HYDROLOGY OF THE PALO DURO BASIN, TEXAS PANHANDLE

by

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Prepared for the
U.S. Department of Energy
Office of Nuclear Waste Isolation
under contract no. DE-AC-97-83WM46615

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1982

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5.6.1 Hydrogeologic Units

The heterogeneous aquifer/aquitard system in the Palo Duro and Dalhart Basins is the result of long-lived cycles of different sedimentation styles. The sedimentary sequence is effectively divided into deep and shallow flow systems. The relatively permeable formations are vertically separated by a thick interval of Middle and Upper Permian evaporites and fine-grained red beds which acts as an aquitard.

Using concepts developed by Maxey (1964) and Toth (1978), Bassett and Bentley (in press) defined several hydrogeologic elements in the Palo Duro Basin (Table 1). The elements are designated according to their relative water-conducting or water-retarding character (e.g., Ogallala Aquifer or Evaporite Aquitard). In the case where a hydrogeologic element contains a permeable lithology interbedded with a mudstone, the aquifer/aquitard designation is based on the properties of the more permeable strata.

Hydrogeologic units are assemblages of vertically adjoining strata that have the same general hydraulic properties, though they may have different primary lithologies (Bassett and Bentley, in press). Each hydrogeologic unit consists of one or more hydrogeologic elements. Bassett and Bentley identified five hydrogeologic units in the Palo Duro Basin: (1) a Basement Aquiclude, (2) a Deep-Basin Brine Aquifer, (3) a Basin Shale Aquitard, (4) an Evaporite Aquitard, and (5) an Upper Aquifer (Figure 1 and Table 1). The permeabilities of a unit shown in Table 1 and on Figure 1 are representative values derived from the literature or determined by the analysis of drill-stem tests.

The following sections describe the Deep-Basin Brine Aquifer, the Evaporite Aquitard, and the Upper Aquifer in detail. The Basement Aquiclude and Basin Shale Aquitard have not been studied. The following descriptions of hydrogeologic units are based primarily on Bassett and Bentley's (in press) preliminary regional analysis of the Palo Duro Basin hydrogeologic system.

5.6.1.1 The Deep-Basin Brine Aquifer

Although tectonism and basin infilling resulted in irregular sedimentation patterns and lateral changes in lithology, all pre-Leonardian formations have been combined into one hydrogeologic unit (Figure 2). The upper stratigraphic limit of the Deep-Basin Brine Aquifer is at the top of the Wolfcampian (lower Permian) dolomite. The lower limit is at the top of the Basement Aquiclude. There are six hydrogeologic elements within the Deep-Basin Brine Aquifer: (1) a Lower Paleozoic sandstone aquifer, (2) a Lower Paleozoic carbonate aquifer, (3) an Upper Paleozoic granite wash aquifer, (4) a basin shale aquitard, (5) a Pennsylvanian carbonate aquifer, and (6) a Wolfcamp carbonate aquifer.

Sediments of the Deep-Basin Brine Aquifer are largely open-marine shelf carbonates and fluvial and deltaic arkosic sandstones (granite wash) interbedded with mudstone (Figure 2). The distribution of sandstone was controlled by the erosion of faulted granitic and gabbroic Precambrian-basement highlands that formed the basin boundaries (Figures 3 and 4). Downdip from these peripheral sandstones, and intertonguing with them, are shelf carbonates which grade basinward into the thicker, more vertically persistent shelf-edge carbonate buildups that border the central basin (Figure 4). Above these sandstones and shelf carbonates is a Wolfcampian shelf-carbonate system that covers the entire basin, including the arches and uplifts that mark the basin boundaries (Figure 4). The hydrologic characteristics of the Deep-Basin Brine Aquifer are described in Section 5.6.4.

5.6.1.2 The Evaporite Aquitard

The bottom of the Evaporite Aquitard is at the Wolfcampian-Leonardian boundary. The Permian-Triassic boundary marks the top of the aquitard. The Middle and Upper Permian strata of the Evaporite Aquitard consist almost entirely of halite, anhydrite, dolomite, and fine-grained silici-clastic red beds (Figure 2), which grade southward into shallow-marine carbonates in the Midland Basin (Dutton et al., 1979). There are eleven formations in the Evaporite Aquitard (from oldest to youngest): (1) Red Cave, (2) Clear Fork, (3) Tubb, (4) Glorieta, (5) San Andres, (6) Queen/ Grayburg, (7) Seven Rivers, (8) Yates, (9) Salado, (10) Alibates, and (11) Dewey Lake.

The San Andres Formation is identified in the Pease River Group in east-central New Mexico and the Palo Duro and Midland Basins. The Blaine Formation is equivalent to the San Andres in the Dalhart and Anadarko Basins. Thick salt deposits within the San Andres Formation are of interest as a potential stratigraphic zone for containing a nuclear-waste repository. Where porous and transmissive dolomite or limestone beds occur in the San Andres Formation, they constitute a minor aquifer within the Evaporite Aquitard.

The stratigraphy of the San Andres Formation consists of multiple cycles of porous limestone-and-dolomite rocks interbedded with non-porous carbonate rock, shale, anhydrite, and salt (Presley, 1981) (see Section 3.5). Effective porosity tends to be greater and more widespread in the cycle-4 than in other cycles of the San Andres. The cycle-4 and cycle-2 carbonates extend farther north through the Palo Duro Basin than do carbonates in the other units (Presley, 1981). Carbonate cycles in the San Andres Formation coalesce southward into the single, thick, porous, marine limestone found in the Midland and Delaware Basins (Ramondetta, 1982).

The San Andres Formation crops out west of the Palo Duro Basin between the Pecos River and the Guadalupe Mountains in New Mexico, and east of the Palo Duro Basin in north-central Texas and southwest Oklahoma (Figure 5). The structure of the formation is a broad syncline with a gentle southward plunge into the Midland Basin (Nicholson, 1960; Core Laboratories, 1972; Ramondetta, 1982).

There is a lateral change from carbonate-shelf facies to sabkha and halite brine-pan facies in the lower San Andres Formation that correlates with a reduction in the porosity and permeability of the San Andres Aquifer. Porosity in carbonate units in the center part of the Palo Duro Basin is often occluded by anhydrite and halite cements (Bein and Land, 1982). The distribution of carbonate-rock transmissivity (bed thickness times hydraulic conductivity) in the San Andres Aquifer has not been measured, to date. The hydrologic characteristics of the San Andres Aquifer are presented in Section 5.6.4.2.

5.6.1.3 The Upper Aquifer

The dissolution zone on top of the evaporite section marks the lower limit of the Upper Aquifer, and the hydrogeologic unit extends upward to the land surface. The Upper Aquifer contains two major hydrogeologic elements: the Dockum Aquifer and the Ogallala Aquifer (Figure 2). The sandstones, conglomerates, and red shales in the Triassic-age Dockum Group were deposited in fluvial, alluvial-fan, and lacustrine environments. Sand percentage maps of the Dockum Group detail complex anastomosing and branching patterns (Figure 6) (McGowen et al., 1982). The Tertiary Ogallala Formation is an extensive alluvial apron of sand, gravel, and clay that extends eastward from the Rocky Mountains in the form of coalescing alluvial-fan lobes (Seni, 1980). The upper part of the Ogallala Formation is cemented with calcium carbonate (caliche) and forms the cap rock found on the High Plains.

The regional extent of hydrologic continuity between transmissive zones in the Dockum and those in the overlying Ogallala has not been determined. Depending on the degree of separation between transmissive zones, the response of fluid pressure in the Dockum to change in the Ogallala is expected to be delayed or absent. Further information on the hydrologic characteristics of the Dockum Aquifer is given in Section 5.6.4. The Ogallala Aquifer is being treated in a separate study.

5.6.2 Relationships Among Hydrogeologic Units

As of July, 1982, the hydrologic relationships between the hydrogeologic units in the Palo Duro Basin are not well known. The distribution of hydraulic heads, and therefore the patterns of flow, in mature, compacted basins may be controlled to a significant degree by the surface topography and consequent configuration of the top of the saturated zone (Toth, 1978). This means that the Evaporite Aquitard, over geologic time, may permit vertical and cross-formational flow between the Upper Aquifer and the Deep-Basin Brine Aquifer. The presence of a minor aquifer (the San Andres Aquifer) within the Evaporite Aquitard means that lateral as well as vertical flow may take place in the aquitard.

