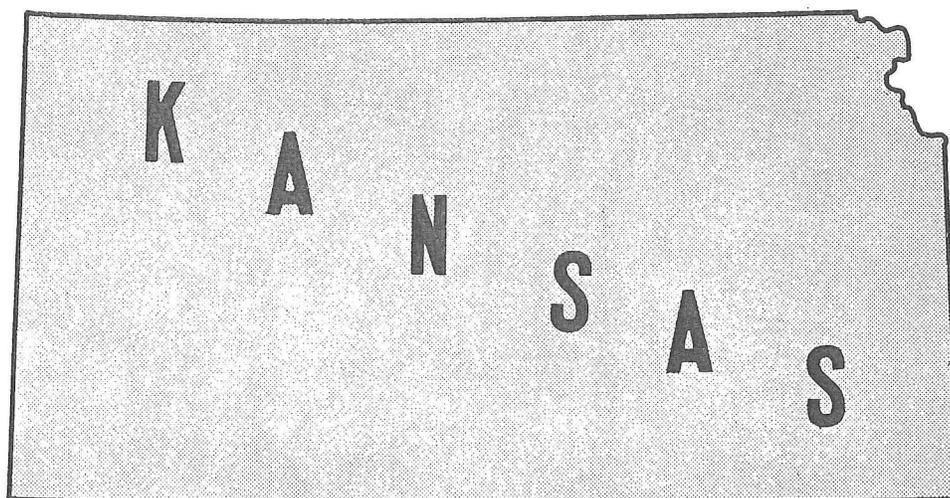


RESIDUAL SALT STUDY OF BRINE AFFECTED SOIL AND SHALE

POTWIN AREA - BUTLER COUNTY, KANSAS

By

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and Ralph E. O'Connor



KANSAS STATE DEPARTMENT OF HEALTH  
ENVIRONMENTAL HEALTH SERVICES

Topeka, Kansas

May 1966

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## ABSTRACT

This report presents the results of a study of residual salt concentrations beneath and near an abandoned oil field brine disposal pond. A decade after the use of the pond was discontinued, chemical analyses of test hole cores indicate an excess of 434 tons of soluble residual salts still remain to be leached out of the soil and shale in the pond area. Solutions alter in chemical composition during transportation away from the source. The degree of alteration is determined by the seepage environment and the volume of fresh water available for transportation and dilution. Findings indicate that residual salt removal is a very slow process.

The use of clay minerals as parameters of ion adsorption are discussed. The degree of adsorption depends upon the cation exchange properties of the clays which favor adsorption of calcium and magnesium over sodium. Clays with expansion properties adsorb sodium; as a result sodium frequency, as an adsorbed cation in montmorillonite, can be determined by use of X-ray diffraction patterns. From these patterns, paths of seepage too small to be detected by chemical methods can be outlined.

The correlative value of the chemical analyses and X-ray diffraction data on clay minerals is discussed. The chloride ion concentration is the most important dissolved constituent in detection of oil field brine pollution. The necessity of using complete chemical analyses in pollution studies is stressed.

## INTRODUCTION

Source identification of mineralization in ground water aquifers has long been an enigma to those engaged in water quality studies. All water carries a degree of natural mineralization. These inorganic constituents in many instances are of predictable concentrations for a given formation water in a given area.

Increasing interest has recently been shown in developing suitable statistical guidelines and quantitative methods by which naturally occurring mineralization in ground water reservoirs can be differentiated from commingled oil field brine contaminants. Jeffords (1948) suggests that in Kansas oil field brine concentration ratios of calcium, magnesium, and sodium to chloride are virtually constant despite wide differences in dissolved solids concentration. Leonard (1964) indicates that chemical analyses of water samples can be used to determine load percentages of dissolved solids contributed by oil field brines to the Walnut River in Kansas.

Formerly, petroleum companies used unsealed surface ponds extensively in Kansas for oil field brine disposal. This practice resulted in the introduction of brine contaminants into formations containing fresh and usable ground water. Inorganic pollution of the aquifer has resulted rendering it chemically unsuitable for human or animal consumption. The chloride ( $\text{Cl}^-$ ) concentration of the water is presently the decisive factor in characterizing pollution from oil field brine. An abnormally high chloride concentration may be indicative of oil field brine pollution. The Oil Field Section of the Kansas State Department of Health has investigated many cases involving suspected pollution from oil field brine in which the original quality of the subsurface was characterized by high mineralization, or where more than one possible source of contamination was involved. After considering such factors as time, dilution, original chemical composition of ground water, chemical composition of the brine, and lithology of the seepage medium, it became apparent that erroneous interpretations could result from sole reliance upon the chloride concentration and could lead to mistaken opinions regarding the source and degree of pollution.

To establish better methods of understanding and classifying water pollution, the Oil Field Section of the Kansas State Department of Health formulated a pilot research study. The purpose of this project was designed to investigate:

1. The amount of leachable salts which remain in the soil, rocks, and aquifers surrounding an abandoned surface brine pond of a well known history.

2. The importance of bedrock lithology in sorption of brine contaminants and subsequent chemical alteration of brine seepage.
3. The changes in chemical composition of the brine seepage in various directions away from the pond source and the effect of ground water on the brine seepage.
4. The necessity of utilizing complete chemical analyses determining pollution sources rather than dependency upon chloride concentration as an indicator of oil field brine pollution.
5. The movement of brine seepage through a specific lithologic environment.
6. The usefulness of clay mineralogic information as a supporting tool to chemical methods in pollution investigations.

#### FIELD INVESTIGATION AND GENERAL INFORMATION

The abandoned brine pond used in this study is located in the southwest quarter of Section 36-24S-3E, Butler County, Kansas on the McCraner 'B' lease in the Potwin oil field. The pond actually consists of two interconnected ponds which will be considered as one in this report. In February 1963, the Oil Field Section supervised the drilling of a network of test holes in the immediate vicinity of the brine pond. The holes were drilled by the Kansas Geological Survey using a portable power auger.

Eleven test holes were completed and located as shown in Figure 1. Test hole No. 2 was located in the abandoned pond and the others in a pattern to represent the surrounding area. Hole No. 1 is outside the area affected by the pond and was selected for control purposes. Rain soaked soil at the time of drilling somewhat controlled the overall pattern and contributed to the lack of coverage west of the pond.

The surface disposal pond reportedly received brine continuously from March 1937 to December 1955. During this period, an estimated total of 1,800,000 barrels of Mississippian formation brine was put into the pond. The pond is constructed in the lower ten feet of the Wellington formation of Permian age. This part of the Wellington formation is shale and overlies the Herington limestone member of the Nolans formation which outcrops in the gullies that drain the pond area. The Wellington-Nolans contact essentially conforms to the depth of the individual test holes. Lithologic description of the test hole samples are given in the Appendix. Each sample received a

# MAP OF TEST HOLE LOCATIONS

S/2 SW 1/4 36-24S.-3E.

