

**MODELING THE IMPACT OF A PHOSPHOGYPSUM STACK
ON THE GROUNDWATER AQUIFER**

A Thesis Submitted
to the
Temple University Graduate Board

in Partial Fulfillment
of the Requirement for the Degree

MASTER OF ARTS

by

Takashi Thomas Shinkawa

May 1997

DEPARTMENT COPY

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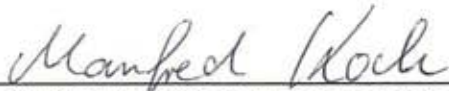
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Dr. Manfred Koch, Primary Advisor



Dr. David Grandstaff, Committee Member



Dr. Peter Goodwin, Committee Member

ABSTRACT

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Primary Advisor: Dr. Manfred Koch

The phosphate industry in the state of Florida is the largest producer of phosphate in the country, producing about one-third of the world's phosphate. By-product gypsum slurry from this industry is allowed to precipitate in large ponds where a topographical "stack" of waste material is created. Environmental concern for this practice is two-fold, involving the hydraulic impact of the topographic mound on the surficial aquifer, and the contaminants (radionuclides and hydrofluoric acid) contained within the highly acidic (pH = 1.0-3.0) process water (most stacks are unlined).

This study has characterized hydrologic parameters (i.e. transmissivity and storativity) of this gypsum stack, and has mathematically modeled volumetric fluxes of water in the system. Results can be used to determine the chemical impact of contaminants through further geochemical speciation and transport modeling, although none has been attempted here.

Although the water budget analysis of the stack indicates a large flux of process water from its base (1591 m³/day), only a small portion (~1%) of this total is modeled as

having an impact on regional flow. Most of the process water drains into ditches from which it evaporates. When other potential water losses are considered (i.e. drain dewatering from the stack interior and flank evaporation) the actual impact of stack waters may be even less.

Sensitivity of the modeled environment shows that leakage rates from the gypsum stack are the most critical values determined in this research. Assumption of steady state water volumes in stack ponds provides a direct calculation of the leakage rate (3.0×10^{-4} day⁻¹) from evaporative losses; essentially, output rates equal input rates.

Findings in this research are in support of the topographical mounding theory, and provide a model upon which volumetric water flux from above-ground tailings piles can be determined. This groundwater model has been tailored to fit the site-specific characteristics of the situation considered, but can be applied to virtually any medium of groundwater flow in the same configuration.

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Saving the largest debts of gratitude for last, I would like to thank my primary advisor, *Herr Director* Manfred Koch, for the unending patience as well as the vast academic knowledge that he has given to me. Finally, I thank my mom, sister, and father for their support and guidance that each has lovingly given to me. It is to them that I dedicate this thesis.

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CHAPTER 1

INTRODUCTION

Phosphate mining in Florida is currently one of the state's largest industries, processing approximately 30-50 million tons of ore per year (Burnett and Hull, 1996). Estimates from previous studies indicate that over 700 million tons of phosphatic waste have been stockpiled in above-ground formations called "Phosphogypsum Stacks" (defined as such by the source and product of their existence). Gypsum and silicon hexafluoride make up the slimy waste that is pumped out to large evaporating ponds, where the former is allowed to precipitate. Over time, accumulation at the bottom of the pond is dug out and piled on the embankments of the pond. This practice is intended to strengthen the walls of the pond as it grows in size and elevation. Approximately eighteen such industrial facilities are located in the Tampa area, with an average area of 90 hectares and a range of heights from 10 to 45 meters. As the stockpile of gypsum stacks grow to a projected billion-plus tons by the year 2000 (Burnett and Hull, 1996), high concentrations of radionuclides, acid, and fluoride within these stacks become an increasingly problematic characteristic of this material, with the potential for groundwater pollution inherent.

The primary focus of this study was to investigate the hydrologic controls of the phosphogypsum stack, and to provide a model of groundwater flux. From these results, transport and geochemical models can determine the migration and fate of possible contaminant leachate plumes. Particular objectives of the research include quantification of the vertical and horizontal flow rates in the phosphogypsum stack and in the surficial

aquifer, as well as determination of the hydraulic impact the phosphogypsum stack on the surficial aquifer.

CHAPTER 2

ENVIRONMENTAL SETTING

Geography

The Piney Point Phosphates facility, located along the coast of western Florida, lies approximately 30 kilometers south of downtown Tampa in Manatee County, along Florida Route 41 (Figure 1). The study area is in a rural setting with cattle ranches, citrus groves, and vegetable farms making up a majority of the businesses close by. Topographically, the area is relatively flat with drainage waters flowing either to the Manatee River in the north, McMullen Creek in the south, or to the Gulf of Mexico in the west (Figure 2). The Piney Point Phosphates complex is at an elevation of 3 - 8 m. above mean sea level, and is about two kilometers from the shoreline of the Gulf of Mexico.

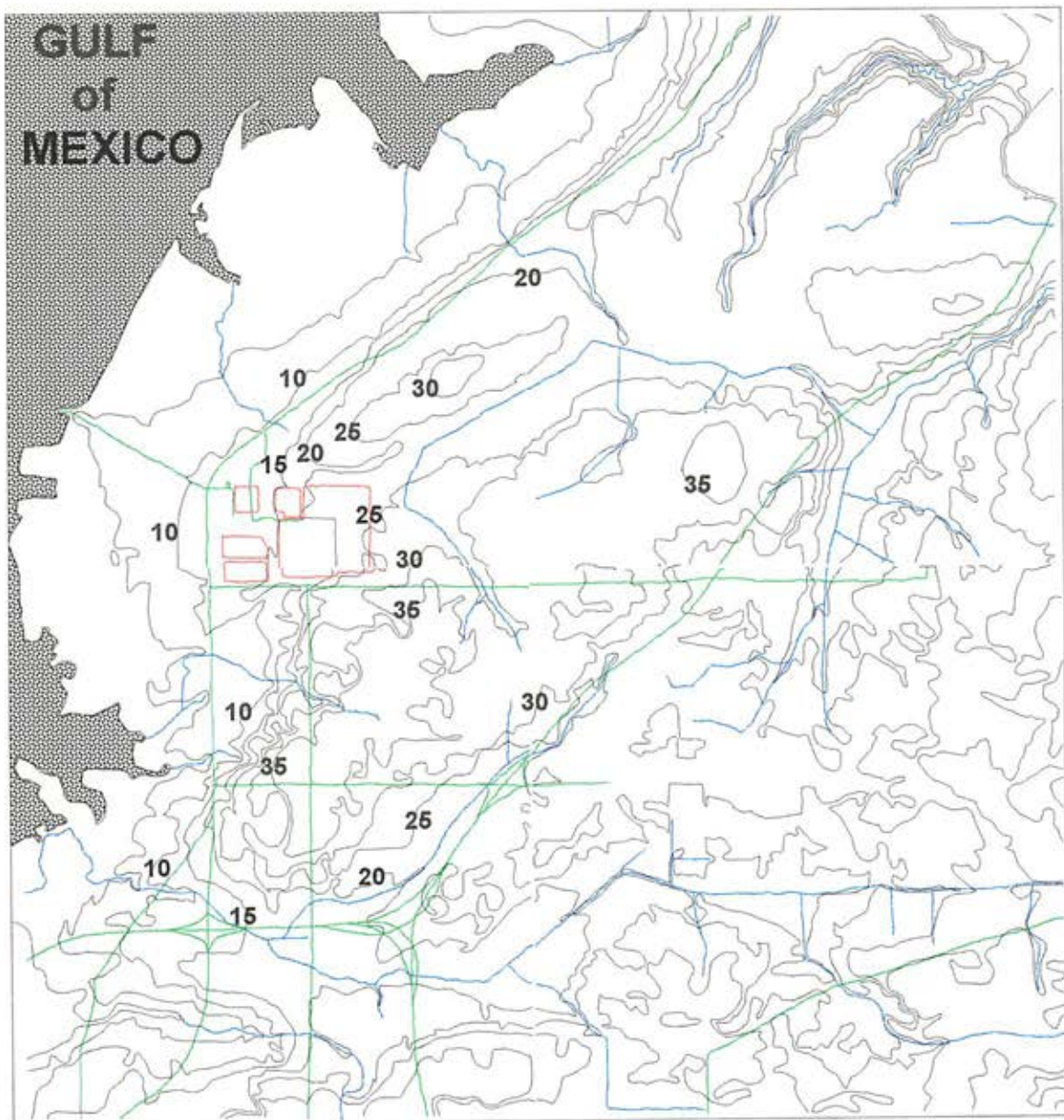
The climate of the research area is subtropical. Convective thunderstorms dominate the rainy weather of the summer months, while winter and spring are fairly dry. Consequently, irrigation demands on the groundwater reach a peak from March through May. This particular site, although presently inactive, is an ideal location for studying fluid migration from phosphogypsum stacks, owing to the fact that local groundwater movement is toward the Gulf of Mexico and away from any large population in the area.

Stratigraphy




Major lithologies of stratigraphic units in the area define three distinct groups of formations (Figure 3). Each group's hydrologic importance is defined by its lithology.



Figure 1. Location of Research Area on Florida State Map



LEGEND

-  Piney Point Complex
-  Waterways
-  Roads

SCALE



Figure 2. Topographical Map of Research Area. Data were taken from USGS 7.5 -minute maps using 5 foot contour intervals.

Although each group contains heterogeneous lithologies (Table 1), generalized lithology is sufficient for the purposes of this study.

The base of the stratigraphic column (Figure 3) is made up of the Suwanee, Ocala, and Avon Park Limestones. Together, these formations comprise a 150 - 250 m thick limestone unit which is commonly referred to as the Floridan Aquifer. The lower boundary of this limestone group is defined by a carbonate unit containing intergranular evaporites, and the upper boundary by another carbonate unit with higher percentages of clays (Miller and Sutcliffe, 1984).

Overlying the Floridan Aquifer are alternating sandy limestone and clay layers. This alternation of layers, classified as the intermediate aquifer, is composed of the Tampa and Hawthorne Formations. Although this intermediate group can be used as a source of water, its high clay content reduces its ability to supply water. The upper portion of the group is a confining unit of phosphatic clay known as the Bone Valley Formation. It is this unit which is used as the ore for the phosphate industry in the area and has been called "one of the world's most important sources of phosphate" (Miller and Sutcliffe, 1984). Thickness of the intermediate unit is from 75 - 125 m , with the phosphatic clay composing the upper 10 - 20 m. At the top of the section, a 10-20 m thick unit of undifferentiated sands and constitutes the third lithological group, the surficial aquifer. It consists primarily of surficial sands with occasional clay lenses, and is lithologically distinct from the other two units.

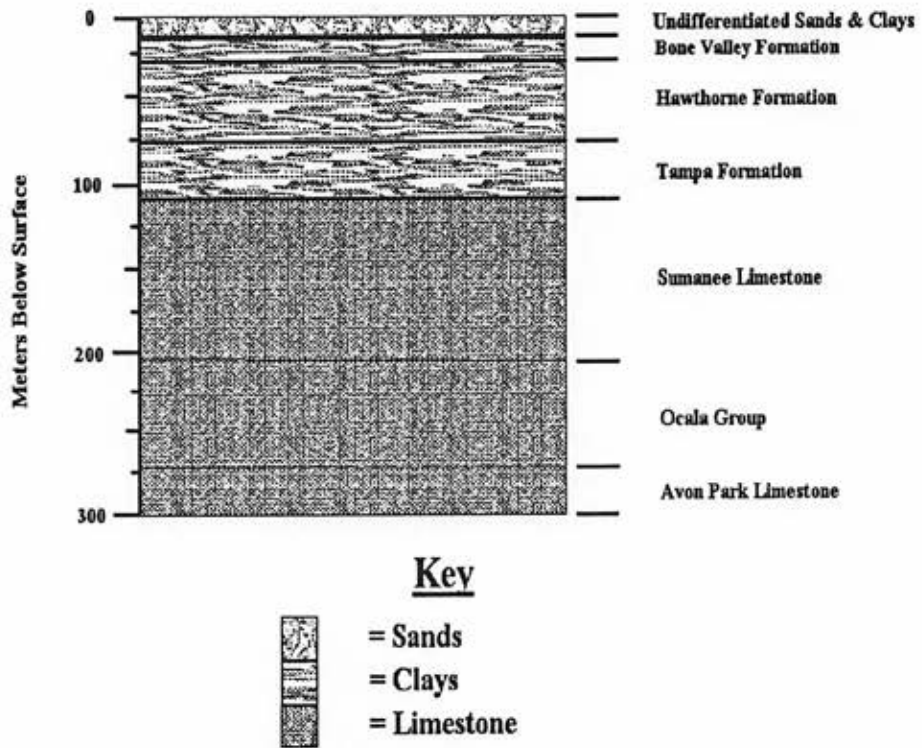


Figure 3. Stratigraphic Cross Section of Regional Geology. A Generalized Lithological Representation of Stratigraphic Units below Piney Point Phosphates, INC.