The relationship between fluid pressure and depth below land surface provides some information about the relationships between hydrogeologic units. The hydrostatic relation between fluid pressure and depth below land surface is governed by the specific weight of ground water (fluid density times the acceleration of gravity) (Hubbert and Rubey, 1959; Toth, 1978). A departure from the hydrostatic pressure-versus-depth curve implies that there is non-horizontal flow. If a pressure-versus-depth curve lies above the hydrostatic line, the potential exists for upward-directed flow of ground water. A subhydrostatic curve indicates that ground-water flow may be directed downward (Toth, 1978) (Figure 7).

The Ogallala Aquifer is hydrostatically pressured (Cronin, 1961), and this condition is thought to be true for the Dockum Aquifer as well. The San Andres aquifer and the Deep-Basin Brine Aquifer are subhydrostatically pressured (UTBEG, in press). The pressure-versus-depth gradient in the San Andres Formation in the western and along the southern edge of the Palo Duro Basin is 8597 Pa/m (0.38 psi/ft), less than the hydrostatic pressure-versus-depth gradient for both fresh water (9796 Pa/m, 0.433 psi/ft) and brine (11,311 Pa/m, 0.50 psi/ft) (Figure 7).

A subhydrostatic pressure-versus-depth gradient indicates that there is a potential for downward flow. For example, there may be a component of flow moving from the Wolfcamp Aquifer into deeper elements of the Deep-Basin Brine Aquifer. The Deep-Basin Brine Aquifer is also artesian, that is, the potentiometric surface is above the top of the aquifer. Water in boreholes open to the Deep-Basin Brine Aquifer will typically stabilize at elevations above the San Andres Cycle-4 and Cycle-5. The potential exists for water to flow upward through unplugged boreholes from the deep aquifer into potential mines in the San Andres salt.

The potentiometric surface of the Deep-Basin Brine Aquifer is significantly below the potentiometric surface of the Ogallala Aquifer. This creates a downward-directed fluid potential gradient between the two aquifers. The large head difference between the hydrostatically pressured Ogallala and the subhydrostatically pressured Deep-Basin Brine Aquifer could allow improperly cased or plugged boreholes connecting them to conduct fresh water downward, resulting in salt dissolution around the well bore. Dissolution under similar conditions has resulted in subsidence and collapse in the Hutchinson Salt Basin in Kansas (Bentley, 1981). Because salt dissolution could drastically reduce the integrity of a nuclear waste repository, the exact relationships between the hydrogeologic units in the Palo Duro Basin need to be determined.

Information on potentiometric levels can be found in Section 5.6.3. Estimates of average interstitial ground-water velocities are in Section 5.6.4. Recharge, discharge, and leakage are discussed in Section 5.7.1. Hydrochemical facies are identified in Section 5.7.3.

5.6.3 Potentiometric Level

Relative to the size of the aquifers in the Palo Duro Basin, the amount of reliable data on fluid pressure is small. Data are lacking because few wells are drilled to depths below the Ogallala Aquifer and hydraulic measurements are more difficult to obtain at greater depths. Potentiometric levels are vital to the understanding of a hydrogeological system. As of July, 1982, the potentiometric surfaces of none of the hydrogeologic units in the Palo Duro Basin are known in sufficient detail to adequately describe the hydrogeologic system. Ongoing field work will provide additional information to help describe the potentiometric surfaces.

Fluid-pressure data have come almost exclusively from the results of drill-stem tests (DSTs) conducted in petroleum exploration wells and from bottom-hole pressures measured in oil fields. Because there has been no petroleum production in the central Palo Duro Basin, data points are clustered around the basin margins with a scarcity of information available on the central region. However, the lack of petroleum production means that accurately measured fluid pressures can be assumed to approximate natural pre-stress conditions (Bassett and Bentley, in press).

Equivalent fresh-water heads were computed by dividing the formation pressure by 9796 Pa/m (0.433 psi/ft) and correcting for elevation. Though each well report usually had records of several DSTs at different depths, only one head value per well could be used when a particular potentiometric map was drawn. In order to systematically choose between several head values from the same well, a hierarchy of well data was established (in order of descending quality): (1) pressure-time charts (which could be examined to confirm proper performance of the test tools), (2) multiple similar head values recorded in different tests in the same zone, (3) multiple dissimilar head values recorded in different tests in the same zone, and (4) one head value from a zone (in which case there was no way to judge the quality of the value). Out of a group of values from different depths in the same well, the head value which belonged in the highest-quality category was chosen to represent the site. If there were several values in the highest-quality category, the largest head value was used to make the potentiometric map.

Kriging was used to define potentiometric surfaces for the Wolfcampian element of the Deep-Basin Brine Aquifer and for the San Andres element of the Evaporite Aquitard. Kriging is a geostatistical technique of estimating plane surfaces (e.g., potentiometric surfaces) with spatially distributed data. There are two basic advantages of kriging over the trend-surface method: (1) kriging measures probable error at each point, rather than over the surface, and (2) kriging bases predicted values on moving block averages to minimize error in areas of sparse data (Davis, 1973).

The potentiometric data for the Deep-Basin Brine Aquifer, the Evaporite Aquitard, and the Upper Aquifer will now be treated separately.

5.6.3.1 Potentiometric Level of the Deep-Basin Brine Aquifer

Potentiometric maps of only two of the hydrogeologic elements in the Deep-Basin Aquifer (the Pennsylvanian carbonate aquifer and the Wolfcampian carbonate aquifer) could be drawn from existing data. Most of the head values are from wells along the Palo Duro Basin margins, with few values available from the basin interior (Figure 8). The drill-stem test results from the Deep-Basin Aquifer are in Appendix A.

The hydraulic head map for the Pennsylvanian carbonate aquifer (Figure 9) was drawn by Bentley (1981), and shows that the principal flow direction in this unit is from west to east through the Palo Duro Basin.

The potentiometric surface of the Wolfcampian carbonate aquifer has been hand-mapped by Bentley (1981), and, more recently, mapped by kriging (Figure 10). The two maps depict similar general pressure conditions and magnitudes of potential gradient, but the map obtained by kriging shows a more northerly component of flow across the Palo Duro Basin. The more northerly flow component suggests that deep-basin flow is toward the Amarillo Uplift and that hydrologic conditions along the uplift may control regional flow through the basin.

The potentiometric level in deep-basin aquifers is higher than the level of the San Andres cycle-4 and cycle-5 salts in the Palo Duro Basin. However, this level is far below the hydraulic head in the Ogallala Aquifer, so there is a potential for water movement down through the salt. More information on the pressure-versus-depth conditions in the Deep-Basin Aquifer is found in Section 5.6.2.

5.6.3.2 Potentiometric Level of the Evaporite Aquitard

Potentiometric studies of the Evaporite Aquitard have focused on the San Andres Aquifer because it may be one of the more transmissive elements in the aquitard and it is adjacent to a potential stratigraphic target for a repository. Ninety-eight percent of the data on San Andres' fluid potential comes from outside of the Palo Duro Basin and is based on water-level measurements in the San Andres outcrop in New Mexico and on the results of drill-stem tests (DSTs) in San Andres oil fields south of the Palo Duro Basin (Figure 11). Elevation, pressure, and head data for the San Andres Formation can be found in Appendix B.

The results of kriging the potentiometric surface of the San Andres Aquifer show that kriging minimizes the error in the surface through those areas with a high density of data and that the number of DSTs in the interior of the Palo Duro Basin (at DOE/SWEC wells in Deaf Smith and Swisher Counties) is insufficient to define a statistically valid surface.

The potentiometric surface obtained by kriging is similar to the hand-drawn map of McNeal (1965) (Figure 5). The potentiometric surface of the San Andres Formation dips from northwest to southeast. Theis (1965) and Dinwiddie and Clebsch (1973) defined the recharge zone for the San Andres as the area between the Pecos River Valley and the San Andres outcrop. This is supported by the high hydraulic heads west of the Pecos River. There are not sufficient head data to directly measure the amount of recharge to the San Andres by downward seepage from ground water in alluvium in the Pecos River Valley.