BUTLER COUNTY

KANSAS

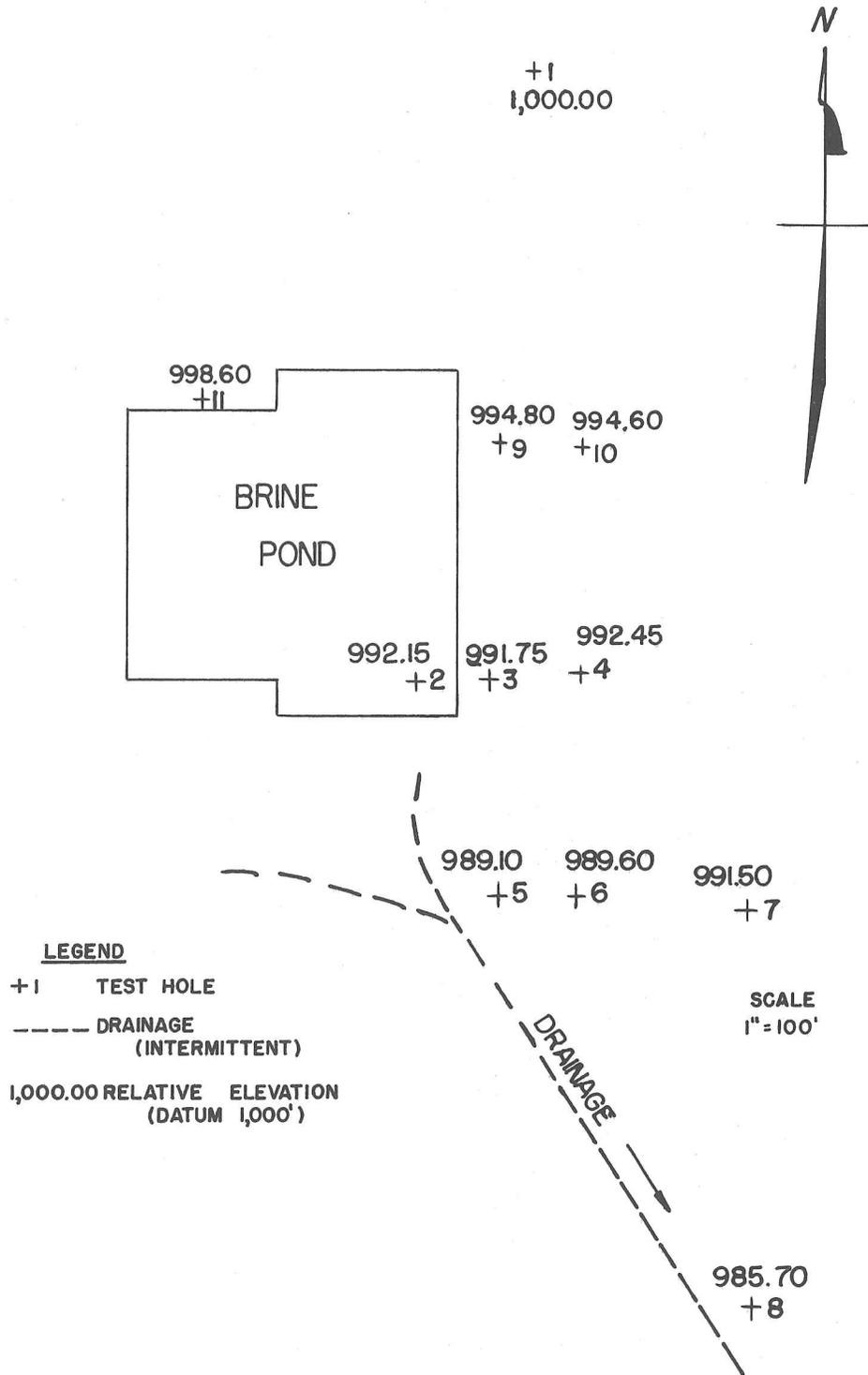


FIGURE I.

KANSAS STATE DEPT. OF HEALTH  
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OIL FIELD SECTION  
RESIDUAL SALT STUDY

number which denotes both the hole number and the footage interval. For example, the two-to-four foot zone in hole 3 is shown as sample 3-2.0-4.0. This type of designation is used in reference to all sample numbers in the report.

The available water samples represent seepage that would not be available during periods of drought at the depth of the test holes. Samples of soil or shale were collected from intervals ranging from 1.5 to 4.0 feet in each hole.

## LABORATORY ANALYSES

Sample Preparation and Chemical Analyses. The soil and shale samples collected from the test holes were air dried for two weeks at room temperature. Then each sample was mechanically ground in an electric grinder to a uniform powder size. A portion of each sample was dried in an electrical oven at 105°C for 24 hours.

The dried material was sieved to retain particles ranging in size from .35 mm to .50 mm. This eliminated small particles, thereby preventing formation of colloidal suspension when water was added. A 40 gram (gm.) portion of each sample was placed in a 1/2 pint glass bottle and 200 milliliters (ml.) of deionized water was added for purposes of obtaining a 1:5 soil-water extract. The samples were agitated on a mechanical shaker for 15 minutes. Agitation was repeated for a two minute period for each of three successive days. Then the samples were allowed to settle out of suspension. The supernatant was filtered off and collected in a clean 200 ml bottle for major ion determinations.

The major ion determinations were conducted on the supernatant by the following analytical methods: (1) Calcium and magnesium by titration with ethylenediaminetetraacetic acid, (2) chloride by titration with silver nitrate, (3) bicarbonate by titration with sulfuric acid, (4) sulfate by the turbidity method using barium chloride, (5) sodium by flame photometry and then calculated by difference between cations and anions for uniform values, (6) total dissolved solids by stoichiometry.

Sample Preparation and X-ray Analysis of Clay Minerals. A 50 gm. sample from each soil or shale interval was weighed out on an analytical balance and then placed in a 600 ml beaker with sufficient deionized water to cover the sample. A 10 ml portion of Calgon was added as a clay dispersing agent and the mixture was allowed to set and slake overnight.

The sample was then placed in a Waring blender and agitated for five minutes and processed through a size 270 wet sieve so that particles of less than 53 microns were collected. The mixture was then placed in a 1,000 ml. graduated cylinder, hand shaken for one minute, and allowed to set in a water bath for 24 hours. The clay suspension, containing particles of less than 2 microns in size, was then siphoned off for X-ray analysis of clay minerals. Glass slides of oriented clay mineral aggregates were prepared from each sample suspension.