Table 1. Stratigraphic Framework (Miller and Sutcliffe, 1984)

<u>System</u>	<u>Series</u>	<u>Stratigraphic Unit</u>	<u>General Lithology</u>	<u>Major Lithological Unit</u>	<u>Hydrogeologic Unit</u>
Quaternary	Holocene, Pleistocene	Surficial Sand, terrace sand, phosphorite	Predominantly fine sand; interbedded clay, marl, shell, limestone, phosphorite	Sand	Surficial Aquifer
		Bone Valley Formation	Clayey and Pebbly Sand; clay, marl, shell, phosphatic	Phosphatic Clay	Confining unit
Tertiary	Pliocene	Hawthorn Formation	Dolomite, sand, clay, and limestone; silty, phosphatic	Carbonate and Clastic	Intermediate Aquifer system (Includes First and Second Aquifers)
		Miocene	Tampa Limestone	Limestone, sandy, phosphatic, fossiliferous; sand and clay in lower part in some areas	
	Oligocene	Suwanee Limestone	Limestone, sandy limestone, fossiliferous	Carbonate	Floridan Aquifer
		Ocala Limestone	Limestone, chalky, foraminiferal, dolomitic near bottom		
		Eocene, Paleocene	Avon Park limestone		
		Lake City, Oldsmar, and Cedar Key Limestones	Dolomite and chalky limestone, with intergranular gypsum and anhydrite	Carbonate w/ intergranular evaporites	lower confining bed of Floridan Aquifer

Hydrogeology

Groundwater in the area is commonly drawn from one of the three water producing units described above. Flow within these aquifers is, for the most part, in the horizontal direction with little leakage between layers. The water table in the unconfined unit varies with precipitation and evaporation, while underlying units modulate their potentiometric yields according to changing lateral flow from inland areas of recharge and local points of discharge. The seasonal high (September) and low (May) of the potentiometric surface are mainly associated with groundwater pumping for agricultural irrigation (Johnson et al., 1981).

Comparison of the potentiometric surfaces in the southeastern United States before and after development has shown a regional trend in the vertical flow between aquifer units (Johnston et al., 1980, 1981). Following extensive development of the area in the late 1970's, Polk County to the East had become an area of recharge whereas the coastal area along Tampa Bay had become a zone of discharge to the Gulf of Mexico. This trend dictates a downward flow to the Floridan Aquifer in the area of recharge, and an upward flow in the area of discharge. Because the Piney Point facility is in the area of discharge, there exists an upward flow gradient in the water-bearing units through their confining beds.

Locally, groundwater is drawn primarily from the Floridan Aquifer, although the surficial and intermediate aquifers are occasionally important. The surficial unit is used for domestic lawn irrigation, while the intermediate aquifer system is tapped for use as a rural domestic source of water and agricultural irrigation. Additionally, the Floridan Aquifer

south of the Piney Point facility contains water having high salinity (>250 ppm TDS), making the intermediate aquifer the primary source for municipal water.

Previous Work

Miller and Sutcliffe (1984) studied the aquifer system beneath the Piney Point complex in great detail. About forty test wells investigated aquifer units ranging from the surficial aquifer down through the intermediate aquifer to the Floridan aquifer. Various geophysical well-logging techniques were applied in some of the boreholes to determine lithologies of the aquifers. Potentiometric elevations for most wells were taken weekly, while three wells monitored continuous fluctuations of the hydraulic heads. Hydrographs for the three continuously monitored wells showed sporadic evidence of an upward hydraulic head gradient between the intermediate and the surficial aquifer. During the dry season (April to June), when the intermediate aquifer is heavily pumped for agricultural irrigation, the situation can be reversed and a downward gradient may be observed. Although the aquifer system varies, a majority of the data was interpreted as an indication of low leakage rates into the intermediate aquifer. Data from the surficial aquifer also show a topographic mounding effect of the gypsum stack on the regional groundwater flow.

Quarterly reports of the groundwater monitoring program for the Florida Department of Environmental Protection (FDEP) provide some evidence for the direction of regional groundwater flow in the stack vicinity. Gerathy & Miller Inc. was consulted on the installation of 7 monitor wells drilled for this program into the surficial aquifer. Most

of these monitor wells are still in use today and are being sampled on a regular basis. Contouring results for these data in the last six years show that groundwater flow is primarily to the northwest, and that flow in this system has reached a steady-state condition.

The only hydrogeologic study of the phosphogypsum stack itself was a geotechnical study on slope stability by Oaks Geotechnical Inc. in 1980, a study which provided rudimentary clues on water flow within the stack. During this study, boreholes were drilled into the stack flanks and water levels were monitored over a period of several months. Because the exact well construction data have not been reported, precise inferences on stack flow cannot be made.

CHAPTER 3

GEOCHEMICAL PROFILE

The Florida Department of Environmental Protection has initiated a program to close gypsum stacks by the year 2001. Because the guidelines of this program could demand a multi-million dollar effort from the industry, the highest priority and immediate objective of research is to ascertain whether the fluxes of radionuclides from stacks to the underlying groundwater aquifers are environmentally significant.

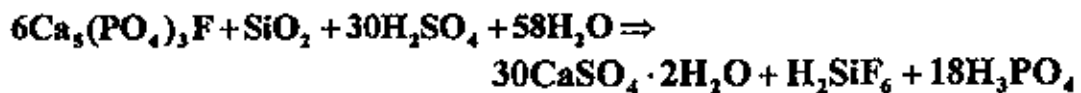
The evaluation of the chemical impact that process waters have on water quality beneath the phosphogypsum stack is the basis for this hydrologic study. Determining hydrologic flux of gypsum stack waters to the surficial aquifer is the first step in deciding whether radiochemical mobilization controls and pertinent transport processes for individual radionuclides will be significant factors in determining the environmental impact of stack waters on the surficial aquifer. Site-specific characteristics will determine the relative importance of each radionuclide on the groundwater, but the collective radiotoxic impact of leachate on ambient conditions in the Floridan terrane will be important in the application of these results to the seventeen other waste gypsum accumulations.

Phosphate Ore Processing

The average composition of phosphate ore processed at the Piney Point Phosphate facility has been reported by Miller and Sutcliffe (1984) to be 65.5% fluorapatite [$\text{Ca}_5(\text{PO}_4)_3\text{F}$], 23% calcite, 8.5% fluorite, 3 % dolomite and 0.35% clay (primarily sodic

and ferric aluminosilicates). Also present in the ore are the radioactive elements Uranium, Thorium, and Actinium, which have a total concentration of approximately 50 to 500 parts per million (Sweeney and Windham 1979). Although these radionuclides combine to provide a total radioactivity of over 5.41 Bq/L, ²³⁸U of the Uranium series decay chain supplies 95.9% of this total (5.18 Bq/L). Thus, the daughter products of the uranium series are the only ones of concern at hazardous levels.

Beneficiation of the phosphate ore to its useful form follows a rather lengthy preparation and separation process, but can be summarized in the following manner :



Phosphoric acid is precipitated as Na₃PO₄, and the gypsiferous solution of fluorosilicic acid, radionuclides, clay, excess sand and water, and other trace elements are removed from the reaction vessels. The resulting waste products are transported to tailings piles after excess water and sand are removed (for reuse). Once the process water has been pumped to the storage ponds, particles settle and the solution evaporates.

Process Water Infiltration

Fluid samples collected from monitoring wells drilled into gypsum tailings piles have a high ionic strength and low pH ranging from 1.4 - 2.5 (Burnett and Hull, 1996). The solutions contain appreciable amounts of HF, SiF₆, and sulfuric acid, with specific activities of up to 18 Bq/L for ²³⁸U and ²³⁴U (greater than three times the activity found

in phosphate ores) and 0.08 - 0.30 Bq L⁻¹ for ²²⁶Ra. Dissolved ²²²Rn is typically 400 - 1,200 Bq L⁻¹, while ²¹⁰Po activities are much lower at about 5 Bq L⁻¹. The activity of dissolved ²¹⁰Pb can be as high as 65 Bq L⁻¹. Burnett and Hull (1996) suggested that ²¹⁰Pb is the most mobile radionuclide in the stack.

A number of studies which address leaching of radiochemicals and other species from phosphogypsum or various aspects of groundwater interactions near phosphate ore bodies, phosphogypsum stacks, and gypsum ponds in Florida have been published (May and Sweeney, 1982, 1983; Miller and Sutcliffe, 1982, 1984; PEI Associates, Inc., 1986; Oural and Brooker, 1986; Oural *et al.*, 1988a, 1988b; Berish, 1990; Burnett, 1988; Kennedy *et al.*, 1991; Upchurch *et al.*, 1991; Carter and Schneider, 1992; Carter *et al.*, 1993a, 1993b; Burnett *et al.*, 1995; Hull *et al.*, 1995; Hull and Burnett, 1996). However, with the exceptions of Miller and Sutcliffe (1982, 1984), Upchurch *et al.* (1991), Burnett *et al.* (1995), Hull *et al.* (1995), and Hull and Burnett (1996), compositional and radiochemical data are not provided for the same samples. Detailed compositional and radiochemical analyses of solutions actually circulating within Florida phosphogypsum stacks are critical to understanding the actual processes of chemical mobility. Conclusive findings presented in this chapter are the results of efforts made at Florida State University (Burnett), and are taken from material presented in literature as well as from a project conducted in parallel with the hydrologic investigation presented here.

Solubility of ions in stack solutions, as well as the groundwater beneath it, is highly dependent upon solution pH. Thermodynamic data show most compounds to precipitate

at higher pH's (>3); however, free energies of some important species (such as Ra-Ba-Sr complexes) are still unknown (Rutherford, 1996). The most mobile of potentially hazardous species are those radioactive compounds with high solubility and low sorptive properties. Presently available literature values for radionuclides of concern do not provide evidence for such a combination of these properties (Burnett and Hull, 1996).

Analysis of the Piney Point waters has included radiochemistries of stack and surficial waters in an attempt to characterize the internal environment of the structure. Analysis as a function of depth within the stack was intended to illustrate pathways of mobile particles as well as to identify critical nuclides of interest.

Concentrations in the surficial aquifer (Burnett, 1997) are similar to those of waters reported by Upchurch (1991), who investigated radionuclide impact from the phosphatic clay unit. Of particular significance in basic chemistry of the non-potable water are high levels of aluminum (71.5 ppb) and iron (5.4 ppm), as well as high TDS readings (496 ppm). Although this water is certainly above EPA standards for human consumption, primary use is for agricultural purposes.

Results of the radiochemical analyses from Piney Point will be used in a comparison with background levels determined by Upchurch (1991) through utilization of concentrations found for the stack waters with hydrologic flux from this project's analysis. Upchurch (1991) concluded that elevated radionuclide concentrations were of concern (above EPA standards) only in highly fractured areas. Thus, the radioactivity of process water from the phosphogypsum stacks will be compared to ambient levels of water in the surficial aquifer as well as with federal regulation standards.

Radiochemistry

Uranium

The uranium ion is most commonly found as a uranous (U^{+4}) or uranyl (UO_2^{+2}) ion, or as their hydroxyl or carbonyl complexes. Chemical relationships of both species are complex; however, the uranyl ion is the only one of concern in the oxidizing stack waters. Although UO_2^{+2} is highly soluble, it can also be strongly sorbed and coprecipitated with certain minerals (in this case, gypsum). Thus, because of conditions in stack waters, uranyl will be fairly immobile.

Although elevated activities of the uranyl ion are present within the stack, concentrations of the ion in the surficial aquifer of the Piney Point site were low (<3 Bq/L). The low concentration in the surficial aquifer is most likely because of limited transport through the gypsum stack, owing primarily to the sorptive quality of the ion. Thus, only the daughter products pose a threat to the surficial aquifer.