The boundary between the Pecos River Valley and the western caprock escarpment area appears to coincide with a change in the hydraulic gradient from about 5 m/km (26 ft/mi) west of the Pecos River to about 2.5 m/km (13 ft/mi) under the cap rock (Figure 5). The decrease in gradient may reflect a large increase in fluid density across the Pecos River Valley. Variation in fluid density was not taken into account in the calculation of equivalent fresh-water head.

The pressure-versus-depth gradient is about 8597 Pa/m (0.38 psi/ft) (Figure 7). The gradient is less than that for fresh (9796 Pa/m, or 0.433 psi/ft) or brine (about 11,311 Pa/m, or 0.5 psi/ft) ground water without a component of vertical flow. This gradient was calculated by using data from the Northern Shelf and from the western and southwestern edges of the Palo Duro Basin. The cause of the apparent underpressuring is still under investigation, though it may be a reflection of the downward dip of the San Andres Formation in this region. Pressure-versus-depth curves are discussed more fully in Section 5.6.2.

In Deaf Smith and Randall Counties, the hydraulic head of water in the San Andres is greater than the hydraulic head of water in the Deep-Basin Brine Aquifer. The difference in head decreases toward the south so that in Lamb and Hockley Counties there is no appreciable difference. Hydraulic head in the Upper Aquifer is only a few hundred feet higher than that in the San Andres (Cronin, 1969). This difference in head may be insignificant considering the uncertainty in the position of the San Andres potentiometric surface. The existence and magnitude of vertical differences in hydraulic head between the hydrogeologic elements in the Palo Duro Basin is still under investigation as of July, 1982.

Data on the fluid potential in the Palo Duro Basin are too sparse to allow statistical resolution of the potentiometric surface of the San Andres. The six data points from drill-stem tests in Oldham, Deaf Smith, Randall, and Swisher Counties are not sufficient to establish a krig-block. Potentiometric contours obtained by kriging cannot be quantitatively extended across this area (note their termination in Figure 5) without a large increase in error (Gustavson et al., in preparation). However, if the values of these data are mapped, the dip of the potentiometric surface would be changed from east, in Guadalupe and Quay Counties (New Mexico), to southeast in Deaf Smith, Randall, Parmer, and Castro Counties (Texas). Ground-water flow paths through the aquifers in the Palo Duro Basin are discussed in Section 5.7.2.

5.6.3.3 Potentiometric Level of the Upper Aquifer

The regional potentiometric surface of the Dockum element of the Upper Aquifer is assumed to be similar to the more well-known surface of the Ogallala Aquifer. However, this assumption lacks any solid basis because few data exist with which to define the hydrologic relationship between the Dockum and Ogallala elements in the Texas Panhandle. The water in the Ogallala is unconfined and the gradient of the water table beneath the High Plains surface is about 0.002 (2 m/km or 10 ft/mi) (Simpkins, 1980). The water-table gradient in the Ogallala increases with the changes in relief and lithologic properties at the eastern Caprock Escarpment (Figure 38).

5.6.4 Hydraulic Characteristics of Principal Hydrogeologic Units

Values have been estimated for the hydraulic characteristics (hydraulic conductivity, permeability, storage coefficient, effective porosity, saturated thickness, and ground-water flow rates) of many of the hydrogeologic elements in the Palo Duro Basin. Further research is needed to refine these estimates into valid, acceptable measurements.

The appropriateness of assuming Darcian flow conditions, i.e., that discharge is linearly proportional to the gradient of energy potential, is sometimes questioned for flow in rocks of very low permeability and flow in fractured rock. In rocks of very low permeability, molecular forces may be important relative to the gravitational force. In fractured rocks, nonlaminar flow may take place through fractures that have appreciable space between adjoining walls. Although both low-permeability rocks and fractured rocks occur in the Palo Duro Basin, no data are available for evaluating the appropriateness of assuming Darcian flow conditions.

The hydraulic characteristics of the Deep-Basin Brine Aquifer, the Evaporite Aquitard, and the Upper Aquifer will be treated separately in the following sections.

5.6.4.1 Hydraulic Characteristics of the Deep-Basin Brine Aquifer

The mean permeability of the Deep-Basin Brine Aquifer, estimated from available drill-stem test data, is 49.3 millidarcys, with a range between 0.02 and 694 millidarcys. There are no estimates of the storage coefficient available as of July, 1982. The porosity of permeable intervals of Wolfcampian and Pennsylvanian age rocks in three test wells in the Palo Duro Basin is between 10 and 25 percent. An upper estimate of the saturated thickness of the Deep-Basin Brine Aquifer is 1830 meters (6004 ft). Porous carbonates and granite wash constitute about 1070 meters (3511 ft) of this estimate. The flow rate of ground water in the Wolfcamp carbonate aquifer is estimated to be between 3 and 30 cm/yr (1.2 and 12 in/yr).

5.6.4.1.1 Permeability of the Deep-Basin Brine Aquifer

As of July, 1982, the only information available on the permeability of the deep-basin aquifers comes from the analysis of drill-stem test reports obtained from petroleum company operators and from the analysis of drill-stem tests and pumping tests performed as a part of the National Waste Terminal Storage (NWTS) program in the Texas Panhandle. To date, pumping tests have been completed in only the Sawyer #1 test well in Donley County.

Sixty-nine of the test records received from operators in the Texas Panhandle were complete enough to analyze. As of July, 1982, six drill-stem tests have been performed in the deep-basin aquifers as part of the NWTS program in West Texas. Five of these six tests were suitable for permeability analysis. Table A-1, in Appendix A, lists the results of the analyses of available drill-stem test records. Figure 8 shows the locations of these tests and the permeability measurements obtained from their analysis. Figure 8 also presents frequency histograms for the permeability values of Ellenburger-Mississippian, Pennsylvanian, and Wolfcampian rocks, as well as for the granite wash facies rocks and all the deep-basin permeability values together.

The number of values available is insufficient to describe in detail the permeability of the deep-basin aquifer system. The calculated permeability values are within the range expected for these formations, though biased on the high side. There is a higher-value bias because most of the drill-stem tests were performed in the more permeable layers.

The distribution of calculated permeability values is approximately log-normal in each formation within the Deep-Basin Aquifer. The mean and variance for each of the five populations (Ellenburger-Mississippian, Pennsylvanian, Wolfcampian, granite wash facies, and all deep-basin permeability values together) was estimated by the method described by Krumbein and Graybill (1965). Table 2 lists the range, mean, and variance for each population.

Pumping tests were performed in five zones in the Sawyer #1 test well in Donley County (Table 3). The testing was conducted in order to obtain estimates of permeability and formation pressure and to obtain formation fluid samples. The extended pumping time necessary to obtain clean water samples allowed multiple transient pressure tests to be done in each test zone. Pumping tests and fluid sampling are complete in each of these five zones. Well completion problems prevented transient pressure testing in Production Zone 1 (Ellenburger sand), although fluid samples were collected. Pump testing has been completed and analyzed in Production Zones 2 through 4 (Upper Ellenburger, Mississippian limestone, and Pennsylvanian granite wash). Though testing is complete in Zone 5 (Permian Wolfcamp), the data analysis is incomplete at this time.

The average permeability results of analyses of the pumping tests in the Upper Ellenburger, Mississippian limestone, and Pennsylvanian granite wash are listed in Table 4. The pressure-time charts were analyzed according to the methods outlined by Earlougher (1977). The data and analyses of the pump tests will be included in the Sawyer #1 Summary Well Report (UTBEG, in press).

Deep-basin pumping tests will be conducted in at least three more test wells as part of the NWTS program in the Palo Duro Basin. Testing is underway in the first of two Permian Wolfcamp zones in the Mansfield #1 well, Oldham County. A Pennsylvanian carbonate and two Permian Wolfcamp intervals will be pump tested in the Zeeck #1 test well. Up to four deep-basin intervals will be pump tested in the J. Friemel test well, Deaf Smith County (to be drilled in FY1983), possibly including a Pennsylvanian granite wash, a Pennsylvanian carbonate, and two Wolfcampian intervals. Permeability tests will be conducted on core plugs from Wolfcampian and Pennsylvanian rocks.