The X-ray diffraction patterns of the clay samples were obtained by use of a North American Phillips diffraction unit and a North American Phillips electronic circuit panel. Each slide was exposed to nickel-filtered copper radiation, using 20 milliamperes and 40 kilovolts with a one degree Soller slit system. The goniometer was traversed through an angle of 30 degrees to 2 degrees two theta for untreated slides, and 15 degrees to 2 degrees two theta for slides receiving ethylene glycol ( $\text{CH}_2\text{OHCH}_2\text{OH}$ ) applications. Ethylene glycol forms an organic complex with certain clay minerals and is used in the identification of montmorillonite, vermiculite, and other clay minerals which have expansion properties. The diffraction angles were read directly from the chart graph paper in degrees two theta. These degrees were then converted to angstrom units of the d-spacing of the reflection by the use of tables (U. S. Dept. of Commerce 1950).

#### DISCUSSION OF RESULTS OF CHEMICAL ANALYSES

The results of the chemical analyses for both water and soil samples are presented in Table I. These data indicate that most of the area bounded by the test holes received some contamination from oil field brine solutions. The area surrounding test hole 10 apparently did not undergo the extensive seepage of brine typical of the rest of the area. Shale samples from test hole 10 were characterized by a predominance of calcium ( $\text{Ca}^{++}$ ) and bicarbonate ( $\text{HCO}_3^-$ ) in the upper part and sodium ( $\text{Na}^+$ ) in the lower part. The lower part of test hole 10 apparently received some brine seepage during the time of pond usage. The dry condition of the hole at the time of sampling limits interpretation of present brine seepage activity. There is the possibility that the upper part of hole 10 was contaminated and has returned to normal. The total amount of leachable salts in samples from test hole 10 is small, however, compared to the other test hole samples. By contrast, the chemical composition of the salts from test hole 10 appear to resemble the pre-pollution conditions in the Lower Wellington formation more than the samples from other test holes. For purposes of natural comparison, hole 10 can be used as a control hole instead of hole 1.

TABLE I  
 ANALYSIS OF WATER FROM TEST HOLES - SW SECTION 36-24-3E., BUTLER COUNTY  
 In Milligrams per Liter and Millequivalents per Liter

Sample Hole No.	Feet	Ca++ mg/l	Mg++ mg/l	Na+ mg/l	Cl- mg/l	HCO <sub>3</sub> mg/l	SO <sub>4</sub> <sup>=</sup> mg/l	Total Solids (Stoichiometrical) mg/l
1	0 - 4.0	32.	7.7	12.	30.	116.	1.	199
	4.0- 6.0	39.	4.6	57.	120.	83.	2.4	306
	6.0- 9.0	51.	6.	140.	286.	60.	4.	547
	9.0-11.0	58.	8.1	203.	380.	85.	13.	747
2	0 - 2.5	264.	47.	1570.	3450.	90.	148.	5570
	2.5- 5.0	172.	23.	1700.	2880.	81.	90.	4940
	5.0- 7.5	86.	12.	1490.	2420.	75.	26.	4120
	7.5- 9.0	21.	7.7	530.	825.	75.	11.	1470
	Water	1090.	295.	7070.	13600.	111.	14.	22200
3	0 - 2.5	34.	20.	19.	80.	125.	1.0	279
	2.5- 4.0	30.	5.0	130.	280.	94.	2.4	541
	4.0- 6.0	12.	3.1	241.	344.	92.	6.4	699
	6.0- 9.0	21.	1.0	173.	244.	99.	6.4	544
	Water	835.	256.	5440.	10500.	198.	0.70	17200
4	0 - 2.5	16.	3.1	139.	140.	166.	20.	484
	2.5- 5.0	21.	3.3	142.	172.	137.	19.	494
	5.0- 6.0	26.	5.2	117.	158.	132.	10.	448
	6.0	30.	5.0	65.	182.	78.	12.	372
5	0 - 2.5	18.	0.0	100.	80.	180.	2.6	381
	2.5- 4.5	9.2	1.4	114.	130.	105.	6.0	368
	4.5- 5.0	8.4	0.0	173.	196.	120.	20.	517
	Water	701.	221.	4790.	9080.	346.	0.70	15100
6	0 - 2.5	31.	4.6	277.	328.	285.	2.0	928
	2.5- 4.0	30.	1.7	221.	326.	93.	25.	697
	4.0- 6.0	21.	3.1	218.	330.	86.	3.0	661
	6.0- 8.0	11.	2.4	258.	360.	96.	13.	740
	8.0	32.	3.9	131.	224.	66.	10.	467
Water	1010.	211.	4040.	8470.	180.	17.	13900	