Radium

Although radium has 16 different isotopes, only two are important in Floridan waters (^{226}Ra & ^{228}Ra). ^{226}Ra is the principal isotope of interest, as it is in the ^{238}U decay chain. Radium will exist in solution as Ra^{+2} and as $RaSO_4^0$ complex. Radium is brought into solution through ion exchange, leaching, and alpha recoil; however, sorption is thought to control the concentration of the ion in solution. Additionally, higher ionic strength solutions can release the ion from sorbed sites (Upchurch, 1991).

²²⁶Ra concentration in solution at the Piney Point site is shown to be generally less than 0.12 Bq/L. Within the interior of the stack, this is expected due to the presence of gypsum, but findings in the surficial aquifer for the most part suggest little influence of the ion from waters interacting with the confining Bone Valley Formation. The highest activity of ²²⁶Ra was found in the surficial aquifer at monitoring well 3 (0.56 Bq/L). The fact that this value is greater than activities in the stack (Burnett and Hull, 1996) suggests that the source of the radium was not the stack, but possibly from high concentrations of pelletal phosphate below the surficial aquifer.

Radon

The chemistry of radon has been of relatively great interest in recent years, because radon is hazardous to human health. Although radon's impact on human health is important, research concerning aqueous mobility of the ion is mostly related to its capability to redistribute itself, and provide a source of its decay products, ²¹⁰Pb and ²¹⁰Po. The short half life ($t_{1/2} = 3.8$ days) limits its migration to approximately 5 m, depending on grain size and direction/magnitude of flow. Diffusion is negligible.

Radon is found to be one of the three most important radionuclides in the surficial aquifer at Piney Point (the other two being its daughter products). Activity levels for radon increase with depth in the stack (Burnett and Hull, 1996), as a function of flow patterns. The high concentration of radon at the base of the stack is of primary interest as a source mechanism for ²¹⁰Pb and ²¹⁰Po, because of radon's short half life. Levels in the surficial aquifer were found to be elevated in well USGS 9 and monitoring well 2, two

wells located south of the stack, approximately 10 m from confining ditches. Whether the high concentrations are the result of input from the stack may be determined from flow patterns in the stack and surficial aquifer (see Chapters 5 & 6).

^{210}Pb

The most common lead minerals found in natural environments are cerussite (PbCO_3), anglesite (PbSO_4), and galena (PbS). Although the concentrations of these minerals are limited by their solubilities in natural waters, the ability of the lead ion to adsorb onto colloids, clays and organics results in lower concentrations of the element in stack and surficial waters. The presence of lead is thus generally believed to control the quantity of its granddaughter, Polonium-210.

The presence of ^{210}Pb at the Piney Point complex is of the highest concern in the stack waters. Typical activities of lead in samples are between 6.7 - 67.0 Bq/L, which makes lead the largest contributor to radioactive flux next to radon levels. Increasing levels of the element with depth indicate that leaching does occur, although elevated concentrations in the surficial aquifer are limited to the same wells for which radon was found in larger quantities (USGS 9 and monitoring well 2).

Polonium 210

^{210}Po is the last member of the uranium series decay chain of importance as an environmental hazard. Concentrations of this species are believed to be primarily controlled by sorptive properties of the ion (Upchurch, 1991) although specific behavior of

the element is debatable, owing to the disparity of research in natural systems. The ion concentrations are also pH sensitive. Formation of radiocolloids at lower pH's is particularly important.

Concentration of dissolved polonium in samples taken from Piney Point waters has been shown to closely correlate with those of radon and lead, which are the element's parent source. High concentrations of both ^{210}Po and ^{210}Pb in the stack and in the two wells to the south of the stack indicates that occurrence is directly correlated with its source material. Movement of this ion in the surficial aquifer as of yet is restricted to the known transport within acidic environments.

Discussion

Migration of any environmentally hazardous radionuclides will be closely linked to radioactive decay and the pathways of transport associated with the group of ions in question. Conditions in groundwaters that control the mobility of particular ions are particularly important. Although the geochemical behavior of these elements is very complex, the most important factor for all of them is their tendency to sorb onto solid particles. This limits their mobility. In addition, dilution of stack waters in the surficial aquifer also contributes to lower radioactivities. Determination of the actual environment on a smaller scale will provide clues to the actual processes that control ions in solution. In summary, except for wells USGS 9 and MW 2, the migration of radionuclides is promptly and effectively retarded by ion adsorption onto clays.

Additional X-ray diffraction analysis of clays in the area may provide information on the presence of radionuclides in the surficial aquifer. For one, the analyses may show preferential dissolution of material in the surficial aquifer by fluoride in stack solutions (Arocena et al., 1995). If such interactions were to occur, propagation of the dissolution trail would be seen in the direction of regional flow. Secondly, high sorptive properties of smectites would attenuate the ions.

Preliminary investigation of a drill core from MW 11 showed small quantities of montmorillonite, which is a smectite. Conceivably this clay could adsorb radionuclides migrating from the stack, thereby limiting the presence of contamination to the area immediately surrounding the stack. Systematic analysis of samples from cores around the stack is necessary to determine the validity of this hypothesis.

CHAPTER 4

METHODS OF DATA ANALYSIS

Compilation of the data and computation for the analyses were conducted in spreadsheet format using Microsoft Excel. Representation of these data as graphs, in addition to a regression for the topographical analysis were done in Axum 5.0. Modification of some figures was accomplished through use of Microsoft Paint, and Hijaak Pro.

Phosphogypsum Stack

Identification of hydrologic flow within the phosphogypsum pile itself was carried out through a series of investigations centered around quantifying the hydrologic parameters of the stack material and identifying vertical gradients between stratigraphic layers. Ten partially screened wells and one fully screened well were drilled into the oldest portion of the stack. The wells were set at various depths (Table 2) in two clusters of four wells and one cluster of three. Cluster one in the west wall and cluster two in the south wall had four wells, while cluster three in the center dividing wall had only three wells (Figure 4). The gypsum-aquifer interface (base of the stack) is at a depth of 20.8 m from the surface, so there is only one well which taps the surficial aquifer through the gypsum stack.



Figure 4. Locations of Monitoring Wells.
Piney Point Phosphates, Inc. Palmetto, Florida

Table 2. Depths of Sampling Wells Drilled into the Stack

Cluster # - Well #	Total Well Depth (in m. from top of riser)	Cased Section (m. depth)	Screened Section (m. depth)
1 - 1	18.0	0 - 14.8	14.8 - 18
1 - 2	14.8	0 - 12.5	12.5 - 14.8
1 - 3	12.5	0 - 9.5	9.5 - 12.5
1 - 4	9.5	0 - 6.6	6.6 - 9.5
2 - 0	23.6	0 - 22.0	22.0 - 23.6
2 - 1	18.0	0 - 14.8	14.8 - 18.0
2 - 2	14.8	0 - 12.5	12.5 - 14.8
2 - 3	11.5	0 - 8.2	8.2 - 11.5
3 - 1	18.0	none	0 - 18.0
3 - 2	14.8	0 - 12.5	12.5 - 14.8
3 - 3	11.5	0 - 8.2	8.2 - 11.5

All wells were constructed with a 10 cm. diameter PVC pipe. Screens for most of the wells were packed in 20-30 mesh sand with approximately 50 cm (except for well 2-0 which was 2m thick) of a bentonite plug overlying the sand pack. The cased sections of the wells were grouted to the surface with a bentonite-cement mixed grout compound. For the fully screened well (3-0), grout-plugs were set at intervals of 1.5 m in order to reduce cross-stratificational flow outside the well and increase accuracy in the borehole flowmeter tests.

Quantification of hydrologic parameters within the stack was determined by one of the most commonly used non-equilibrium pump tests, the Cooper-Jacob (straight-line) method. This method was used over the more popular Theis-curve match for its asymptotic approximation of the well function within a small radius and over longer times.

Additionally, it was considered important to rule out the bias of values representative of the region directly surrounding the well. A Grundfos 1.2-amp machine was used to pump water out of the well at an approximate rate of 6 L/min., and head measurements were taken with an electrical head level indicator.

Hydraulic gradients within the stack were determined by using a pressure transducer, an electromagnetic borehole flowmeter (Molz et al., 1994) , and a comparison of hydraulic head values. Owing to the significance of hydrologic gradients in the understanding of flow within the stack, the use of multiple methods to determine such information should lead to the increased reliability of the results.

In situ vertical head measurements were made using a set of inflatable packers from the Tennessee Valley Authority and a 20 psi pressure transducer from Telog Instruments, INC. Inflation of the packers above and below the pressure transducer allowed a section of the well to be isolated, and a reading to be taken. Measurements of the *in situ* pressure were taken at all screened intervals available, along with 3 - 5 readings from cased intervals (to provide a standard hydrostatic gradient upon which to compare the screened readings). Variations of anomalous readings in the screened sections were correlated to the presence of a pressure perturbation (i.e., a flow gradient).

Borehole flowmeter tests were conducted by the Quantum Engineering Corporation (Tampa) using the deepest well of each stack cluster. Ambient flow, induced flow, and pump test measurements were conducted at all wells; however, a complete analysis was only done for well 1-1. Results for wells 2-1 and 3-1 were incomplete, owing to the onset of a thunderstorm the day that measurements were taken. Results from this

testing have provided data for ambient flow direction and magnitude, as well as stack response to induced flow conditions. Computation of these induced flow rates with the measurements for net flow can be utilized to calculate hydraulic conductivities.

Hydraulic head measurements for the monitoring wells on the stack were taken approximately every three months. Because wells in the same cluster were fairly close to each other, comparison of the head measurements between wells in the same cluster were used to indicate possible variations of vertical gradients. Organization of the data as a cross-sectional view provided information on internal stack-stratification.

Surficial Aquifer

Analysis of the hydrology of the surficial aquifer includes calculations of hydraulic conductivities and transmissivities, a contour analysis of monitoring well head levels, and a determination of the regional flow trend. For this study the primary interest in the surficial aquifer was to quantify horizontal flow rates as well as to establish the direction of flow, so that the hydraulic impact of the phosphogypsum stack on the surficial aquifer could be determined.

Hydraulic conductivity analyses were conducted by two different analytical methods, allowing for respective well geometries that were available. USGS well #9 (Figure 4) was treated as an auger hole, while all other research wells were drilled to be partially screened for their lowest 3 meters.

The hydraulic conductivity for the auger hole was calculated according to a method prescribed by Boast and Kirkham (1971). The well was pumped out by a Grunfos

machine, and the water table allowed to recover over the next hour. Measurements of the rebounding head elevation were taken with an electrical head level indicator, and entered in a spreadsheet file.

The analysis for the partially penetrating monitor wells was conducted on monitor wells 1 and 8, and research wells 11, 18, 21, 22, and 24, using a method described in Bouwer and Rice (1976). A volume of approximately 200 liters was pumped out of each well using a Grunfos machine, and then the well was allowed to recharge. As the hydraulic head rebounded, elevation measurements were taken at logarithmic intervals and inserted into a spreadsheet file.

Contours of the water table for the site were compiled every three months using hydraulic head elevations taken from the following wells : monitor wells 1 - 5, 8-11; research wells 8 - 24; U.S.G.S. wells 8, 9, 34, 36, 37, 39; and stack well 2 - 0. Data files were entered into the Surfer program, and contours were generated using the Kriging method. The significance of the head measurement at well 2-0 (which wasn't drilled until March 1996) demanded that only contours for months that include this measurement are presented.

The standard assumption for regional flow of the unconfined aquifer to be partially controlled by the topographic slope of the land surface was used to determine direction and gradient of the surficial aquifer. A lack of monitor wells further away from the phosphogypsum stack restricted a more precise determination of the groundwater flow gradient. A three-dimensional regression of the drainage basin was made using an equidistant-node grid of elevations, which led to a first-order representation of the ambient

regional flow. The calculation of the regression plane was determined in the graphing program using a collection of data points taken from topographical maps of the area (figure 2). Transects for the data point collection were made using a one unit interval (representing 200 m.) of plotted data from an AutoCAD drawing.