5.6.4.1.2 Porosity of the Deep-Basin Brine Aquifer

The porosity of core plug samples from Deep-Basin Aquifer rocks in basins adjacent to the Palo Duro was determined by Core Laboratories, Inc. (1972). A summary of the porosity ranges determined can be found in Table 5. In wells drilled in the Palo Duro Basin for the NWTS program in the Texas Panhandle, the porosity estimated from geophysical logs and from inspections of core is similar to the porosity found in oil fields in basins adjacent to the Palo Duro. The porosity of permeable Wolfcampian and Pennsylvanian age rocks in the Zeeck #1 test well ranges between 10 and 25 percent, while the porosity of the same units in the Sawyer #1 well ranges between 10 and 20 percent. In the Mansfield #1 well, the porosity of permeable Wolfcampian-age rocks ranges between 10 and 25 percent. These porosity values cannot be assumed to be representative of Wolfcampian and Pennsylvanian age rocks throughout the Palo Duro Basin. More data, from more points spread throughout the Palo Duro Basin, are needed to characterize the porosity of deep-basin rocks.

5.6.4.1.3 Saturated Thickness of the Deep-Basin Brine Aquifer

The principal conduits of flow through the Deep-Basin Aquifer in the Palo Duro Basin are porous carbonate and granite wash of Permian and Pennsylvanian age. The upper limit of the saturated thickness for the Deep-Basin Aquifer system can be derived by combining the isopach map of the Pennsylvanian-age rocks (Figure 12) with the isopach map of Wolfcampian-age rock (Figure 13). Pennsylvanian-age rocks range in thickness from less than 120 meters (394 ft) near the western edge of the basin to greater than 970 meters (3183 ft) adjacent to the Amarillo Uplift in Carson County (Dutton et al., in press). Wolfcampian-age rocks range in thickness from less than 250 meters (820 ft) near the western edge of the Palo Duro Basin to greater than 850 meters (2,789 ft) in northeast Oldham County (Dutton et al., in press).

A large part of this thickness is shale of low permeability and shaley limestone and dolomite. The thickness of rock through which fluid can flow is better estimated by the thickness of granite wash and of porous carbonate of both Permian and Pennsylvanian age. The net thickness of both Permian and Pennsylvanian granite wash varies from greater than 500 meters (1641 ft) along the downthrown side of a major fault in Carson County to areas of nondeposition of granite wash along the Matador Arch, in the southern Palo Duro Basin (Figure 14). The thickness of porous, Pennsylvanian-age carbonate is greater than 150 meters (492 ft) in some parts of the Palo Duro Basin (Figure 15). The Wolfcampian-age shelf-carbonate system covers the entire Palo Duro Basin and porous carbonate is more than 300 meters (984 ft) thick in some areas (Figure 16) (Dutton et al., in press). The isopach maps of porous carbonate are based on the number of feet of carbonate denoted as porous on sample logs; however, the cutoff-porosity value is not recorded on these logs. The porosity trends delineated by examination of sample logs coincide with porosity values of eight to ten percent on the few, and scattered, density, sonic, and neutron logs available.

Though most ground water in the Palo Duro Basin deep-aquifer system flows through Pennsylvanian and Permian age rocks, the discontinuous porosity reported in Ellenburger and Mississippian carbonates may allow these rocks to contribute flow to the system. However, the total thickness of Mississippian and Ellenburger age rock (Figures 17 and 18) is greater than the thickness of rock through which fluid flow could take place, because there are impermeable zones within these units.

5.6.4.1.4 Ground-water Flow Rates in the Deep-Basin Brine Aquifer

The average linear velocity of ground water in the Deep-Basin Brine Aquifer as a unit is undetermined. An estimate of the average linear velocity of ground water in the Wolfcamp carbonate aquifer was calculated by assuming an average permeability of 2 millidarcys (1.6 x 10^{-3} m/day or 5.3 x 10^{-3} ft/day), a porosity range between 0.5 and five percent, and a head gradient of 0.0027. The flow rate was estimated to be between 3 and 30 cm/yr (1.2 and 12 in/yr). If the hydraulic gradient has remained unchanged since the late Cretaceous, and the permeability and porosity averages are correct (Bentley, 1981), the fluid from western recharge zones could replace the Wolfcamp carbonate brines in cycles of about one million years (Bassett and Bentley, in press). However, the calculated flow rate and replacement time are rough estimates at best and should be considered cautiously because the parameters used to evaluate them are not known with any certainty.

5.6.4.2 Hydraulic Characteristics of the Evaporite Aquitard

The hydraulic characteristics of the Evaporite Aquitard as a whole have not been determined. Work to date has concentrated on determining the properties of the San Andres Aquifer within the Evaporite Aquitard.

The permeability of the San Andres cycle-4 dolomite in the center of the Palo Duro Basin is estimated to vary between 0.04 and 0.4 millidarcys. As of July, 1982, there are no storage coefficient values available from hydrologic tests of the San Andres Aquifer in the Palo Duro Basin. Within the Palo Duro Basin, San Andres porosity appears to be less than 10 percent and limited to thin zones. Quantitative measurements of the total porosity or effective porosity in San Andres carbonate rocks in the Palo Duro Basin have not been made as of July, 1982. An upper estimate of the saturated thickness of the San Andres Aquifer is 18 to 31 meters (60 to 100 ft). Order-of-magnitude estimates of the average linear velocity of a water particle in the San Andres aquifer range from 0.1 to 10 cm/yr (0.04 to 4 in/yr).

5.6.4.2.1 Hydraulic Conductivity and Permeability of the San Andres Aquifer

As of July, 1982, available information on the hydraulic conductivity and permeability of San Andres carbonate rocks comes from: (1) the analysis of one drill-stem test (DST) chart supplied by an independent oil company, (2) published information derived primarily from the analysis of core from San Andres oil fields, and (3) the analysis of three DSTs in DOE/SWEC hydrostratigraphic test wells in the Palo Duro Basin.

The permeability of San Andres carbonate rocks, determined in core from oil field reservoirs, varies from one to thirty millidarcys (md) and may reach several hundred millidarcys (Core Laboratories, Inc., 1972; Ramondetta, 1982). These values are biased on the high side because the tested rocks were usually from the more permeable layers. Values of permeability determined from the center of the Palo Duro Basin range from 0.04 to 0.4 md (Table 6). The drill-stem test results given in Table 6 assume a kinematic viscosity of 1 cm^2 sec^{-1} (0.16 in^2 sec^{-1}). The hydraulic conductivity of the San Andres Aquifer has not been determined because the water conditions (salinity, temperature) are not known.

5.6.4.2.2 Effective Porosity of the San Andres Aquifer

The porosity in carbonate rocks of the San Andres Formation varies from two to sixteen percent in oil fields on the northern shelf of the Midland Basin (Core Laboratories, Inc., 1972). Within the Palo Duro Basin, San Andres porosity appears to be less than ten percent and limited to thin (less than three meters) zones (Table 6). As of July, 1982, quantitative measurements have not been made of the total porosity or effective porosity in San Andres carbonate rocks in the Palo Duro Basin.

5.6.4.2.3 Saturated Thickness of the San Andres Aquifer

Because most of the other units either pinch out or have their porosity occluded, the San Andres cycle-4 carbonate unit is assumed to be the principal conduit for ground-water flow in the San Andres through the Palo Duro Basin. The thickness of the cycle-4 carbonate unit (18 to 31 meters, 60 to 100 ft) is an upper estimate of the saturated thickness. However, the transmissive portion of the aquifer may be less than the thickness of the rock (Pitt and Scott, 1981). Research in progress seeks to estimate the thickness of transmissive rock in the San Andres.