Sample Hole No.	Feet	Ca++		Mg++		Na+		Cl <sup>-</sup>		HCO <sub>3</sub>		SO <sub>4</sub> <sup>=</sup>		Total Solids (Stoichiometrical) mg/l
		mg/l	meq/l	mg/l	meq/l	mg/l	meq/l	mg/l	meq/l	mg/l	meq/l	mg/l	meq/l	
7	0 - 2.5	91.	4.5	14.	1.2	43.	1.9	118.	3.3	256.	4.2	0.80	0.02	523
	2.5- 4.0	36.	1.80	5.6	0.46	23.	0.99	28.	0.79	136.	2.2	11.	0.23	240
	4.0- 6.5	16.	0.80	2.7	0.22	110.	4.8	112.	3.2	136.	2.2	20.	0.42	397
	6.5- 8.5	14.	0.70	1.4	0.12	211.	9.2	280.	7.9	111.	1.8	13.	0.27	630
	8.5-10.5	15.	0.75	0.50	0.04	344.	15.	500.	14.1	89.	1.5	8.8	0.18	957
	10.5-12.5	29.	1.5	3.1	0.25	427.	19.	660.	18.6	94.	1.5	4.8	0.10	1220
Water	12.5-13.5	97.	4.8	14.	1.2	647.	28.	1160.	32.7	67.	1.1	15.	0.31	2000
		2650.	132.	630.	52.	11700.	510.	24500.	691.	126.	2.1	1.0	0.02	39600
8	0 - 2.5	125.	6.2	15.	1.2	37.	1.6	178.	5.0	248.	4.1	0.40	0.00	603
	2.5- 4.5	44.	2.2	3.1	0.25	28.	1.2	60.	1.7	120.	2.0	0.80	0.02	256
	4.5- 5.0	15.	0.75	1.2	0.10	77.	3.3	52.	1.5	144.	2.4	17.	0.35	306
9	0 - 2.5	28.	1.4	6.2	0.51	42.	1.8	32.	0.90	176.	2.8	2.8	0.06	287
	2.5- 4.5	36.	1.8	5.2	0.43	49.	2.1	84.	2.4	120.	2.0	0.80	0.02	295
	4.5- 7.0	47.	2.4	8.1	0.67	111.	4.8	214.	6.0	106.	1.7	2.9	0.06	489
	7.0- 9.0	27.	1.4	2.7	0.22	278.	12.	430.	12.1	90.	1.5	3.0	0.06	831
	9.0-11.0	11.	0.55	0.70	0.06	200.	8.7	250.	7.1	110.	1.9	17.	0.35	589
	Water	236.	12.	74.	6.1	2610.	118.	4590.	129.	386.	6.3	0.50	0.01	7900
10	0 - 2.5	98.	4.9	13.	1.1	16.	0.69	48.	1.3	332.	5.3	0.20	0.00	507
	2.5- 4.0	40.	2.0	6.2	0.51	22.	0.93	36.	1.0	137.	2.3	8.0	0.17	249
	4.0- 6.0	21.	1.1	2.1	0.17	34.	1.5	20.	0.56	110.	1.9	10.	0.21	197
	6.0- 8.0	10.	0.50	0.70	0.06	48.	2.1	54.	1.5	102.	1.7	5.6	0.12	220
Water	16.	0.80	1.0	0.08	95.	4.1	92.	2.6	120.	2.0	22.	0.46	346	
11	0 - 2.5	142.	7.1	21.	1.7	77.	3.4	294.	8.3	233.	3.8	3.0	0.06	770
	2.5- 4.5	38.	1.9	3.3	0.27	36.	1.6	64.	1.8	116.	1.9	1.0	0.02	258
	4.5- 6.0	53.	2.6	7.4	0.61	4.0	0.18	36.	1.0	146.	2.4	0.80	0.02	247
	6.0- 9.0	16.	0.80	0.50	0.04	47.	2.0	32.	0.90	111.	1.8	7.2	0.15	214
PRODUCED BRINE		4970.	248.	1480.	121.	25500.	1110.	65100.	1480.	67.	1.1	95.	2.0	97200

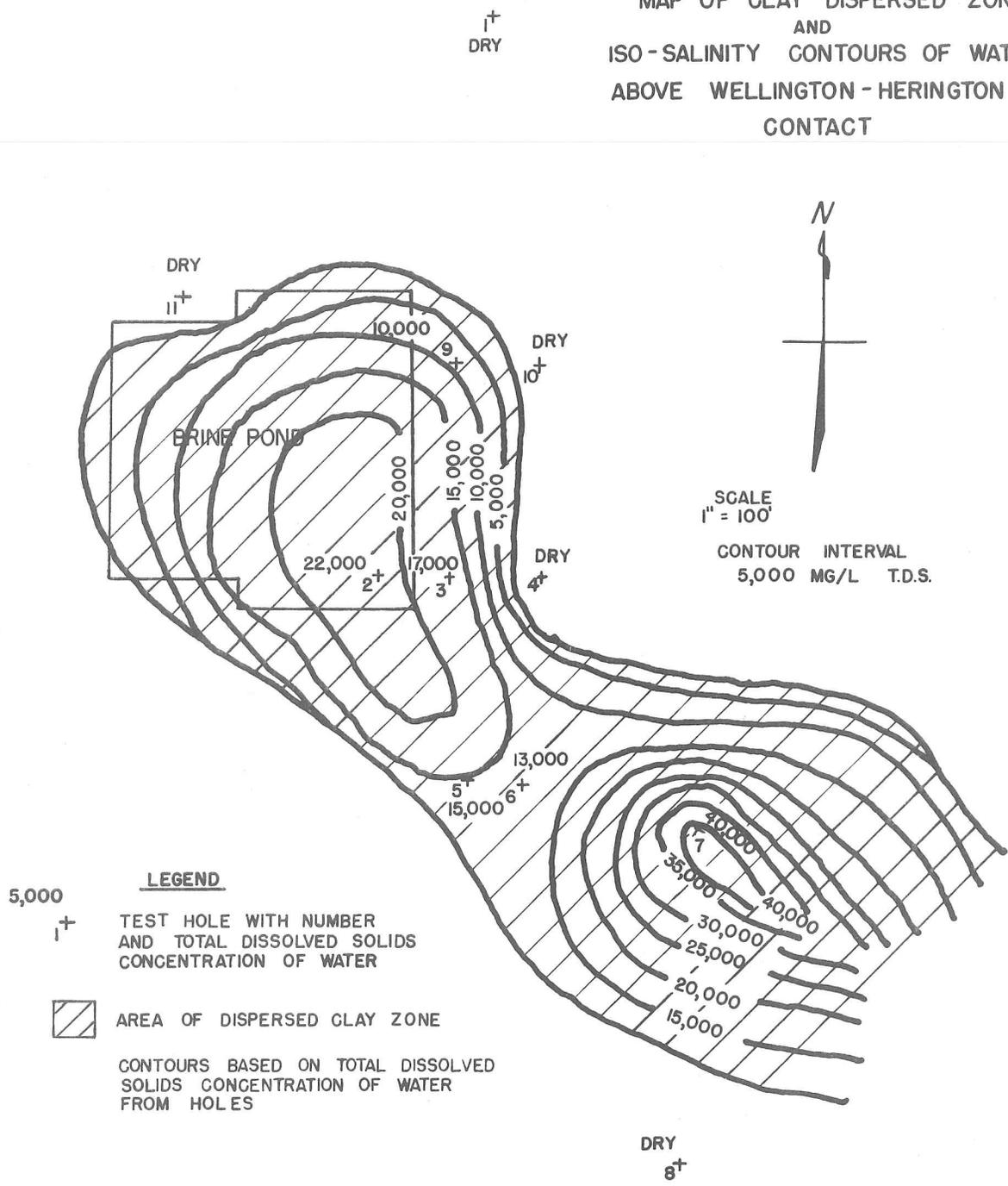
Ratios of sodium/chloride, calcium/chloride, and calcium/sodium were used to trace chemical alteration patterns across the study area. All quantities comprising these ratios are expressed in milliequivalents per liter. The sodium/chloride ratio for the original brine solution is 0.75. Water samples from test holes 2, 3, 5, 6 and 9 carry ratios ranging from 0.80-0.90 and hole 7 water is 0.74 or comparable to the brine. This is considered significant in that  $\text{Na}^+$  cations are apparently leached and transported at slightly lesser rates than are  $\text{Cl}^-$  anions. Whether differential transportation is restricted to the period after the use of the pond was discontinued is not known. This suggests that moderate alteration in brine compositions probably occur during seepage movement.