Precipitation records of the area were measured daily at stations on site, and at the U.S.G.S. stations in Ruskin (10 miles to the north), and Bradenton (5 miles to the south). These sets of data were compared in hydrograph format to monitoring well heads and stack pond levels, so as to qualify existence of a possible recharge pathway. In addition, the hydrographs were analyzed for temporal and spatial relevance.

CHAPTER 5

CHARACTERIZATION OF THE HYDROLOGICAL ENVIRONMENT

This chapter presents the results of efforts to characterize the gypsum stack and underlying surficial aquifer, as well as an analysis of regional precipitation data. These characterizations are necessary for parameter adjustments of the groundwater model presented in the following chapter. Additional data are presented in Appendices A, B, C, and D.

Stack Analysis

Analysis of Hydraulic Heads

Hydraulic head measurements for all three well clusters demonstrate a downward flow in all instances. Specific gradients between stratigraphic layers of the gypsum stack can be made for each of the well regions, as well as a determination of the flow gradient to the surficial aquifer. Patterns of relative head do not change over time, but can be correlated to the precipitation record.

Well cluster 1 (Figure 5) typifies the standard pattern for gradualized downward flow in the stack. The occurrence of a slight plateau between wells 1-2 and 1-3 points to a region of slower flow when compared to neighboring head gradients to wells 1-1 and 1-4.

Well cluster 3 (Figure 6) depicts a flow gradient toward the screening depth of well 3-2. This is conceptually consistent with the results from well cluster 1, because

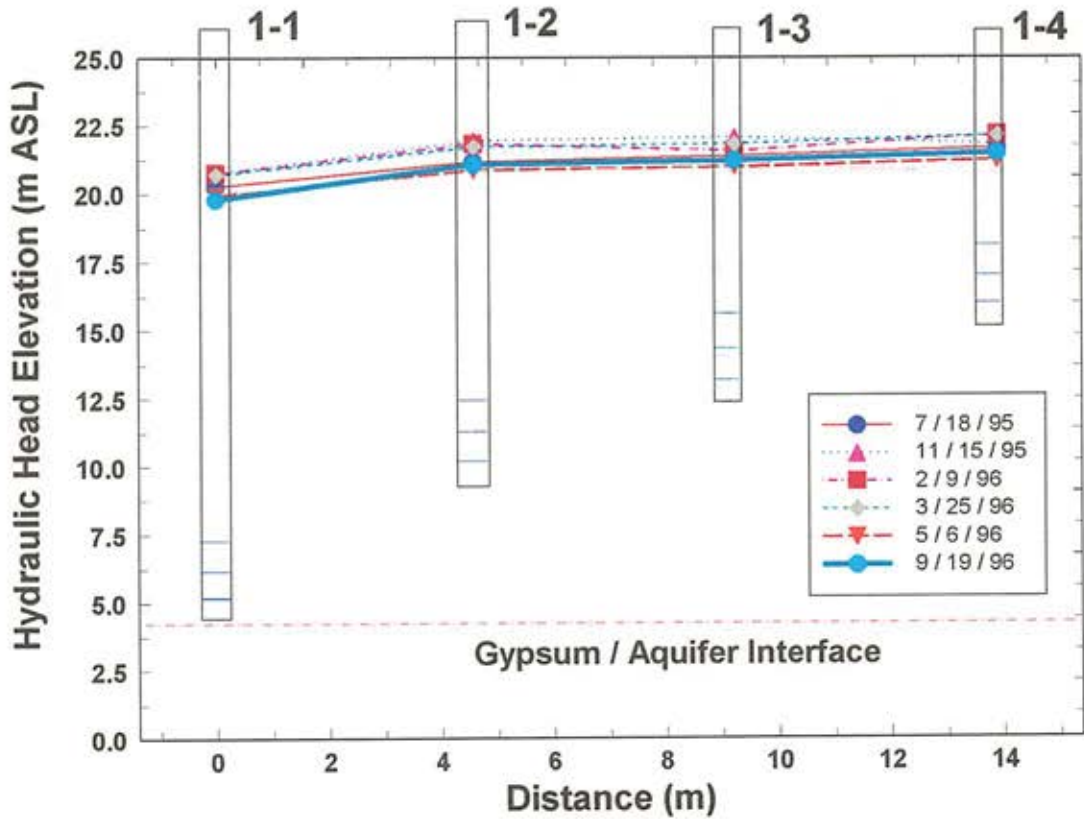


Figure 5. Hydraulic Head Comparison for Well Cluster 1. Well cluster one is located on the west flank of the old stack. Symbols and lines represent observed hydraulic head elevations for each well on a specific date. Horizontal lines within each well indicate the screened portion of that well. A general downward gradient is found in consecutively deeper wells.

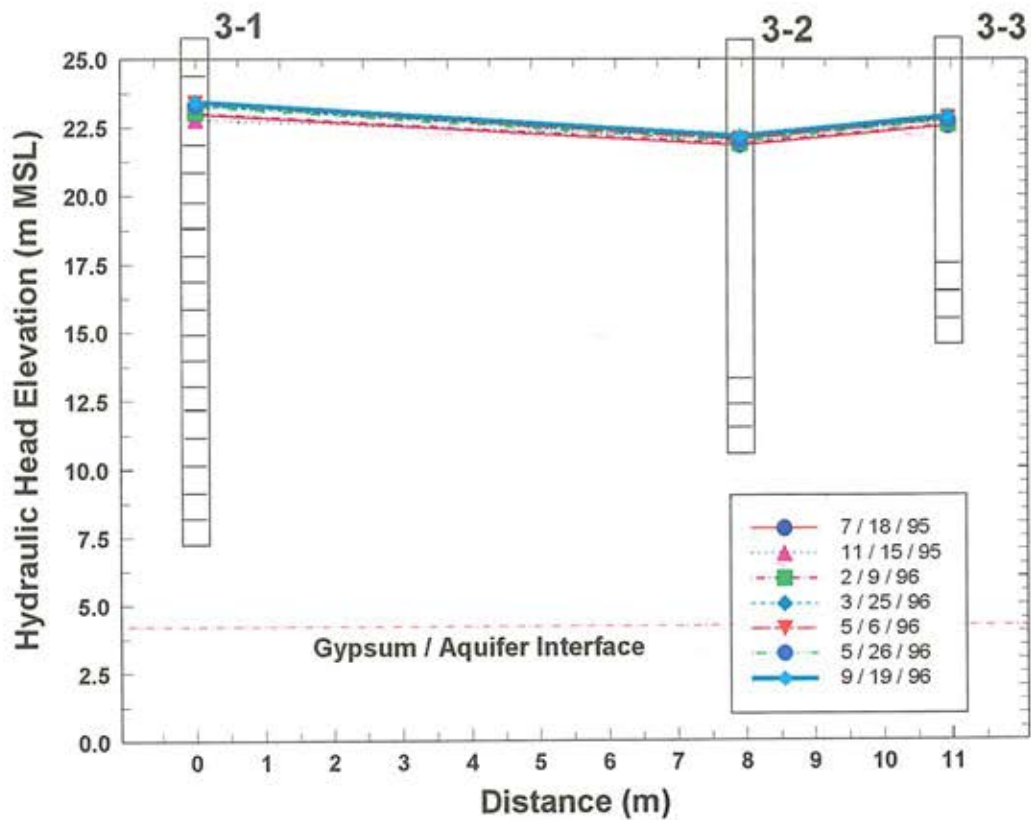


Figure 6. Hydraulic Head Comparison for Well Cluster 3. Well cluster three is located on the center dividing wall of the old stack. Symbols and lines represent observed hydraulic head elevations for each well on a specific date. Horizontal lines within each well indicate the screened portion of that well. A downward gradient is found toward well 3-2, which represents a head level for the deepest section of screening in the gypsum stack.

although well 3-1 is the deepest of the three wells, it is fully screened. Thus, head measurements are responding according to their highest screened elevations and force downward flow gradients toward the well containing the deepest representation of the stack.

Well cluster 2 (figure 7) is of particular significance because it contains the only well (2-0), which is drilled into the surficial aquifer. Gradients between all wells are still downward, which also includes into the surficial aquifer. The presence of a gradient toward well 2-0 provides one of the most critical factors needed for a distinction of flow into the surficial aquifer. However, the relative magnitude of the actual gradient suggests a nonlinear flow into the surficial aquifer, indicating that additional factors may be involved. A comparison to surficial aquifer head levels, as well as quantitative modeling of flow rates, will provide a clearer picture of the factors controlling the hydrologic environment.

Cooper-Jacob Straight-line Method

Transmissivity and storativity values were determined through a modification of the Cooper-Jacob equation. This formulation represents an asymptotic solution of the Theis equation for large time intervals, and describes the radially symmetric, non-equilibrium head-drawdown ($s(r,t)$) in a confined aquifer. Thus, the Cooper-Jacob equation is a function of the radius to time under the influence of pumping (Driscoll, 1986):

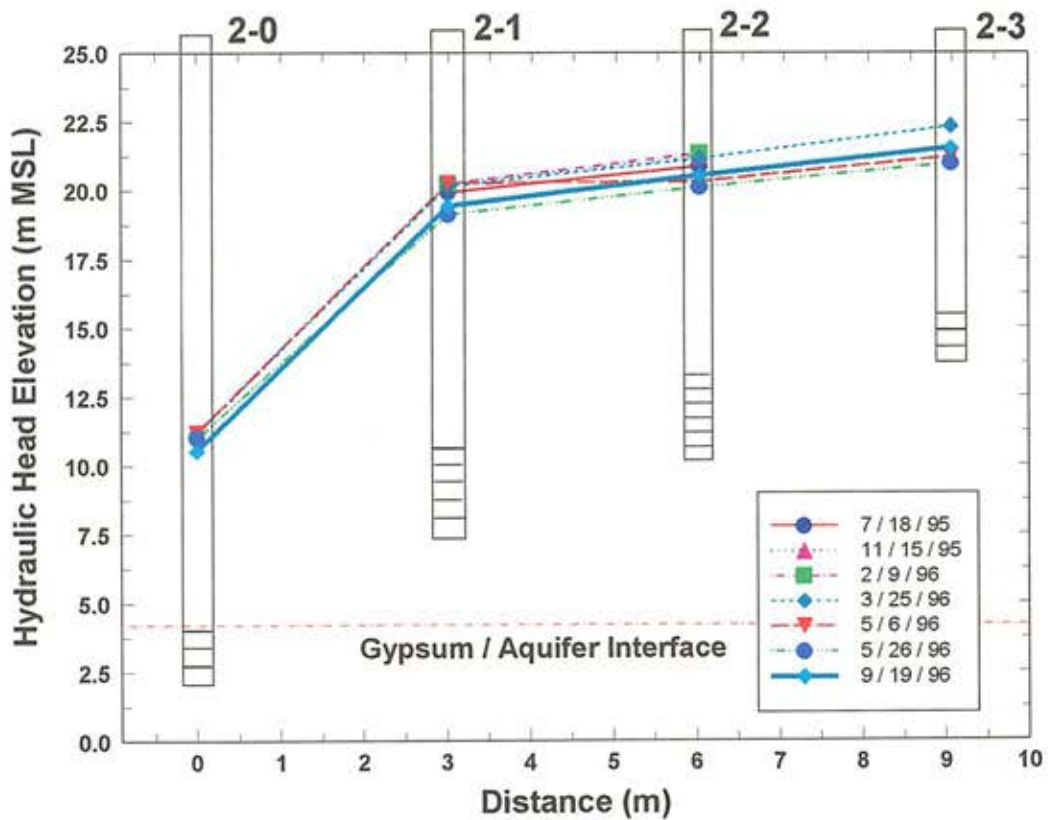


Figure 7. Hydraulic Head Comparison for Well Cluster 2. Well cluster two is located on the south flank of the old stack. Symbols and lines represent observed hydraulic head elevations for each well on a specific date. Horizontal lines within each well indicate the screened portion of that well. A downward gradient is found into the surficial aquifer represented by well 2-0.

$$s(r, t) = \frac{Q}{4\pi T} \cdot (-0.57772 - \ln u) \quad (4.1a)$$

By substituting for the expression $u = \frac{r^2 S}{4Tt}$, and converting to log base-10 format one gets the following equation:

$$s(r, t) = \frac{2.3Q}{4\pi T} \cdot \text{Log}\left(2.25 \frac{Tt}{r^2 S}\right) \quad (4.1b)$$

By obtaining the drawdown $s(r, t)$ observed in one log unit (Figures 8 and 9), and a known value for the pumping rate Q , a value for the transmissivity can be calculated.