5.6.4.2.4 Ground-water Flow Rates in the San Andres Aquifer

The hydraulic head gradient, hydraulic conductivity, fluid viscosity and density, and aquifer thickness vary significantly along the ground-water flow path through different areas of the Palo Duro Basin. Because of this variation, values of average and regional ground-water velocity can be estimated with only a three-dimensional, variable density, numerical model. As of July, 1982, knowledge of flow velocity in the San Andres in the Palo Duro Basin consists of order-of-magnitude upper estimates of average linear velocity ranging from about 0.1 to 10 cm/yr (0.04 to 4 in/yr). An order-of-magnitude estimate of the specific discharge through the San Andres carbonates in the Palo Duro Basin is 0.01 to 1.0 cm/yr (0.004 to 0.4 in/yr). These values were calculated by assuming a permeability of 0.1 to 10 md, a hydraulic conductivity of 2.71 to 271 cm/yr (1.07 to 107 in/yr) (estimated by using the conversion: 1 darcy = .7433 m/d, valid only for fresh water at 16^{o}C), a porosity of 10 percent, and a hydraulic head gradient of 0.004. The calculated values of average linear velocity and specific discharge must be considered broad estimates because of the uncertainties in the hydrologic parameters attributed to the San Andres Aquifer.

5.6.4.3 Hydraulic Characteristics of the Upper Aquifer

The transmissivity of the Dockum unit of the Upper Aquifer, as indicated by one pumping test, is about 19.3 m^2/d (16,700 gpd/ft) (Myers, 1969). This one value cannot be assumed to be representative of all Dockum rocks. Data are minimal because aquifer tests are rarely performed in the stock and irrigation wells which typify Dockum water use. The most commonly reported well characteristic is well discharge. An attempt to synthesize transmissivity data from specific capacity data has not been made to date.

Myers (1969) reports a coefficient of storage of 10^{-4} from the one pumping test in the Dockum unit in Deaf Smith County. The absence of additional data prevents this value from being considered to be representative of Dockum rocks.

Most of the Dockum Group is saturated under the High Plains region and the group thickness varies from 120 to 300 m (394 to 984 ft); however, the thickness of the transmissive zones in the Dockum is unknown. Any estimate based on net sand thickness must take mud content into account. The saturated thickness of the Dockum is still under study.

Valid estimates of the porosity and ground-water velocity in the Dockum unit have not been made, to date. The hydraulic characteristics of the Ogallala Aquifer are being treated in a separate study.

5.7.1 Identification of Recharge and Discharge Areas

Other than the Ogallala Aquifer (discussed in another study), the hydrogeologic elements of the Palo Duro Basin are thought to be recharged primarily at their outcrops to the west, in New Mexico. The San Andres Aquifer may also receive recharge by cross-formational flow through rocks of the Delaware Mountain Group (Hiss, 1975a). The Dockum Aquifer may receive recharge from the overlying Ogallala, but this has not been documented.

Some of the meteoric recharge to the Deep-Basin Brine Aquifer, San Andres Aquifer, and Upper Aquifer is undoubtedly captured by the gaining reaches of the Pecos River. The quantity of water that enters the regional flow system is unknown. The amount of leakage between the different hydrogeologic units is also unknown.

The location of deep-basinal discharge has not been identified. Ground water is believed to be discharging from the San Andres Aquifer along the San Andres Formation outcrop, east of the Caprock Escarpment; however, there are no data to support this at present. Ground water from the Dockum is believed to discharge in springs at the formation outcrop along the escarpment. Dockum ground water may also discharge by vertical, downward flow in the salt-solution zone under the edge of the Caprock Escarpment. Pumping takes place from the San Andres Aquifer and the Dockum Aquifer where the units are at or near the surface. Both units yield moderate supplies of water for agriculture.

5.7.1.1 Recharge and Discharge Areas of the Deep-Basin Brine Aquifer

Fluids migrating through the deep basin have entered the system primarily in New Mexico, where the aquifers outcrop. If the hydraulic gradients have remained unchanged since the Late Cretaceous, and if a permeability of 2.0 md and porosity of 0.5 percent can be considered average for the Wolfcampian-age carbonates (Bentley, 1981), then the fluid from western recharge areas could replace the fluid in the Wolfcamp carbonate aquifer once each million years (Bassett and Bentley, in press). The entire volume of fluid in Wolfcampian-age strata from outcrop to basin center may have been replaced more than 60 times during the Cenozoic (Bassett and Bentley, in press).

The volume of vertical leakage across the Evaporite Aquitard in the Palo Duro Basin may be significant because of the large contact area between the aquitard and the Deep-Basin Brine Aquifer. Measuring the distribution and amount of leakage is difficult because of the low density and questionable reliability of data.

The steady eastward decline in hydraulic head indicates that regional hydraulic continuity exists between the outcropping areas in New Mexico and the unidentified discharge areas to the east, probably in Texas or Oklahoma. However, the discharge locations for the Deep-Basin Brine Aquifer have not been discovered at this time.

5.7.1.2 Recharge and Discharge Areas of the San Andres Aquifer

Theis (1965) and Dinwiddie and Clebsch (1973) defined the recharge zone for the San Andres to be between the Pecos River Valley and the San Andres outcrop (Figure 5). Hiss (1975a) postulated that water in the Permian reef facies that outcrop in the Guadalupe Mountains is transmitted through rocks of the Delaware Mountain Group to the buried San Andres Formation in southeast Nex Mexico and West Texas. The potentiometric map (Figure 5) shows the potential for ground-water flow away from the San Andres outcrop, but does not include data from the area studies by Hiss (1975a).

The Pecos River Valley controls ground-water flow in the San Andres Formation at shallow depth. Because of the basin geometry and geological framework of the San Andres Aquifer, the Pecos River is a barrier which limits the amount of water that percolates through the San Andres carbonate rocks in the Palo Duro Basin. The San Andres aquifer is recharged by water from the Pecos River in northern Guadalupe County, New Mexico, as well as by water that has percolated through the overburden between the Pecos River and the eastern boundary of the Pecos drainage basin. However, the Pecos River regains much of this recharge after the ground water passes through the karstic limestone of the San Andres (Dinwiddie and Clebsch, 1973). Therefore, some of the water that recharges the San Andres Aquifer under the Pecos Plains in New Mexico is probably recaptured by the Pecos River.

Recharge can be calculated by the numerical ground-water flow model that generates equipotential and ground-water flow lines for a west-to-east, vertical profile through the hydrogeologic elements in the Palo Duro Basin (Gustavson et al., 1981, and in preparation). Based on known and estimated values of hydraulic head and hydraulic-conductivity, the model has calculated that the maximum recharge to the San Andres Aquifer in the Pecos Plains is about 29 cm/yr (11 in/yr). A large portion of this recharge is gained by the Pecos River. Annual average precipitation in east-central New Mexico is only about 35 cm/yr (14 in/yr) and there is a large evapotranspiration potential. Detailed numerical modeling of the ground-water flow system in the Pecos River Valley is needed to calculate more reasonable estimates of recharge.

An order-of-magnitude estimate of specific discharge through the San Andres carbonate units in the Palo Duro Basin is 0.01 to 1.0 cm/yr (0.004 to 0.4 in/yr) (see Section 5.6.4.2.4). The large difference between estimated recharge and specific discharge may support the conclusion that the Pecos River captures much of the meteoric recharge of the San Andres.

Ground water is thought to discharge from the San Andres Formation east of the Caprock Escarpment in north-central Texas. Carbonate rocks of the San Andres Formation are believed to act as conduits for ground-water discharge under the Rolling Plains (Simpkins and Fogg, in preparation). Ground-water discharge also may include components from downward flow from the Ogallala and Dockum aquifers, as well as upward flow from the more deeply buried rocks of the San Andres. However, there is not enough information from this area to document the water volume derived from these two sources. Some geographic areas along the north-south trend of the San Andres (Blaine) outcrop in north-central Texas are possible discharge sites if radionuclide-contaminants leak into the San Andres from a failed repository. However, there is little hydrologic information available with which to document the location of the active zone of discharge from the San Andres Aquifer.

Where the Evaporite Aquitard crops out east of the Caprock Escarpment, in the Rolling Plains region, the weathered sediments yield moderate supplies of water for agriculture. In this area, the dissolution of halite and resultant collapse and disturbance of bedding have enhanced the permeability and porosity of overlying beds (Gustavson et al., 1980). Salt dissolution has led to the formation of saline seeps and springs along eastward-draining stream courses, degrading the quality of surface waters for tens of miles downstream (Allen et al., 1971; Leifeste et al., 1971). More information on salt dissolution can be found in Section 3.5 and 3.7.