Water from test hole 7 had a higher chloride concentration than that of any other hole. The apparent reversion to chloride dominance in hole 7 might be attributed to: (1) Larger seepage flows which allow more unrestricted passage of contaminants, thus preserving the original sodium/chloride relationship, (2) less sodium due to retention and adsorption by clay material under and adjacent to the pond, (3) the hole 7 area represents a temporary high chloride concentration peak from a prior flushing out period (Figure 2).

The pond area has the highest population of  $\text{Na}^+$  and  $\text{Cl}^-$  ions throughout the nine foot sample interval. This was expected because the shale at this location had received an undiluted concentration of brine constituents over an eighteen-year period. Test hole 2 was located on the low side of the pond and the shale received excessive accumulations of salts during seepage of brine from the pond. Shale material directly overlying and coinciding with the natural spring seeps exhibits decreases in major ion concentrations, particularly  $\text{Na}^+$  and  $\text{Cl}^-$  in holes 2, 3, 6, and 9 and increases in holes 5 and 7. Whether this decrease is solely related to gradual flushing out of constituents by solution with fresh water is not completely defined by the information available. Indications are that sample zones 2 -7.5-9.0, 3 -6.0-9.0, 6 -8.0, 9 -9.0-11.0 have experienced effective leaching, whereas, the strata overlying the leached zone contain dissolved solids in a position more inaccessible to leaching. Undoubtedly the surface pond serves as an efficient catchment and flushing area during and shortly after periods of precipitation. Representative samples of water polluted by oil field brine and those having natural ion concentrations are shown graphically in Figure 3.

Holes 8 and 11 show evidence of  $\text{Na}^+$  and  $\text{Cl}^-$  introduction only to the surface material. Hole 8 is located adjacent to drainage which originates near the south dike of the pond. Most of the pond dike seepage in this direction probably entered the drainage; however, the vicinity of hole 8 undoubtedly received intermittent brine contamination if pond overflow occurred. Such overflows were largely surface runoff phenomena and vertical seepage pro-

MAP OF CLAY DISPERSED ZONE  
AND  
ISO-SALINITY CONTOURS OF WATER  
ABOVE WELLINGTON - HERINGTON  
CONTACT



5,000  
1+

**LEGEND**

TEST HOLE WITH NUMBER AND TOTAL DISSOLVED SOLIDS CONCENTRATION OF WATER

 AREA OF DISPERSED CLAY ZONE

CONTOURS BASED ON TOTAL DISSOLVED SOLIDS CONCENTRATION OF WATER FROM HOLES

SCALE  
1" = 100'

CONTOUR INTERVAL  
5,000 MG/L T.D.S.

1+  
DRY

DRY  
11+

DRY  
10+

DRY  
4+

DRY  
8+

FIGURE 2.

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ENVIRONMENTAL HEALTH SERVICES  
OIL FIELD SECTION  
RESIDUAL SALT STUDY

GRAPHICAL PLOTS OF MAJOR IONS IN WATER  
AND SOIL SAMPLES FROM THE STUDY AREA

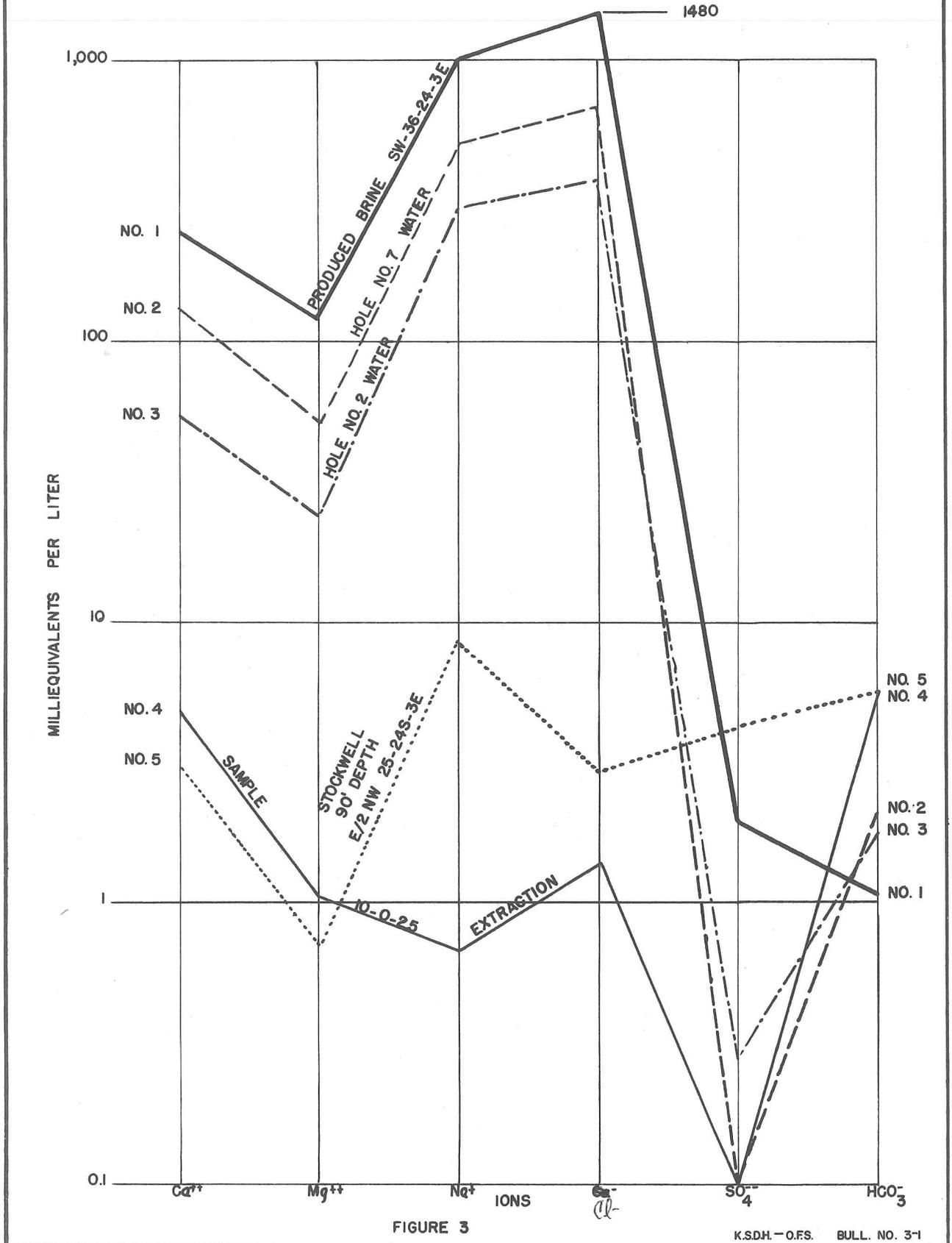


FIGURE 3

K.SDH.-O.F.S. BULL. NO. 3-1

bably did not extend more than three feet below the surface. Hole 11, located on the up-drainage side of the pond, was not directly affected by brine disposed of in the ponds. However, the brine collection system for the lease is located only a few feet from hole 11 and the high chloride concentration in the 11 - 0-2.5 sample is attributed to periodic leakage from tanks and lines rather than from the ponds. Regardless of source, the resulting effect on the shale would be the same.