Storativity is determined from the time intercept (t_0), and corresponds to a zero drawdown (setting the log-term equal to one). The time intercept is depicted graphically as the intercept of the straight line tangent to the drawdown curve with the horizontal axis. Values for storativity cannot be determined for the wells that were pumped, since there is a singularity in the solution for $r = 0$.

Table 3. Transmissivity and Storativity Values for Stack Wells

Well Designation	Transmissivity (m ² /day)	Storativity
1 - 1	-	0.00009143
1 - 2	6.883	-
1 - 3	-	0.00001568
1 - 4	-	0.00008784
2 - 1	-	0.00006698
2 - 2	0.846	-
3 - 1	0.445	-
3 - 2	-	0.00001706
3 - 3	-	0.000008922

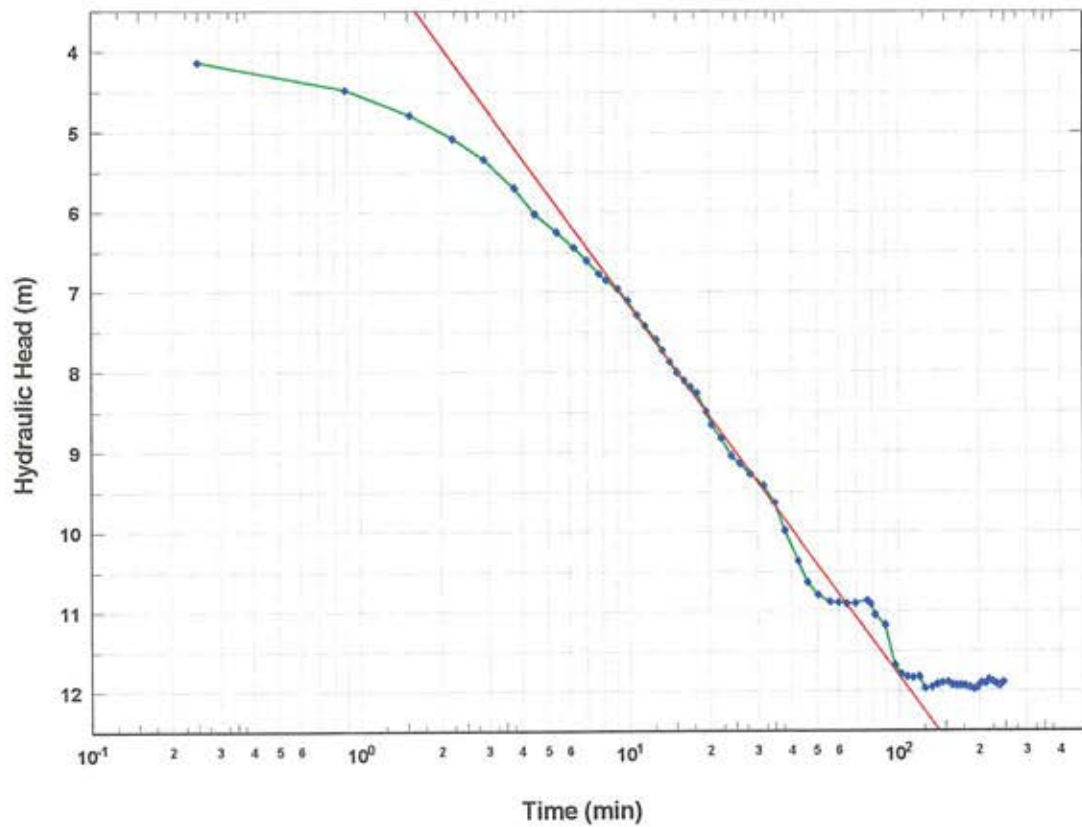


Figure 8. Pump Drawdown vs Time in Stack Well 2-1. Water level is compared to a log plot of time during a pumping test. Of particular note is the recharge that occurs in the data between 50 and 80 minutes of pumping.

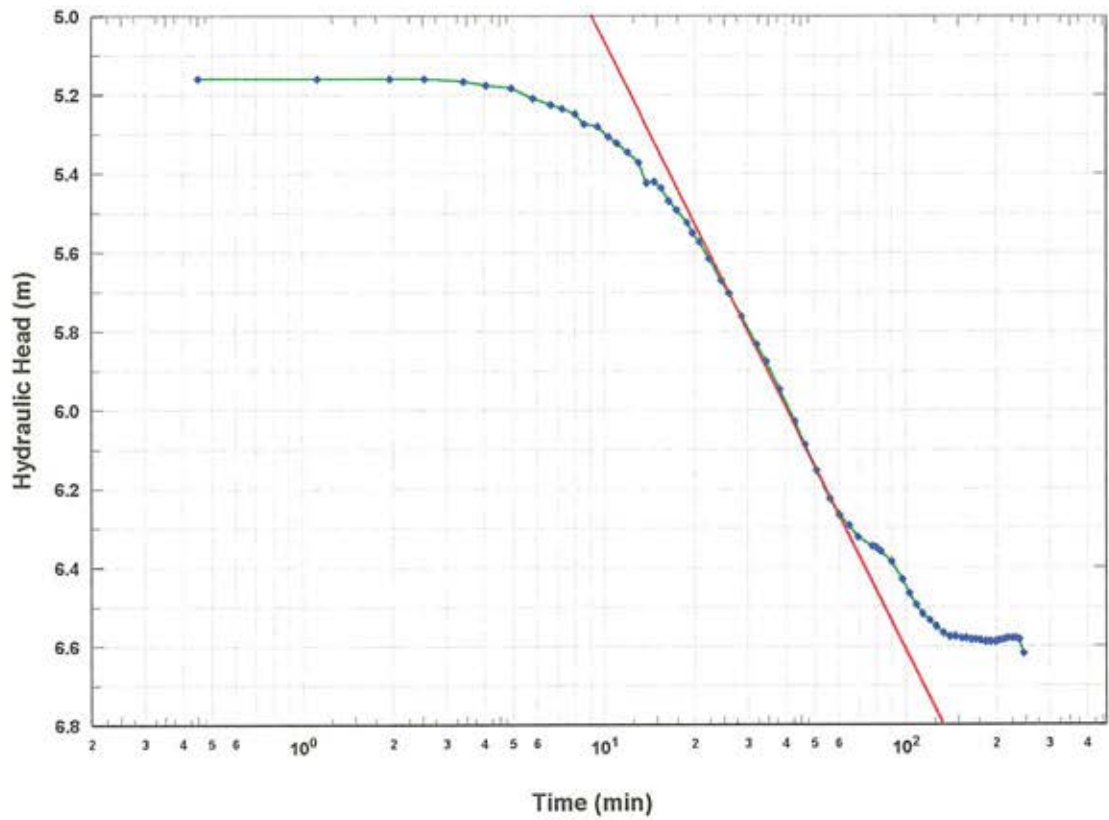


Figure 9. Pump Drawdown vs Time in Stack Well 2-2. Water level is compared to a log plot of time during a pumping test. Of particular note is the recharge that occurs in the data between 65 and 90 minutes of pumping.

Even though transmissivity values for only three of the stack wells were obtained (Table 3), the wide range of values indicates variation in transmissivity throughout the stack. This variation may be caused through modification of the stack structure during structural maintenance, whereby gypsum material from the pond is dug out to strengthen the confining walls. The transmissivity value for well 3-1 is the best representation of conductivity for the stack as an entire unit (owing to the well's representative screened length), while the values for wells 1-2 and 2-2 are more indicative of particular horizons within the stack.

Storativity values are well constrained, with all values falling within one log unit. An average of 4.8×10^{-3} denotes a value comparable to that of natural gypsum, indicating that the waste material maintains storage properties similar to that of its chemically related compound.

Although drawdown curves for most of the analyses are typical of a normal aquifer response, wells 2-1 (Figure 8) and 2-2 (Figure 9) demonstrate a plateau in their data close to the equilibrium stage of pumping. This occurrence has been classified as an influence of recharge, resulting from the proximity to the stack pond. Additionally, the delay observed between the wells is attributed to a source of the recharge being closer to the pump source. The plateau at well 2-2 is also less dramatic because this well is on the perimeter of the drawdown influence.

Pressure Transducer Tests

Investigation with the pressure transducer was intended to provide an identification of horizontal flow within the stack. Complete analysis of the pressure at every depth in all three cluster areas was not possible because of the limited range provided in the screening intervals. Regardless of this restriction, anomalous horizontal flow was identified in three of the wells. Wells 1-3 (Figure 10) and 3-1 (Figure 11) illustrate sections of decreased ambient pressure, while well 3-2 (Figure 12) demonstrates a single section of increased pressure. All other wells showed no deviation from the hydrostatic reference pressure, as computed from the density of the gypsum stack-water solution, indicating no significant vertical variations in the pressure and hydraulic heads at those depths. This means that either there is not a detectable amount of vertical pressure head at that depth, or that the pressure transducer is just not sensitive enough to pick it up.

The low pressure zone found at well 1-3 (on the west wall) indicates the presence of a vertical flow gradient at a depth of approximately 10 m below the surface (Figure 10). Analysis of the same interval in well 2-1 on the south wall does not indicate any flow different from the expected hydrostatic reference. Thus, no support for a conclusive statement on the stack edges can be made, but the possibility for flow still exists.

Measurements made at well 3-1 were conducted in a different manner, owing to the fully screened nature of the well (Figure 11). Comparison to unpacked pressure readings instead of a hydrostatic line allowed a broader interpretation of the readings; however, two areas of pressure anomalies are still apparent. Lower pressures found in the

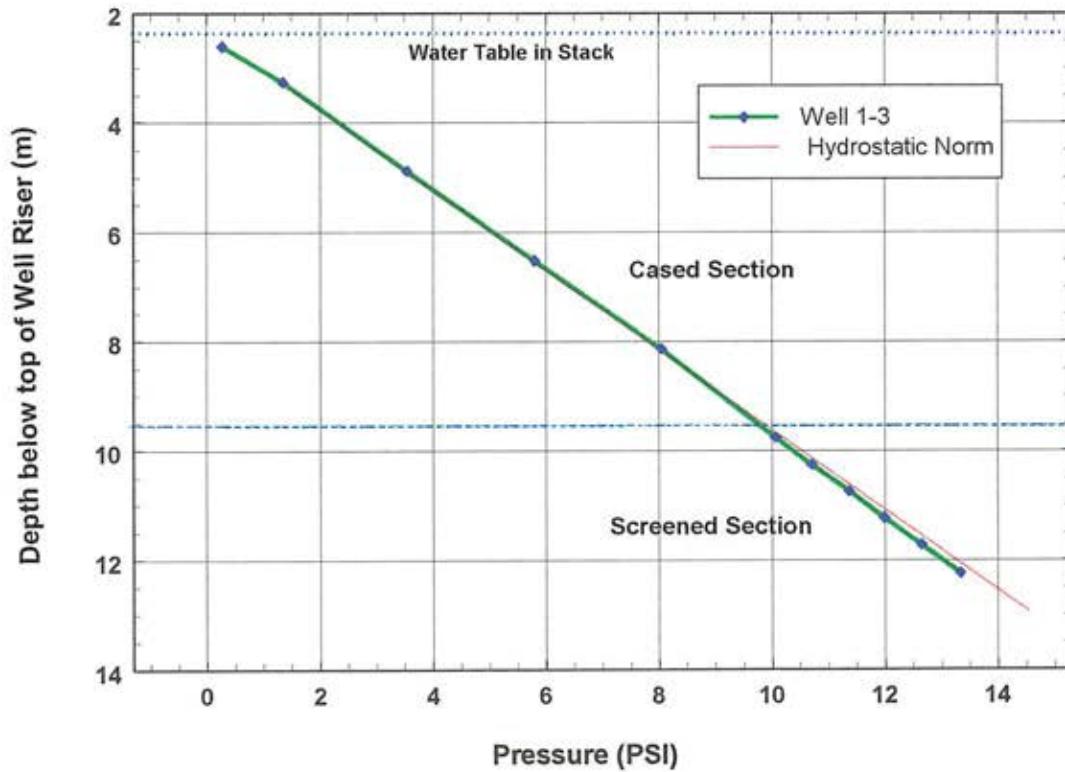


Figure 10. Pressure Transducer Measurements for Well 1-3. Points on the graph represent measurements of pressure at particular depths below the water table. Deviation of readings in the screened section (9.5 - 12.5 m.) below the hydrostatic norm show a regional decrease in ambient pressure.