The residence time of ground water is found by dividing the volume of water present in a section by the specific discharge through the section. For the development of a preliminary estimate, representative values of the major hydraulic characteristics were assumed to be the following: 1) permeability of 0.1 md, 2) average porosity of five percent, 3) hydraulic gradient of 0.004, and 4) hydraulic conductivity of $10^{-3.1}$m/day ($10^{-2.6}$ft/day). The west-to-east distance between recharge and discharge areas in the San Andres is roughly 480 km (298 mi). Using these values, the tentative, order-of-magnitude estimate of ground-water residence time in the San Andres in the Palo Duro Basin is 22 million years. Thus, water in the San Andres has been replaced an estimated three times since the Laramide orogeny (65 mybp). Along the flow path to the south of the Palo Duro Basin, the permeability is higher (Table 6) so the volumetric flux is much greater and the residence time of water much less.

5.7.1.3 Recharge-Discharge Areas of the Upper Aquifer

The Dockum element of the Upper Aquifer undoubtedly receives some recharge by direct rainfall and seepage from streams where the Dockum is exposed on the western side of the High Plains. Some of this water is probably discharged into streams and as springs in local flow systems. The quantity of water that enters into the regional flow system is unknown. To the extent that the Dockum and Ogallala are in hydrologic continuity (see Section 5.6.3.3), the potentiometric surface in the Dockum is maintained by recharge to the Ogallala across the High Plains.

Where the Dockum Group is exposed around the periphery of the Southern High Plains, or where the saturated thickness of the Ogallala is small, ground water in the Dockum is developed on a small scale for domestic, stock, and irrigation uses. The ground water resource of the Dockum in the Texas Panhandle and East New Mexico is summarized by Simpkins (1980).

Some ground water from the Dockum may discharge by vertical, downward flow through brecciated Permian mudstones in the salt-dissolution zone under the edge of the Caprock Escarpment (Simpkins and Fogg, in preparation). Dockum ground water is also thought to discharge in the saline springs that occur in the Rolling Plains region east of the escarpment (Figure 19).

The "brine emission" areas in the Rolling Plains region have been identified and studied extensively by the U. S. Army Corps of Engineers in an effort to improve the water quality in downstream reaches and reservoirs (U. S. Army Corps of Engineers, 1976). The saline spring waters commonly have high Na, Ca, Cl and SO_4 concentrations, due to either the dissolution of Permian evaporites by shallow meteoric ground water, or to discharge of saline waters from the deep aquifers beneath the evaporite section. The integrity of a future nuclear waste repository would be in question, and travel times of radionuclides decreased, if deep-basin waters were found to be discharging in the Rolling Plains region. However, the saline springs immediately east of the Caprock Escarpment are thought to result from shallow meteoric ground waters dissolving bedded salt, not from deep-basin brine discharge. This tentative conclusion is supported by a computer flow model, and chemical and isotopic data.

A conceptual flow model developed by Gustavson, et al., (1980) and Simpkins (1980) links the saline discharge areas in the Rolling Plains directly to the process of salt dissolution by shallow meteoric ground water. Simpkins and Fogg (in preparation) have constructed a two-dimensional finite-element digital computer model that simulates the flow of ground water through the salt dissolution zones. In this model, fresh water enters the system through the higher areas within the Rolling Plains and High Plains regions, then flows through the Periman salt units, and finally discharges as saline water in springs and seeps on the Rolling Plains (Figure 20). The results of several computer simulations indicate that it is possible for all of the saline discharge on the eastern Rolling Plains to have entered the system as fresh water on the High Plains and Rolling Plains.

The salt-dissolution conceptual flow model is supported by the fact that there is a downward hydraulic head gradient between the Upper Aquifer and the Deep-Basin Aquifer (see Section 5.6.2). Saline waters from the deep aquifer could not discharge against the downward-directed gradient. Equivalent fresh water hydraulic heads in the saline aquifers (Wolfcampian, Mississippian, and Pennsylvanian) below the salt section in the Sawyer #1 test well in Donley County, Texas, are at least 275 meters (902 Ft.) below the elevation of the shallow water-table in the region. The mixing of shallow and deep ground waters is possible closer to the saline-discharge points because heads in the Wolfcamp aquifer approach the water-table elevation.

The chemical compositions of the saline ground waters and spring waters also indicate a shallow meteoric origin rather than a deep basinal origin. The chemical and isotopic analyses of these waters are shown in Tables 7 and 8. The ratio of bromide to chloride (Br/Cl) can be used to differentiate between brines of different origins (Whittemore et al., 1981). Brines formed by meteoric waters dissolving bedded salt will usually have Br/Cl ratios between $1X10^{-4}$ and $10X10^{-4}$. Deep-basin brines commonly have Br/Cl ratios greater than $25 X 10^{-4}$. Most of the Br/Cl ratios found in the saline springs and ground waters in the Rolling Plains are within the meteoric-origin range (Figure 21). In contrast, analyses of water samples from the Sawyer No. 1 well in Donley County, Texas, revealed Br/Cl ratios in the Wolfcamp, Pennsylvanian carbonate, Mississippian carbonate, granite wash, and Ellenburger aquifers within the range of deep-basin brines (Figure 21 and Table 7).

The hydrogen and oxygen isotopic compositions of the saline springs and ground waters also support a meteoric origin. A plot of $\delta^{18}O$ and $\delta^{2}H$ (Figure 22) shows that the data are close to the meteoric water line (the line along which the isotopic compositions of nearly all meteoric waters plot). In contrast, the isotopic compositions of the deep formation brines from the Palo Duro Basin are to the right of this line. The isotopic composition of the spring water is significantly different from that of the deep-basin waters.

Though the water in the saline springs just east of the Caprock Escarpment is surely of meteoric origin, there is not enough information available to verify that it is discharge from the Dockum Aquifer. When the analysis of chemical data from Dockum ground waters is complete (F.Y. 1983), the relationship between the saline springs and the Upper Aquifer should be more clear.

5.7.2 Principal Ground-Water Flow Paths

Because of the lack of potentiometric data and the uncertainty in the location of discharge zones, ground-water flow paths through the hydrogeologic elements of the Palo Duro Basin are unknown. Flow paths through the Ogallala Aquifer are treated in a separate study.

In general, water enters the Deep-Basin Brine Aquifer, the San Andres Aquifer, and the Upper Aquifer where these units crop out in New Mexico. Water moves eastward through the formations, reflecting the regional topographic and structural dip away from the Rocky Mountains (Figure 1). Vertical leakage across aquitards may be significant because of the large contact area between formations and the downward flow component predicted by the pressure/depth data and observed at the Sawyer well. Both downward and horizontal flow appear to take place in the Palo Duro Basin.

In the Palo Duro Basin, the abundance of cyclic, impermeable evaporites greatly reduces the transmissivity of the San Andres Aquifer. As a result of the eastward decrease in transmissivity, the ground-water flow direction changes from eastward in east-central New Mexico to southeastward in the Palo Duro Basin. Eastward flow takes place across the Midland Basin, although local patterns of flow are complicated near oil reservoirs.

Approximations of residence times can be found in Section 5.7.1. An estimate of ground-water flow rate is in Section 5.6.4. Continued research is needed in order to delineate the flow paths of ground water through the Palo Duro Basin.

5.7.3 Isotopic and Regional Hydrochemistry

The data regarding chemical compositions of fluids used in this investigation were obtained from petroleum companies, petroleum information companies, and published surveys. The chemical compositions obtained from these sources have to be screened to remove questionable analyses. The unacceptable data are those in the following groups: (1) those suspected of contamination by drilling fluid, (2) those affected by an enhanced recovery operation, and (3) those reported without depth or formation identification (Bassett and Bentley, in press). Data which pass this screening are still subject to unknown errors in collection procedure, sample preservation, and analytic technique. The outgassing of volatiles and the incomplete analysis of dissolved species are common problems (Bassett and Bentley, in press).