Calcium/chloride ratios of the test hole water samples indicate a comparatively lower  $\text{Ca}^{++}$  population in the immediate pond area (holes 2, 3, 5, and 9) than the 0.17 figure for the original brine. Holes 6 and 7 had a higher ratio of  $\text{Ca}^{++}/\text{Cl}^-$  than the brine. In general, the leachable calcium concentrations remain low throughout the area with the exception of the upper samples from holes 2, 8, and 11. Comparison of calcium to sodium values reflected a relationship similar to that of calcium/chloride. The sulfate ( $\text{SO}_4^-$ ) and bicarbonate concentrations in the soil samples are low and appear to be normal values for the area. Small variations can be attributed to heterogeneous selectivity of leaching processes brought about by soil breakdown through weathering. The chemical analyses point out the encompassing nature of this particular pollution movement. Sodium/chloride relationships are by far the most meaningful in unravelling the contemporary effects of brine seepage movement.

In the shale under the pond area there is less clay and silt-sized material than in the surrounding shale. Clay minerals in samples 2 - 0-2.5 and 2 - 2.5-1.5.0 exhibited poor crystallinity. By comparison, the same minerals in hole 7 samples exhibited good crystallinity. Prolonged seepage from the pond due to the constant discharge of brine has degraded the crystallinity of the shale. This effect apparently lessens with distance from the pond.

Low calcium concentrations in the stronger seepage paths are somewhat enigmatic but suggest the following explanations: (1) Much of the  $\text{Ca}^{++}$  cations form insoluble salts which precipitate from the seepage solution and are not present as leachable cations. (2) Adsorption of  $\text{Ca}^{++}$  by montmorillonite during and after the active pollution period. Degradation of illite and subsequent formation of the water layers by removal of the potassium ( $\text{K}^+$ ) cations results in montmorillonite-like lattice structures. The resulting exchange properties are similar to montmorillonite and with the degraded forms, more exchange positions are available. (3) The clay in holes 6 and 7 shows much higher  $\text{Ca}^{++}$  concentrations which indicate transportation of  $\text{Ca}^{++}$  away from the pond has occurred. The area of hole 7 could represent a temporary collecting point.

Magnesium ( $\text{Mg}^{++}$ ) concentrations in the samples are relatively inconsequential and do not contribute greatly to the overall appraisal of brine alteration.

## DISCUSSION OF BRINE SOLUTION - CLAY MINERAL RELATIONSHIPS AND ALTERATION CHARACTERISTICS

Another phase of the study was to investigate environmental factors which cause alteration of the chemical composition of the brine during transportation away from the source. Hanshaw (1962), Grim (1953), and Weaver (1958) have suggested that clay minerals, particularly montmorillonites and vermiculites with their inherent ion-exchange properties, have the ability to adsorb  $\text{Na}^+$  cations under certain conditions of concentration, clay particle size, cation exchange capacity, and clay compaction. Weaver (1958) further states that from the position of the (001) peak of montmorillonite on X-ray diffraction patterns, it is possible to estimate the type of exchangeable cations it contains. A 12.4 peak indicates one layer of water and probably  $\text{Na}^+$ , and a 14 - 15.4-A peak two layers of water and probably  $\text{Ca}^{++}$  and/or  $\text{Mg}^{++}$ . Both types will expand to 17-A when allowed to adsorb sufficient ethylene glycol.

The X-ray method of identification was used in studying clay-sized fractions from all 48 soil and shale samples. The clay mineral species identified are presented in Table II. In order to obtain comparative amounts of each clay mineral present, percentage values were used. These were obtained by computing the area under the curve of the (001) reflection of each clay mineral identified and dividing by the reported reflecting power of the mineral. Brindley (1951) states the (001) reflection of montmorillonite is approximately four times that of illite. Weaver (1958) reports the 7-A kaolinite reflection would be two to three times as large as the 10-A illite peak for equal amounts of the two clays. Quantitative evaluation of clay minerals is extremely difficult. Therefore, only rough estimates can be obtained because the reflecting power differential for each clay mineral is dependent upon the crystallinity of the clay particles, grain size, and composition. Hence, these values should be treated as comparative rather than strict quantitative relationships.

For the purposes of this report, only montmorillonite, illite, and montmorillonite-illite mixed layer clays were studied in detail. Although kaolinite was identified in many of the samples, the amount was too small to be a factor in ion exchange studies. Montmorillonite-illite mixed layer clays were identified by the position of the resolute reflection between 10 - 17-A after glycolation. In the shale samples the peak shifted to 16.0 - 16.7-A indicating that most of the mixed layer clay ratios were 5:1 - 9:1 montmorillonite/illite (Figures 4 and 5). When heated, the layers collapsed to 10-A, indicating that all of the mixed layer clay varieties contained either montmorillonite or illite layers, in probable random stacking sequences. Untreated, the (001) reflection of the mixed layer clays held positions ranging from 13.6 - 13.8-A. To obtain

X-RAY DIFFRACTOMETER SMOOTH LINE TRACINGS OF A  
PATTERN OF SHALE SAMPLE, HOLE NO.2 (75-9.0)