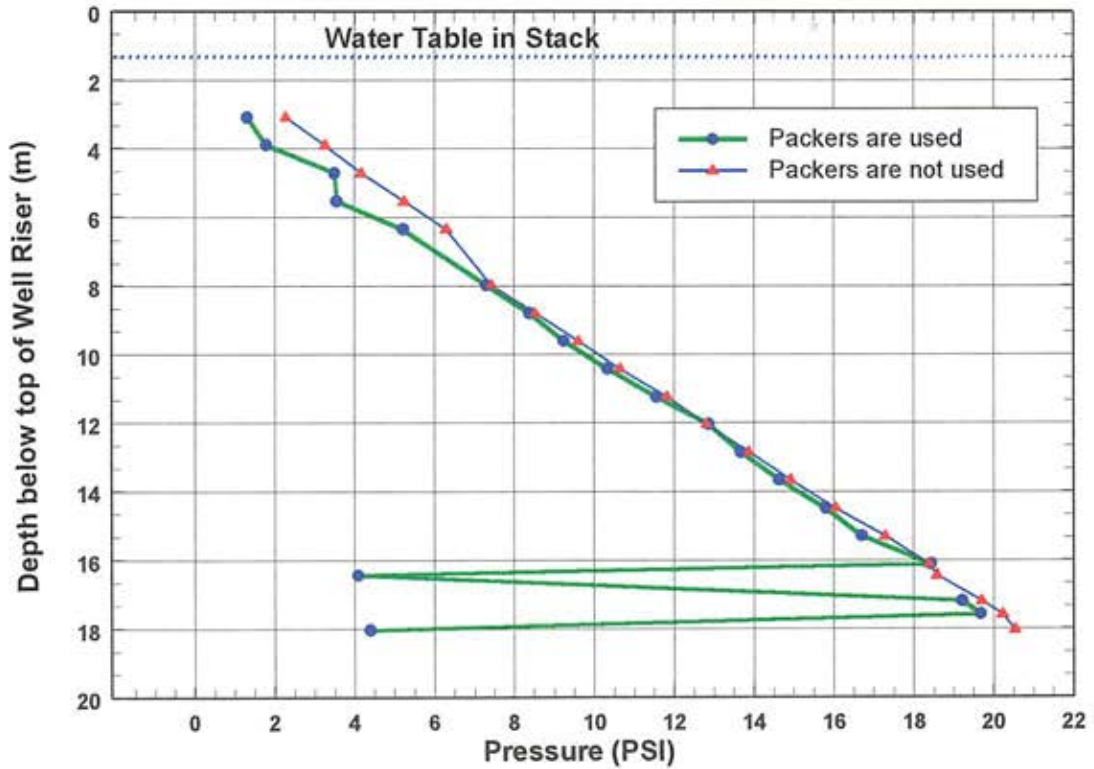


Figure 11. Pressure Transducer Measurements for Well 3-1. Points on the graph represent measurements of pressure at particular depths below the water table. Blue circles are representative of isolated depth readings, while red triangles represent ambient (non-isolated) readings. Deviation of readings in two sections below the hydrostatic norm (no packers used) show a regional decrease in ambient pressure.

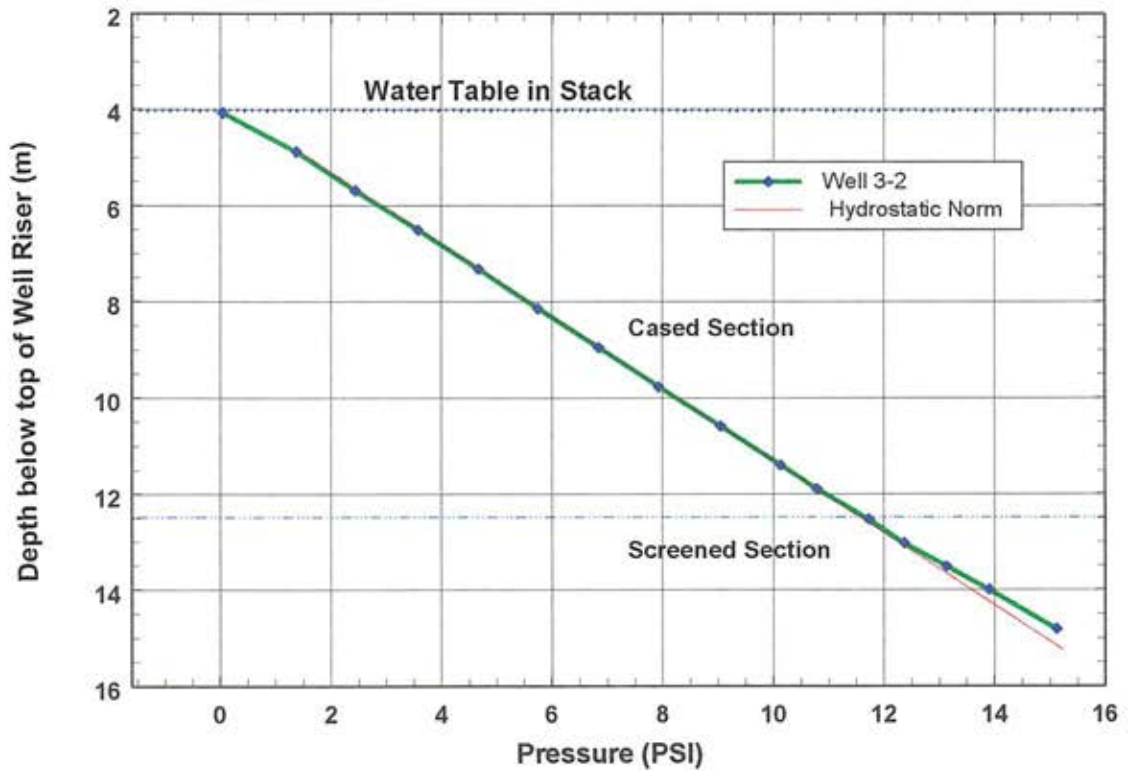


Figure 12. Pressure Transducer Measurements for Well 3-2. Points on the graph represent measurements of pressure at particular depths below the water table. Deviation of readings in the screened section (12.5 - 15.0 m.) above the hydrostatic norm show a regional increase in ambient pressure.

“packed” measurements from 2 - 8 m. most likely can be attributed to an influx of fluid from the nearby pond. Low pressure spikes found at depths of 16.5 and 18.0 m. are more of a mystery. This development is either evidence of poor field methods, or an indication of a flow conduit. The latter would suggest cracks or faulting at the intervals of the spikes, although the large contrast in pressure would suggest that this explanation is unlikely. Therefore, the spikes are interpreted as evidence of poor grouting of the well hole, whereby flow can seep vertically between the outer side of the borehole casing and the back-fill formation..

The high pressure zone of well 3-2, at an approximate depth of 13 - 15 m (Figure 12) is quite important since it is located in the center of the stack between the north and south ponds. This reading is an indication of an increase in overburden pressure and is evidence for the conceptualized flow of a typical groundwater mounding model. Because this anomaly is located close to the low pressure found in well 3-1, the measurements do not support a regional characterization of downward flow. Thus, conflicting evidence from both wells indicates heterogeneity of the gypsum stack at depth. However, because well cluster 3 is located essentially on an old pond construction road, there is also the possibility that some observed anomalies do not reflect influence of the phosphogypsum stack alone, but may also include the influence of the compacted back-fill material of the road.

Borehole Flowmeter Tests

The Borehole Flowmeter Tests (Burnett et. al., 1985) yield three major sources of information:

- 1) Ambient flow in the well under natural conditions. The nature of the ambient flow and its direction, provide clues on anomalous fractures, fault zones, and vertical variations of hydraulic heads.
- 2) Flow rates for each vertical section under steady-state pumping conditions. Results for this test will yield the same clues as in 1), but under stressed conditions.
- 3) Using the results from 1) and 2), vertical variations of the net flow rate in each of the probed intervals can be used as a tool to define the hydraulic conductivity, which is directly proportional to the flow.

Ambient flow measurements for both well 1-1 (Figure 13) and well 3-1 (Figure 14) provide strong support for a natural, downward flow of fluid in the stack. This evidence enhances the theory for topographical mounding of stack waters on the surficial aquifer. Ambient differential readings of both wells further support this point for the entire stack, as readings do not fluctuate very much at depth. Absence of inconsistencies in the data indicate that there are no anomalous flow regimes under ambient conditions, and that flow in the stack is similar to flow in an unconfined unit.

A general decrease in ambient flow through most of the stack is noted for well 3-1. Although this trend is typical of unconfined units, it could also result from a perched water table above a relatively impermeable interface at the base of the stack. Ambient flow in

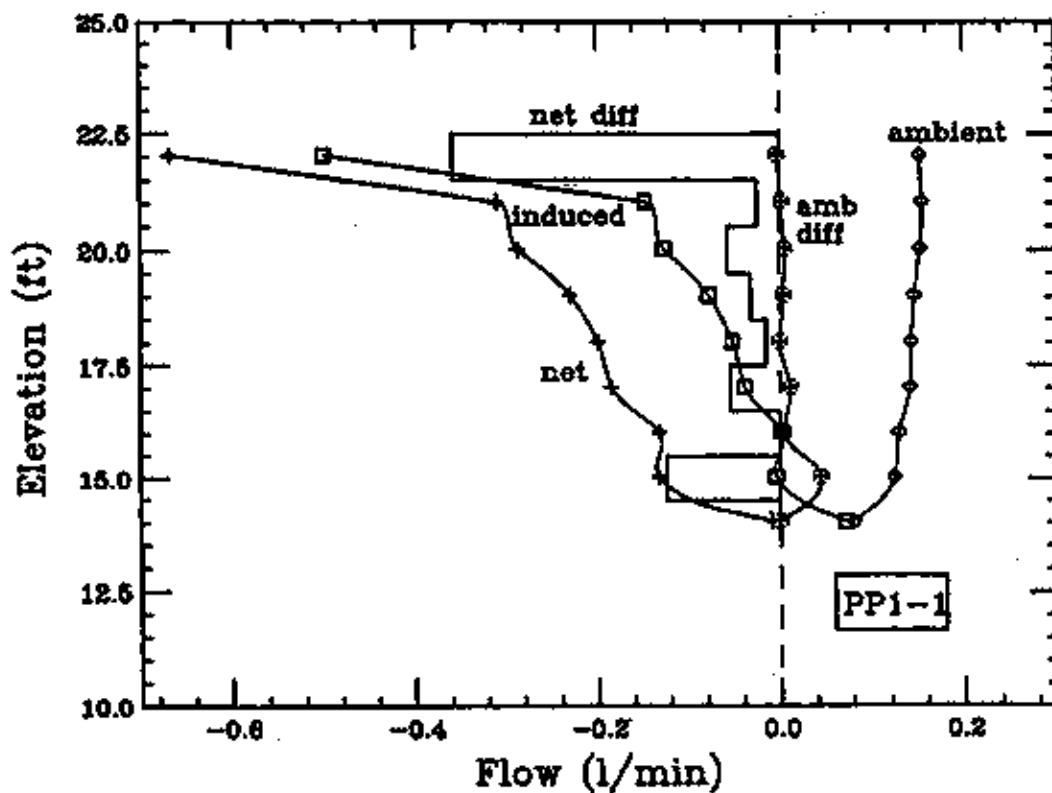


Figure 13. Borehole Flowmeter Results for Stack Well 1-1. Relationships of ambient and net flow are shown in comparison to relative depths as a flow magnitude. Induced flow measurements represent pumping conditions, whereas ambient differential and net differential readings indicate a relative change in the flow to adjacent values. Positive values denote downward flow and negative values upward flow.

