling exercise may provide insight into an otherwise poorly understood system.

The aquifer mineral physical properties (mass and surface area) will be estimated based on Culebra dolomite specific surface area measurements reported in Kelley and Saulnier (1990) and Holt (1997) and scaled to the 1-liter EQ6 volume to reflect the porosity of the Culebra dolomite, and

appropriate kinetic rate laws will be assigned to the mineral phases. In the absence of WIPP-specific laboratory measurements of the mineral surface areas, estimates of this parameter will have to be made and used as input in the EQ6 modeling. Because the mineral surface area directly scales the kinetic rate law, a sensitivity analysis of the effects of this parameter on the model output will be necessary.

The processes which can be modeled include mineral dissolution and precipitation and fluid mixing simulated in the time domain. These types of calculations would provide information about the plausibility and resultant chemistry of brine mixing, including both mixing of Culebra brines belonging to different hydrochemical facies and of waters potentially entering the Culebra from other Rustler members mixing with the Culebra brines. Additionally, mixing calculations may provide information on the relative magnitude of leakage from sources outside of the Culebra.

### 4.5 Task 5—Interpretation of Results and Synthesis

The purpose of this task will be to integrate the results of the geochemical analyses with the flow model output, the geologic data, and the hydrologic data.

Interpretation of the model results, geologic information, and hydrologic information will be facilitated through the use of map-view plots. The geochemical model output (mixing zones, hydrochemical facies, saturation indices, etc.) will be plotted and overlain with the flow model output vectors for comparison. Other information such as halite margins (Figure 5), the occurrence of fracturing, permeability, and flow dimension may also be geospatially plotted. This integrated approach to data interpretation will aid in finding discrepancies between the models and help in making recommendations for future modeling efforts.

## 5. Software List

The following computer codes may be used for different tasks associated with Culebra hydrochemistry:

- AquaChem (commercial off-the-shelf software, Waterloo Hydrogeologic Inc.);
- SNORM (USGS software to be qualified under NP 19-1);
- EQ3/6 Version 8.1 (LLNL software to be qualified under NP 19-1);
- mView 4.0 (acquired software to be qualified under NP 19-1, Intera Engineering Ltd.);
- ArcInfo 8.1 (commercial off-the-shelf software, ESRI);
- MODFLOW-2000 Version 1.6 (qualified under NP 19-1);
- MODPATH (to be qualified under NP 19-1).

Off-the-shelf spreadsheet programs, such as Excel, and graphing programs, such as Grapher or SigmaPlot, may also be used for data manipulation and plotting. Any pre- or post-processors needed for data manipulation and transfer between codes will also be qualified as part of the analysis package.

## 6. Special Considerations

No special considerations have been identified.

## 7. Applicable Procedures

All applicable WIPP quality-assurance procedures will be followed for these analyses. Training of personnel will be done in accordance with the requirements of NP 2-1, *Qualification and Training*. Analyses will be performed and documented in accordance with the requirements of NP 9-1, *Analyses* and NP 20-2, *Scientific Notebooks*. All software used will meet the requirements of NP 19-1, *Software Requirements* and NP 9-1 as applicable. The analyses will be reviewed following NP 6-1, *Document Review Process*. All required records will be submitted to the WIPP Records Center in accordance with NP 17-1, *Records*.

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