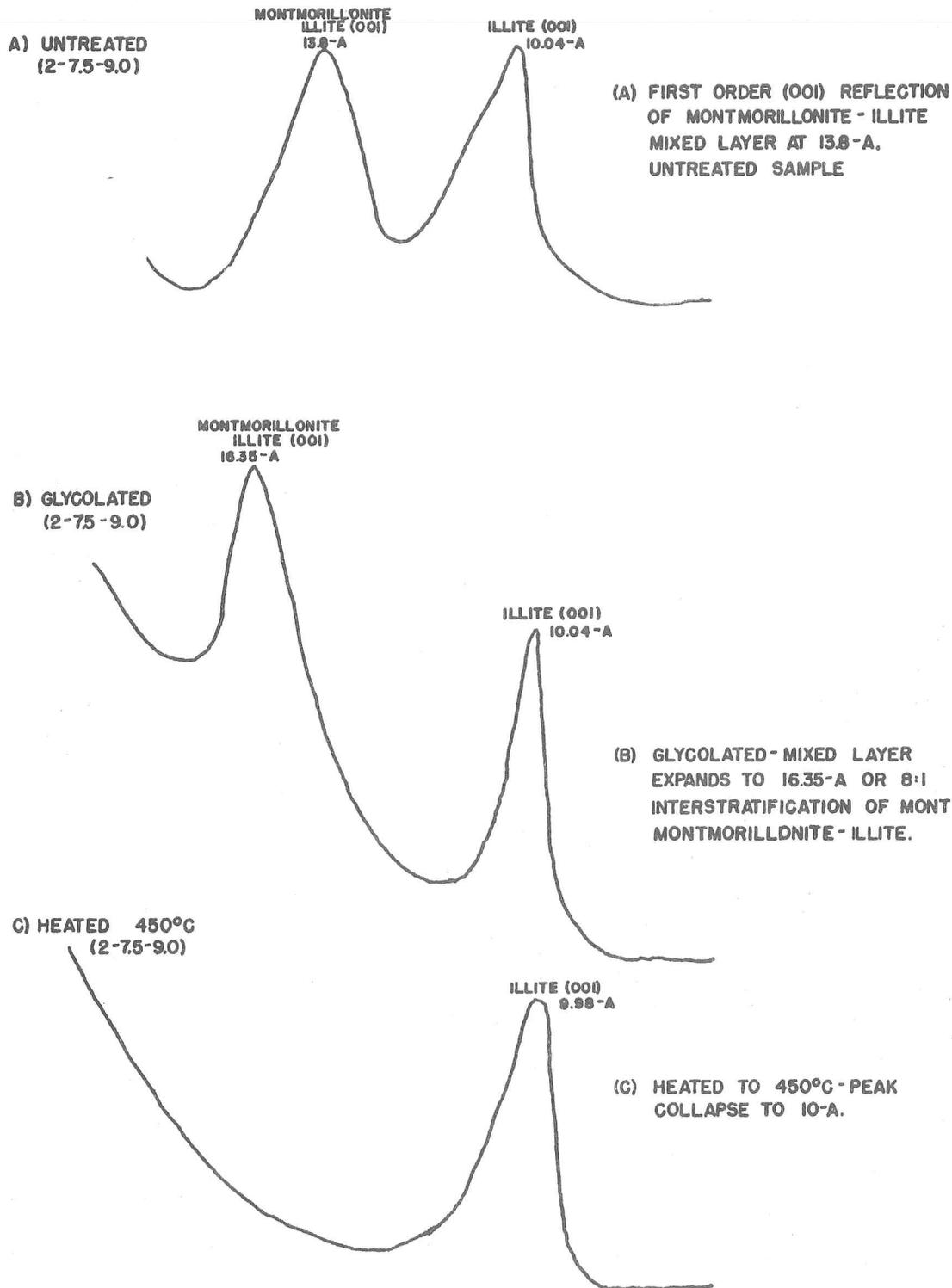


FIGURE 4

KANSAS STATE DEPT. OF HEALTH  
ENVIRONMENTAL HEALTH SERVICES  
OIL FIELD SECTION  
RESIDUAL SALT STUDY

X-RAY DIFFRACTOMETER SMOOTH LINE TRACINGS  
OF A PATTERN OF SHALE SAMPLE, HOLE 7-25-4.0

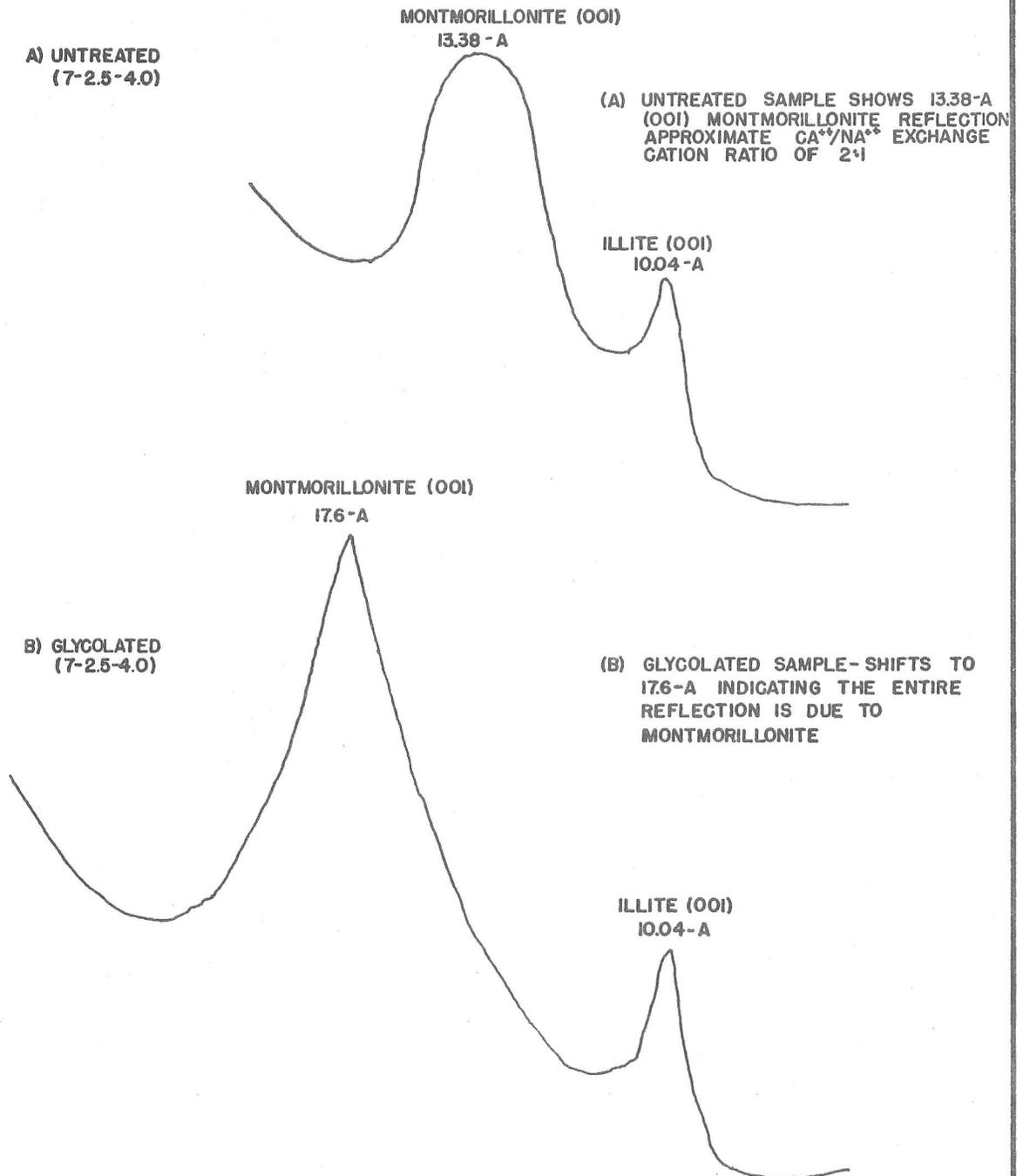


FIGURE 5

KANSAS STATE DEPT. OF HEALTH  
ENVIRONMENTAL HEALTH SERVICES  
OIL FIELD SECTION  
RESIDUAL SALT STUDY

TABLE II CLAY MINERALOGY OF SOIL AND SHALE SAMPLES

Sample No.	CALCULATED PERCENTAGE DISTRIBUTION OF CLAY MINERALS				Ratio M/I in Mixed Layer	Angstroms A		Estimated Crystallinity of Mont. or Mont.-Ill.
	Montmori- llonite	Illite	Kaolinite	Mixed Layer Montmori- llonite- Illite		Untreated (001) Mont. or Mont.-Ill.	Treated Eth- ylene Glycol Mont. or Mont.-Ill.	
1-0 - 4.0	56	16	16	9	1:9	12.3, 13.4	19.2	Poor
1-4.0- 6.0	66	20	14	-	-	13.4	18.0	Moderate
1-6.0- 9.0	74	21	5	-	-	14.3	17.3	Moderate
1-9.0-11.0	83	11	6	-	-	13.8	17.6	Well
2-0 - 2.5	43	51	4	2	1:3	13.2, 14.2	18.0	Poor
2-2.5- 5.0	6	73	2	11	5.1, 1.3	12.6, 13.6 14.7	18.0 16.05	Very Poor
2-5.0- 7.5	17	83	-	-	-	13.4	17 - 19	Poor
2-7.5- 9.0	4	63	T	33	8:1	13.8	16.35	Well
3-0 - 2.5	50	40	10	-	-	14.2	18.8	Poor
3-2.5- 4.0	-	65	1	34	8:1	13.4, 13.8	16.6	Moderate
3-4.0- 6.0	13	55	-	32	9:1	13.8	16.3, 17.0	Well
3-6.0- 9.0	-	67	T	33	9:1	13.2	16.3	Well
4-0 - 2.5	65	27	5	3	3:7	12.8	17.0	Mod.-Well
4-2.5- 5.0	65	27	5	3	8:1	12.0, 13.4 14.0	16.7, 17.2	Moderate
4-5.0- 6.0	73	18	3	6	1:5	13.8	16.7, 17.2	Well
4-6.0	78	20	2	-	-	12.6, 13.4	17.4	Well

TABLE II CLAY MINERALOGY OF SOIL AND SHALE SAMPLES

Sample No.	CALCULATED PERCENTAGE DISTRIBUTION OF CLAY MINERALS				Ratio M/I in Mixed Layer	Angstroms A		Estimated Crystallinity of Mont. or Mont.-Ill.