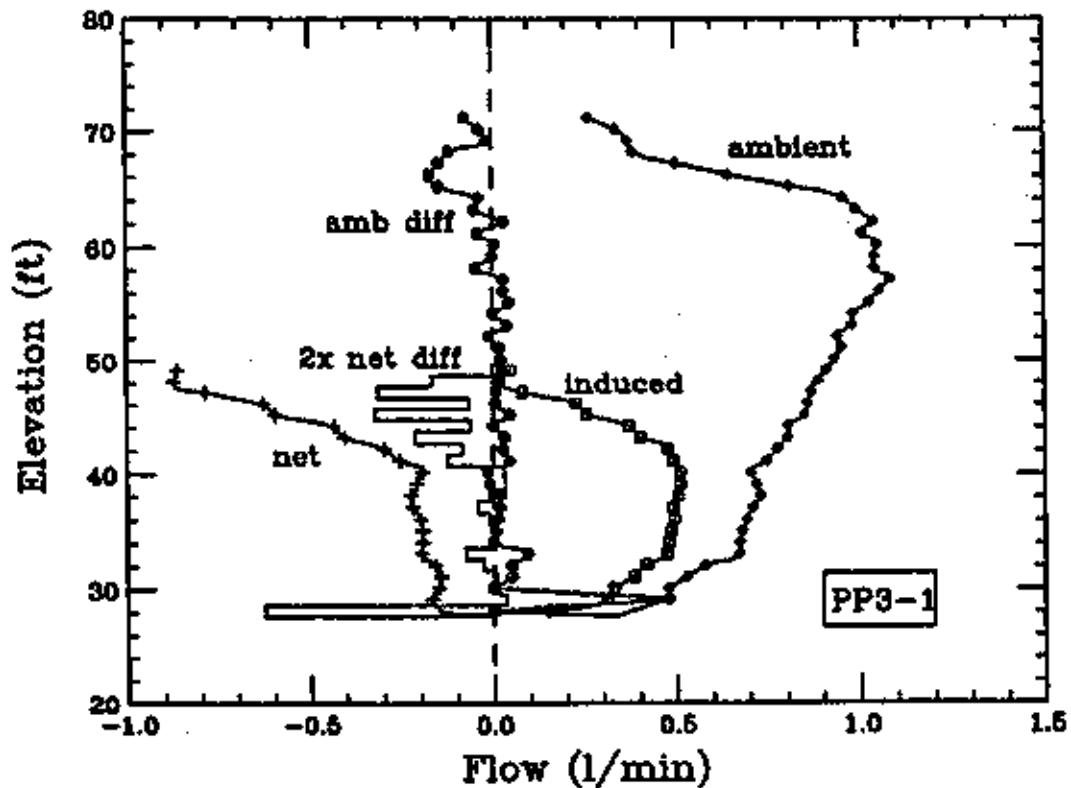


Figure 14. Borehole Flowmeter Results for Stack Well 3-1. Relationships of ambient and net flow are shown in comparison to relative depths as a flow magnitude. Induced flow measurements represent pumping conditions, whereas ambient differential and net differential readings indicate a relative change in the flow to adjacent values. Positive values denote downward flow and negative values upward flow.

well 1-1 ($\sim 0.14 \text{ min}^{-1}$) is much lower than the flow rates in well 3-1 ($\sim 0.2 - 1.1 \text{ min}^{-1}$), and provides evidence for low permeability at the stack base. Although this does not clarify actual permeability at the stack-surficial aquifer interface, an understanding of flow beneath the interface will determine whether this decrease is a product of an impermeable boundary, or the result of an unconfined situation.

Induced pumping of the wells was undertaken in an attempt to quantify possible stratification of the hydraulic conductivity within the stack. Such stratification was visible as horizontal bedding planes intersected by vertical cuts in the stack. Changes in the increase of net flow (or 2x net flow) between a section of well 3-1 ($\sim 28 \text{ ft.}$) and well 1-1 ($\sim 22 \text{ ft.}$) denote a region of increased hydraulic conductivity. This finding supports the theory for conceptualization of the stack as a layered hydraulic structure with varying conductivities at different layers. Although absolute values of conductivities for each layer could be calculated from a more precise analysis (Cooper-Jacob test) of the stack, this task has not been carried out since layered stack conductivities will not be required as an input parameter for the numerical model of flux to the surficial aquifer.

Surficial Aquifer

Regional Flow Trend

The regression plot of topographical data (Figure 15) taken from figure 3 denotes a flow gradient of 1.977×10^{-3} at an azimuthal direction of 303.19° . This gradient is at such a low angle that localized influence of the water table will be a large factor on the

$$z = 21.619485 + 0.001655*x - 0.001083*y$$

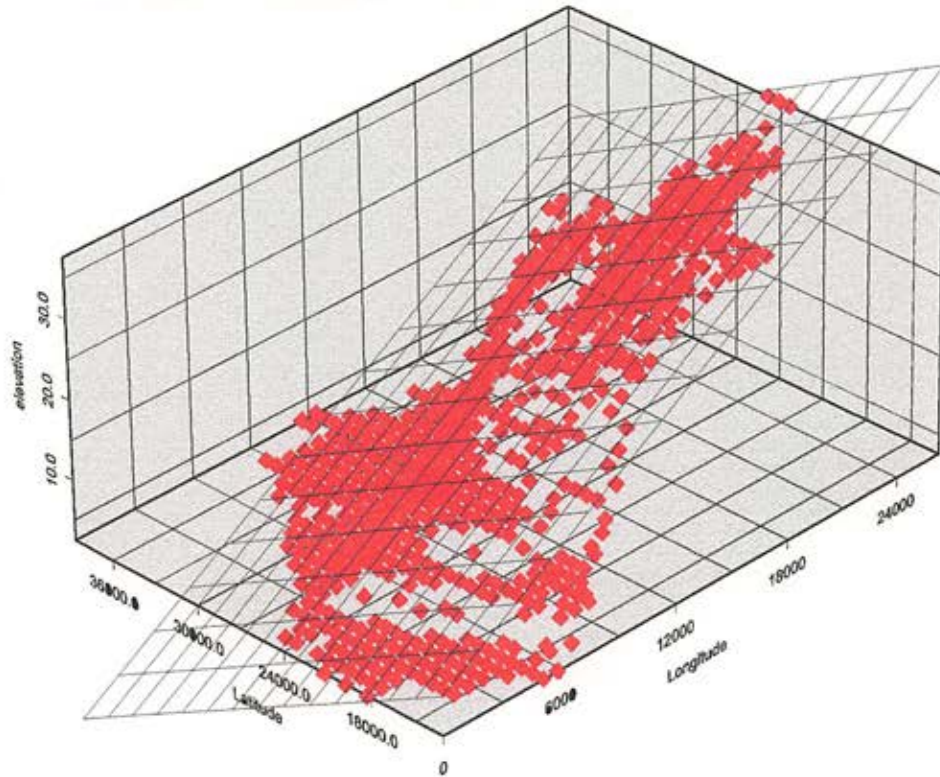


Figure 15. A 3-Dimensional Regression Plot of Topographic Data. Plotted points (red diamonds) represent topographic data taken from 7.5 minute USGS maps for the Piney Point drainage basin. Each point is plotted in terms of its latitude (x-axis), longitude (y-axis), and elevation (z-axis). The above equation represents the regression plane determined for 3-dimensional coordinates of each point considered.

direction and speed of flow. Thus, these results may not represent small-scale flow patterns and gradients for the area, but they do give the best approximation for a generalized regional flow pattern. Topography around the gypsum stack complex is relatively flat, so that the resulting gradient from this calculation is a good representation for ambient conditions of the study area.

Water Table Contours

Contours of hydraulic heads for surficial aquifer monitoring wells are greatly impacted with the addition of well 2-0. Thus, accurate representation of the water table in the unconfined zone cannot be made without inclusion of a measurement taken at this well. Contours for measurements taken on May 6, 1996 (Figure 16) and September 19, 1996 (Figure 17) are typical of other data sets analyzed, and represent the extent of values found in the calculation of the water table for the surficial aquifer. Additional contours drawn from measurements on other sampling dates are depicted in APPENDIX C.

Most significant of the contouring plots is the influence of the head-reading taken at well 2-0 (Figure 16, 17). The gradient between its location and all other monitoring wells is indicative of flow away from the gypsum stack in almost all horizontal directions; flow to the southeast is hindered by the opposing force of regional flow. A water table low in the southwest quadrant may be the result of the cooling pond and the ditch system in that area. As water in the ditches evaporates, additional water is drawn from the surficial aquifer, resulting in a lowering of the local water table.

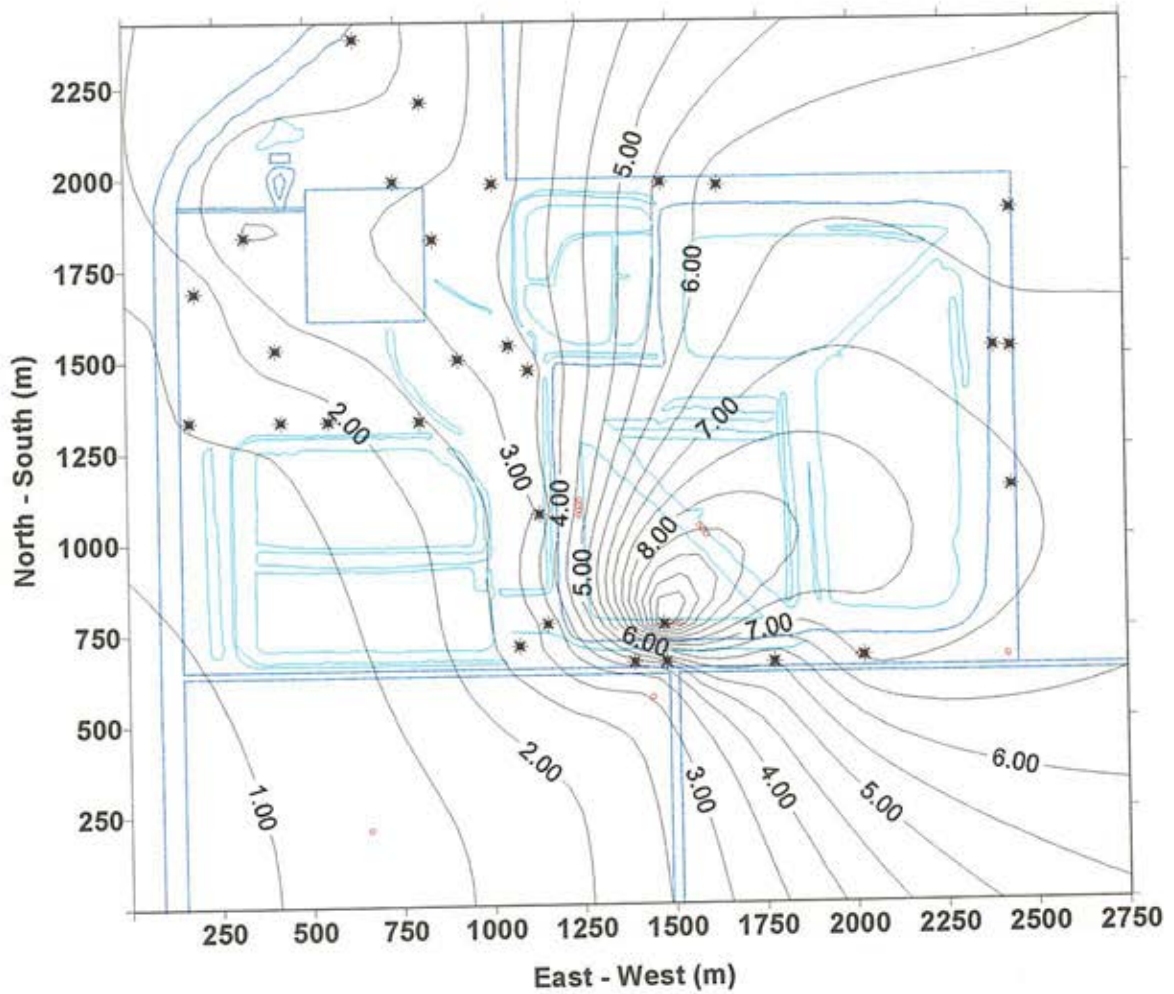


Figure 16. Contour Plot of the Surficial Aquifer on May 6, 1996. Asterisks represent hydraulic head measurements for wells upon which the contours are based. Noteworthy characteristics of the map include a large head value at well 2-0 and regional low in the southwest quadrant.