Formation brine in the Palo Duro Basin has a CO_2 partial pressure (PCO_2) significantly higher than that in the atmosphere (Bassett and Bentley, in press). This causes outgassing of CO_2, elevation in pH, and the possible precipitation of carbonate species in the sample container when the sample is brought to atmospheric pressure. The loss of H_2S, or the exposure of a sample to atmospheric oxygen, will also alter the oxidation state.

Research to be conducted during the next year will attempt to further define the isotopic composition of the ground waters in the Palo Duro Basin. The dissolved gases and organic carbon within the waters will also be examined. The UT/BEG will perform chemical analyses on ground-water samples in order to verify and supplement the analyses obtained from petroleum companies.

5.7.3.1 Isotopic and Regional Hydrochemistry of the Deep-Basin Brine Aquifer

The regional nature of brine migration, lateral continuity of carbonate facies, and long residence and reaction times in the Deep-Basin Brine Aquifer suggest that the brine composition will reflect the composition of the host rock. If the estimated ground-water flow velocity is correct (see Section 5.6.4.1.4), the entire volume of fluid in Wolfcampian-age strata from outcrop to basin center has probably been replaced about 60 times during the Cenozoic (Bassett and Bentley, in press). Any original brine would have been displaced early in the development of the regional flow regime. The brines present today in the Wolfcampian-age carbonate rocks and sandstones cannot be connate water.

The deep-basin brine composition is dominated by sodium and chloride and has a salinity several times that of seawater. The chemical compositions of brines from granite wash and Wolfcampian-age carbonates are listed in appendix C. The chemical compositions of brine samples from within the Palo Duro and Dalhart Basins are in Table 9. Total dissolved solids (TDS) in Wolfcampian-age carbonates range between 50,595 and 340,432 mg/l. The TDS in the granite wash facies range between 108,904 and 261,453 mg/l (Bassett and Bentley, in press). Brine in both the Wolfcampian-age carbonates and the Pennsylvanian and Permian granite wash ranges from a Na-Ca-Mg-Cl type to a Na-Cl type (Figures 23 and 24).

If halite is the primary source of sodium and chloride in a ground water, the ratio of sodium to chloride by weight should be near the theoretical value of 0.65. Departure from this value can be due to mixing of fluids from different sources, or to rock and water interactions. The ratio in the Wolfcampian carbonate brine, which occurs adjacent to the evaporite facies, is only slightly offset from the theoretical ratio (Figure 25). The compositional shift in granite-wash brine is more pronounced (Figure 26), indicating that sodium is depleted relative to chloride. The sodium depletion could be caused by ion exchange with clays, or by albitization (exchange of sodium for calcium in feldspars).

Bassett and Bentley (in press) used the computer model AQ/SALT to identify the thermodynamic constraints on the composition of Wolfcamp and granite-wash brines. The model is discussed in more detail by Bassett and Griffin (1981). By comparing calculated activity products with thermodynamic equilibrium constants, the reaction state of a brine with respect to the minerals of interest can be determined. AQ/SALT calculates ion-activity products and determines whether a given mineral phase is stable or has the potential to dissolve in a given water. There were not enough data available to apply Pitzer's equations (1979), upon which AQ/SALT is based, to the carbonate species in the deep-basin brines. To calculate the carbonate species, AQ/SALT was interfaced with an ion-pairing model, SOLMNEQ (Kharaka and Barnes, 1973). Granite-wash and Wolfcampian carbonate brine data were computer processed separately.

The Wolfcampian carbonate brine is near equilibrium with respect to anhydrite, but is significantly undersaturated with respect to halite (Figure 27). In contrast, the composition of the deeper granite-wash brine appears to be shifted away from saturation with anhydrite and grouped near saturation with respect to halite (Figure 28).

An explanation for the shift away from anhydrite equilibrium is sulfate reduction. The sulfate concentration in the granite wash brine is significantly lower than that in the Wolfcampian carbonates, commonly by two orders of magnitude (Bassett and Bentley, in press). Production reports note that fields developed in granite wash, particularly north of the Amarillo Uplift, produce hydrogen sulfide. Sulfate reduction, with continued dissolution of anhydrite, would effectively increase calcium and deplete sulfate concentrations. The oxidation potential of ground water in the Deep Basin Aquifer has not been determined, as of July, 1982 (information on the importance of oxidation potential to radionuclide transport can be found in Section 5.7.3.2).

The Wolfcampian carbonate brine is in equilibrium with respect to calcite, but not with respect to dolomite (Bassett and Bentley, in press). Magnesium-to-calcium ratios are generally low (0.3), and salinity is elevated. Magnesium-to-calcium ratios of 0.5, or higher, are usually interpreted as being necessary for the stable, two-phase equilibrium between calcite and dolomite at 25^{o} C (Folk and Land, 1975). It is unlikely that the present-day brines cause continued dolomitization in the basin (Bassett and Bentley, in press).

The outgassing of carbon dioxide at the surface during sample collection elevates the pH of the sample and results in an apparent saturation with respect to carbonate minerals. Thus, Bassett and Bentley's (in press) calculations using the measured PCO_2 indicate that most Wolfcampian carbonate brine is supersaturated with respect to calcite (Figure 29) and dolomite (Figure 30), although the brine is actually at saturation with respect to calcite and undersaturated with respect to dolomite. Bassett and Bentley (in press) used a mass-transfer approach to simulate the stepwise addition of CO_2 back into the sample in order to estimate the _in situ_ brine PCO_2 (Table 9). They supported this simulation by finding an analogy with the PCO_2 in natural gas fields near the Palo Duro Basin. Their estimate of the actual pH range in the Wolfcampian carbonate brine in the Palo Duro Basin is 5.70 to 6.63 (as opposed to the measured values between 6.24 and 8.60) (Table 9). Uncorrected pH values for granite-wash brine range from 4.0 to 7.9 (appendix C).

Several mechanisms have been proposed to describe the evolution of brine in sedimentary basins: (1) membrane filtration, (2) dissolution of evaporites, and (3) mixing with metamorphic or magmatic waters (Berry, 1958; White, 1965; Hanshaw and Bredehoeft, 1968a, b; Carpenter, 1978). The presence of brine in the Palo Duro Basin is probably related to dissolution of evaporites (Bassett and Bentley, in press). There has been no post-Paleozoic magmatic activity and there is no evidence of membrane filtration in the Palo Duro Basin. The mudstone and shale required for membrane filtration are volumetrically of little significance in this basin.

The preliminary results of investigations into the bromide-chloride ratio and hydrogen and oxygen isotopic composition of the deep-basin brine are discussed in Section 5.7.1.3, where they are used to help identify the source of saline springs in the Rolling Plains Region. The data are summarized in Table 7.

Carpenter (1978) suggested that, in sedimentary basins, the composition of brine having more than 100,000 mg/l TDS is influenced by evaporite dissolution. The deeply buried formations in the Palo Duro and Dalhart Basins have been overlain by evaporites since Late Permian time. Fluid migrating through this section would be saturated with sodium chloride. However, the low permeability of the Evaporite Aquitard probably keeps the flux through this section low.

Although there has probably been some mixing with water leaking downward from evaporite lithologies, a more reasonable method of generating high total dissolved solids is to dissolve evaporites earlier in the flow history, near the recharge areas to the west (Figure 1). Ancient salt dissolution zones (originating as early as the Triassic) have been identified near the margins of the basin (Gustavson et al., 1980). The character of the brines is controlled by the dissolution of evaporites early in the flow path and by subsequent modification in transit.

5.7.3.2 Isotopic and Regional Hydrochemistry of the San Andres Aquifer

If the estimated ground water flow rates for the San Andres Aquifer are correct (see Section 5.6.4.2.4), the water in the San Andres has been replaced about three times during the Cenozoic. Certainly, all of the original depositional water and evaporite brine have been flushed from the San Andres system. The brine around the periphery of the Palo Duro Basin is currently a Na, Cl-type that evolved from percolating meteoric water by dissolution of halite.