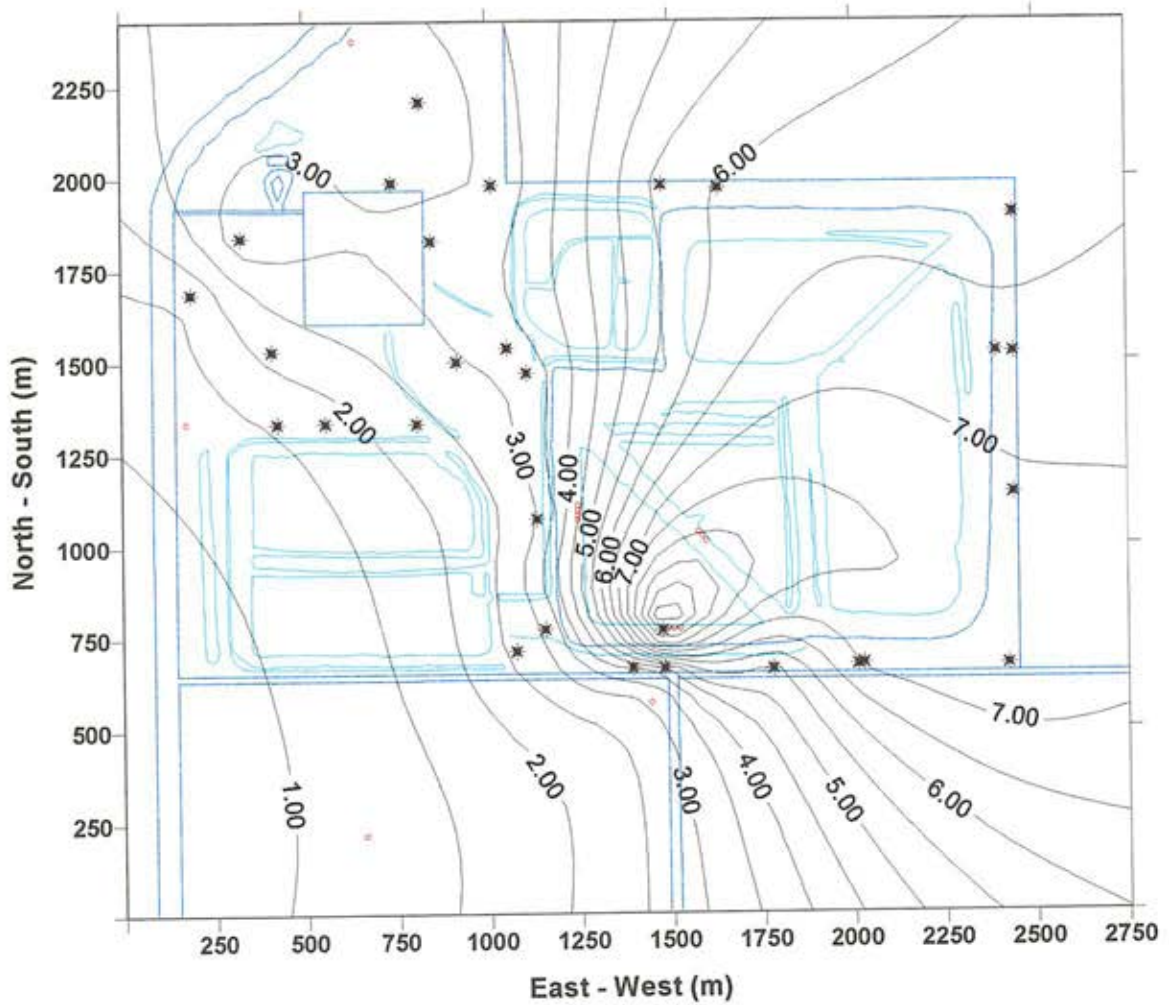


Figure 17. Contour Plot of the Surficial Aquifer for September 19, 1996. Asterisks represent hydraulic head measurements for wells upon which the contours are based. Noteworthy characteristics of the map include a large head value at well 2-0 and a regional low in the southwest quadrant.

Conductivity Analysis

Kirkham Auger Hole Test

Hydraulic conductivity of the well designated as USGS 9 was determined by an auger hole method described by Boast and Kirkham (1971) and Amoozegar and Warrick (1986). This calculation dictates a relationship between the drawdown (y), time (t), and hydraulic conductivity (K) in the following equation :

$$K = \{ \pi r^2 / [C(t_{i+1} - t_i)] \} \ln(y_i / y_{i+1}) \quad (4.2)$$

The hydraulic conductivity is in units of cm/sec, and is compared to known ranges of unconsolidated material (Bear, 1979). C is a shape factor that is commonly referred to as a constant for the equation. Three variables are used to calculate the value of C/r in equation 4.2 :

- 1)- the ratio of the cavity height to the well radius (h/r) ;
- 2)- the ratio of the cased well section to the well radius (hc/r) ; and
- 3)- the ratio of the impermeable layer depth beneath the cavity to the well radius (s/r).

Although the geometry of USGS 9 does not allow the determination of a constant from known values (Youngs, 1968), a log base E curve-fit of the available ranges (figure 18) determined a viable solution for many ratios of the cavity height to the well radius (hc/r). Based on the most likely geometry of the well, the " $hc/r=0$ " curve was selected as the most reliable one. Using this curve, a hydraulic conductivity in the range of 0.00075 - 0.00190 cm./sec. was determined, which is in the range of two geomorphic classifications: clean sand ($1 - 10^{-4}$) and silty sand ($10^{-1} - 10^{-5}$).

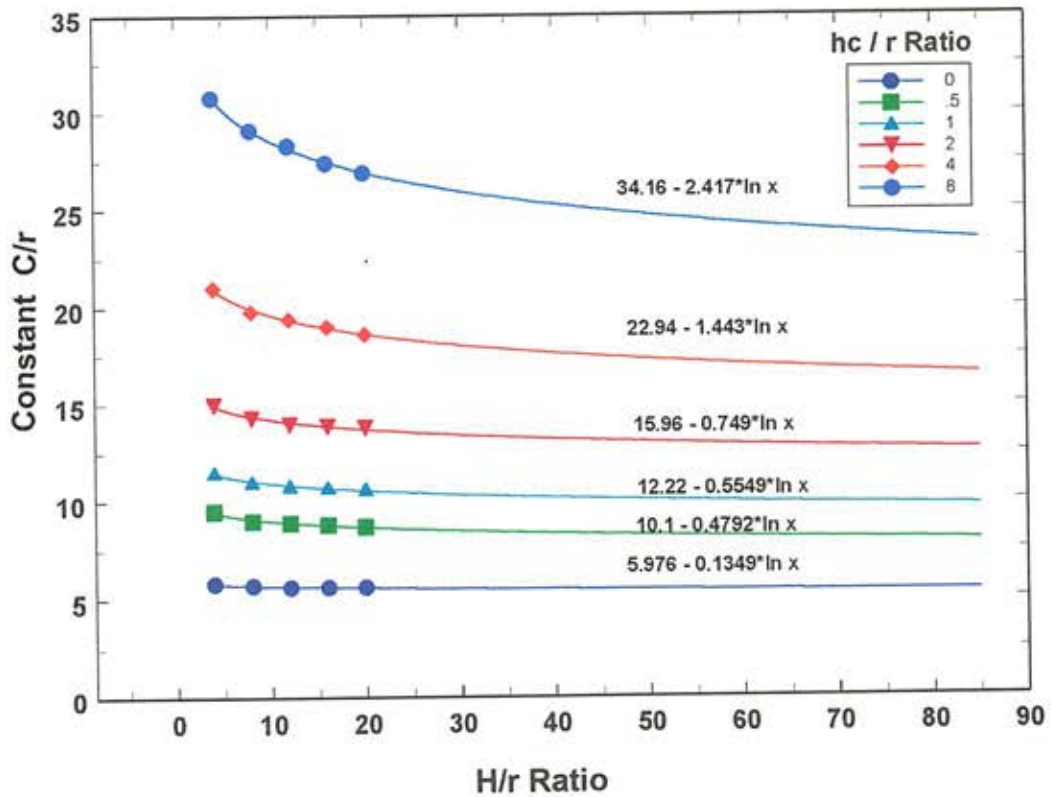


Figure 18. Determination of Shape Factor C/r by a Natural log Curve-fit. Each curve-fit above represents a relationship of H/r to the shape factor (c/r). Approximation of the shape factor for large H/r values was needed in calculating the conductivity for USGS well #9.

Bouwer Rice Test

Procedure for the pump analysis of wells 2-0, MW 1, RW 8, 11, 18, 21, 22, & 24 followed a "slug" recovery method, developed by H. Bouwer and R.C. Rice (1976). This procedure takes into account the partially screened nature of many monitoring wells (Figure 19) for the calculation of hydraulic conductivity, and allows a spatial analysis of conductivities around the site.

The Bouwer / Rice theory is based upon a modification of the Thiem equation to :

$$Q = 2\pi K L \frac{y}{\ln(R_e / R_w)} \quad (4.3)$$

where Q is the volume of water flowing into a well at a specific depth y , K is the hydraulic conductivity, L is the length of the screened section, and R_e/R_w is a ratio of the effective radius of the pumping influence over the effective radius of the well (including the grouted radius). The rate of water level rise (dy/dt) can be represented as :

$$dy/dt = -Q/\pi r_c^2 \quad (4.4)$$

where r_c is the radius of the cased well section. Insertion of equation 4.4 into 4.3, followed by integration will produce :

$$\ln y = -\frac{2KLt}{r_c^2 \ln(R_e/R_w)} + \text{constant} \quad (4.5)$$

Applying this solution for limits y_0 and y_1 where $t = 0$ to t while solving for K yield the finalized equation that was used :

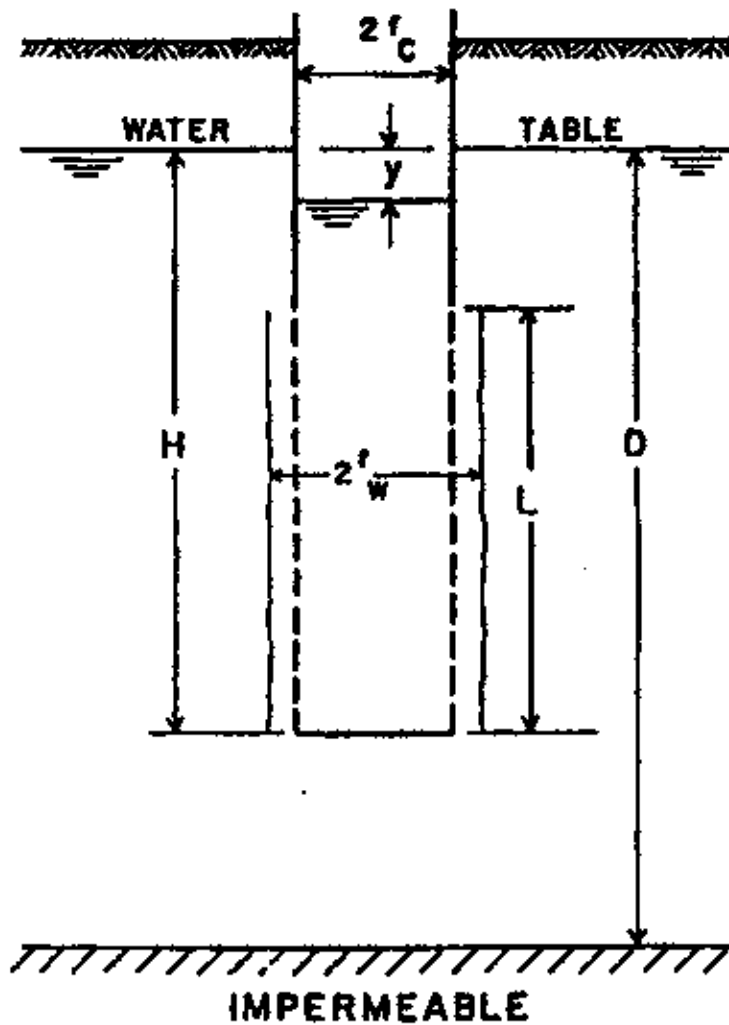


Figure 19. Generalized Well Geometry of a Partially Screened Well. Note values for the total water column (D), effective water column (H), screening height (L), drawdown (y), well radius (r_c), and effective well radius (r_w).