The chemical compositions of San Andres water samples are presented in Appendix D. Total dissolved solids (TDS) in the water of the San Andres Aquifer increases from less than 1000 milligrams per liter (mg/l) at the San Andres outcrop to roughly 5000 to 10,000 mg/l under the Pecos River alluvium (Figure 31). The increase in TDS from 10,000 to over 100,000 along the trend of the Pecos River coincides with the location of a salt-solution zone (Gustavson et al., 1981). Total dissolved solids increase toward the interior of the Palo Duro Basin, and decrease southward out of the Palo Duro Basin and into the Midland Basin.

Ground water in the San Andres Aquifer in New Mexico and Texas is made up of three hydrochemical facies: (1) a $Ca-HCO_3$-type water limited to shallow depths at the San Andres outcrop, (2) a $Ca-SO_4$-type water between the outcrop and the Pecos River/salt solution zone, and (3) a Na-Cl brine in the interior of the Palo Duro Basin (Figures 31 and 32).

The geographical variation in hydrochemical facies is directly related to the increase in total dissolved solids as ground water passes through the salt-solution zone and basin interior. The extremely large increase in total dissolved solids eastward from the San Andres outcrop in New Mexico is probably controlled by the dissolution of salt. The concentrations of Na^+ and Cl^- in ground water approach equilibrium with respect to halite around the periphery of the Palo Duro Basin (Figure 33). If the salinity of water in San Andres carbonate-rock is due to the dissolution of halite, either at the salt-solution zone, or at the bedding contact between halite and carbonate facies, then the Na/Cl weight ratio in the brine should be near 0.65. This is the case for most samples of San Andres water with a salinity greater than that of seawater (Figure 34). But, in many samples with more than 100,000 mg/l dissolved solids, the sodium concentration is depleted relative to chloride for waters in equilibrium with halite (Figure 34). A similar depletion in water from Wolfcampian carbonates and Pennsylvanian granite wash facies in the Deep Brine Aquifer is reported by Bassett and Bentley (see Section 5.7.3.1). The cause of the sodium depletion in highly saline San Andres water is under investigation.

Figure 33 shows that San Andres water does not reach equilibrium with respect to halite. However, this half-order-of-magnitude undersaturation may result because SOLMNEQ was used to calculate the Na-Cl activity product at large values of ionic strength (3 to 5), even though the program was not designed for use on hypersaline brines (Kharaka and Barnes, 1973). The equilibrium state of water in the San Andres is still being studied.

Equilibrium with anhydrite is approached at a concentration of dissolved solids lower than that at which water approaches equilibrium with respect to halite (Figure 35). The saturation index decreases at values of total dissolved solids greater than about 60 g/l. Whether this decrease is an error of the SOLMNEQ program, or an actual event, is under study.

The water at the western and southwestern perimeter of the Palo Duro Basin is nearly saturated with both halite and anhydrite. It is likely that water in San Andres carbonate rock toward the center of the Palo Duro Basin has a similar chemical composition. The decrease in total dissolved solids and in relative saturation with halite seen southward out of the Palo Duro Basin corresponds to the southward change from evaporite to carbonate rock facies. The regional ground-water flow path may also influence the changing water chemistry.

Almost all ground-water samples are supersaturated with respect to calcite and dolomite, as calculated by the computer program SOLMNEQ. Outgassing of CO_2 - gas during fluid production or sample collection is undoubtedly the cause of the apparent supersaturation (Bassett and Bentley, in press). The slope of the relation of the saturation index to pH is about 1.0 for calcite and 2.0 for dolomite (Figure 36). These values are in agreement with the predicted values of the first derivative of saturation index with respect to change in pH (Bassett and Bentley, in press). Reported values for pH of San Andres water (ranging from 4.7 to 8.6) are probably higher than in situ values because outgassing of CO_2 before measurement results in a pH increase. However, ground water around the periphery of the Palo Duro Basin should be in equilibrium with both calcite and dolomite (the dominant components of the San Andres Aquifer). The calcium-bicarbonate-type water in the karstic recharge belt west of the Pecos River appears to be undersaturated with respect to each phase.

Figure 38 shows the variation in the Mg^{2+}/Ca^{2+} ratio in San Andres water with change in salinity. The saline-to-brine formation water lies in the field of preferred occurrence of calcite. Apparently, this water is not currently capable of precipitating dolomite because of its extremely high salinity and low Mg^{2+}/Ca^{2+} ratio. This is true even though the water has dissolved enough dolomite to reach equilibrium with that phase.

The oxidation potential of ground water is an important factor to consider when determining the potential for radionuclide transport. In general, a reducing environment will inhibit transport because many radionuclides are significantly less soluble in reducing water. Two methods are being used to determine the redox condition of the rock matrix and fluid in the Palo Duro Basin. The rock matrix is being examined to identify the presence or absence of authigenic reduced mineral species and the brines are being evaluated to determine if sulfate reduction and subsequent hydrogen sulfide generation have occurred.

Authigenic pyrite is a common constitutent of San Andres anhydrite, dolomite and siltstone. The formation of pyrite probably follows from the bacterial reduction of sulfate and the oxidation of organic matter, and the reduction of ferric iron to ferrous iron (Berner, 1970; Goldhaber and Kaplan, 1974). Sulfate is provided by anhydrite, and ferric hydroxides occur as grain coatings on clastic sediments. The limiting factor in the San Andres rocks is probably the availability of reactive iron.

At 25^{0}C, in dilute water and with all constituents having an activity coefficient equal to one, an Eh of about -200 millivolts (mV) or less is required for pyrite formation (Stumm and Morgan, 1970). Eh values between -100 and -250 mV are typical for modern marine-tidal-flat environments which contain pyrite (Berner, 1964). None of these conclusions can be directly applied to the more saline, warmer water in the San Andres Formation. However, the information presently available suggests that the Eh of San Andres Formation water is between about -100 and -250 mV. Additional petrographic studies of authigenic minerals in the evaporite section are needed to better define the oxidation potential of the rocks.

The isotopic composition of sulfate and bicarbonate is being analyzed to determine if sulfate reduction is occurring. Sulfate in the aquifer is assumed to be the result of anhydrite dissolution. If anhydrite is the sulfate source, the $\delta^{34}S$ of this sulfate is expected to be about +20 o/oo. If the sulfate is being reduced, the residual sulfate should become enriched in ^{34}S. The sulfate in the Wilcox Aquifer near the flank of the Oakwood salt dome in the East Texas Basin appears to originate from the dissolution of caprock anhydrite and is presently undergoing sulfate reduction. The $\delta^{34}S$ of the cap-rock sulfate is approximately +19 o/oo (Feeley and Kulp, 1957), whereas the sulfate in the ground waters on the dome flank (with an Eh of = 150 mV) was +36 o/oo.

Carothers and Kharaka (1980) observed greatly enriched $\delta^{13}C$ values of bicarbonate where sulfate reduction had occurred. They also found greatly depleted $\delta^{13}C$ values of bicarbonate if a methogenesis reaction had occurred (biologic reduction of organic material, producing methane and heavy-carbon CO_2). Both sulfate reduction and methogenesis reactions take place in low-temperature, reducing waters. The $\delta^{34}S$ of sulfate and the $\delta^{13}C$ of bicarbonate will be measured from all San Andres and deep-basin water samples to aid in determining if either reaction is occurring.

Much of the original and secondary porosity in the Palo Duro Basin was plugged by the movement of a residual, evaporative brine early in the burial history (Bein and Land, 1982). The Mg-Ca-Cl-type brine, remaining after the precipitation of $CaCO_3$, $CaSO_4$, and NaCl, moved into the shallow ground-water system and caused calcite dissolution, gypsum precipitation, and dolomitization. Mixing of the Mg-Ca-Cl-type brine with more natural marine water to the south left the brine undersaturated with respect to halite and resulted in a greater residual porosity in the San Andres carbonate rocks over the Northern Shelf than in the Palo Duro Basin.

5.7.3.3 Regional Hydrochemistry of the Upper Aquifer

The analysis of hydrochemical data from the Dockum Aquifer will be performed during Fiscal Year 1982. As of July, 1982, no conclusions can be drawn about the chemistry of Dockum waters. The hydrochemistry of the Ogallala Aquifer is being treated in a separate study.

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