	Montmori- llonite	Illite	Kaolinite	Mixed Layer Montmori- llonite- Illite		Untreated (001) Mont. or Mont.-Ill.	Treated Eth- ylene Glycol Mont. or Mont.-Ill.	
5-0 - 2.5	79	16	5	-	-	13.0	17.6	Mod. - Well
5-2.5- 4.5	56	41	3	-	-	13.0	17.0	Well
5-4.5- 5.0	26	61	-	13	5:1	13.0, 13.6	16.0, 17.0, 18.0	Mod. - Well
6-0 - 2.0	33	28	6	33	7:1	12.0, 12.6, 13.8	17.6, 16.7	Mod. - Well
6-2.0- 4.0	41	59	-	T	1:2	13.4	17.6	Very Poor
6-4.0- 6.0	-	63	-	37	8:1	13.6	16.4	Poor - Mod.
6-6.0- 8.0	-	67	-	33	10:1	13.6	16.6	Mod. - Well
6-8.0	-	61	-	39	8:1	13.7	16.3	Well
7-0 - 2.5	63	27	10	-	-	12.0, 12.4 13.6, 14.0	17.6	Moderate
7-2.5- 4.5	69	22	9	-	-	13.4	17.0	Moderate
7-4.5- 6.5	69	23	8	T	15:1	13.2	16.7, 17.4	Moderate
7-6.5- 8.5	63	31	6	-	-	12.0	17.0, 17.7	Poor - Mod.
7-8.5-10.5	30	36	4	30	15:1	13.6	16.6	Poor - Mod.
7-10.5-12.5	-	70	T	30	8:1	13.4	16.1	Well
7-12.5-13.5	18	62	2	18	6:1	13.8	17.6, 16.1	Mod. Well
8-0 - 2.5	59	31	10	-	-	13.8	17.4	Poor - Mod.

TABLE II CLAY MINERALOGY OF SOIL AND SHALE SAMPLES

Sample No.	CALCULATED PERCENTAGE DISTRIBUTION OF CLAY MINERALS					Ratio M/I in Mixed Layer	Angstroms A		Estimated Crystallinity of Mont. or Mont.-Ill.
	Montmori-llonite	Illite	Kaolinite	Illite	Mixed Layer Montmori-llonite-Illite		Untreated (001) Mont. or Mont.-Ill.	Treated Ethylene Glycol Mont. or Mont.-Ill.	
8-2.5- 4.5	*18	66	1	15	6:1	13.0, 14.0	16.0	Moderate	
8-4.5- 5.0	-	55	2	43	5:1	13.8	16.0	Very Well	
9-0 - 2.5	52	39	9	-	-	12.3, 13.0	17.4	Moderate	
9-2.5- 4.5	65	29	6	-	-	12.3, 13.2 14.2	17.1	Poor - Mod.	
9-4.5- 7.0	75	11	5	9	1:7,7:1	13.8	17.0	Moderate	
9-7.0- 9.0	13	53	-	34	7:1	13.4	16.3, 17.6	Well	
9-9.0-11.0	-	66	1	33	7:1	13.6	16.35	Well	
10-0 - 2.5	62	29	9	-	-	13.2, 14.2	17.0	Poor - Mod.	
10-2.5- 4.5	50	44	6	-	-	12.2, 13.6	17.2	Moderate	
10-4.5- 6.0	84	13	3	-	-	13.4	17.3	Mod. - Well	
10-6.0- 8.0	90	7	3	-	-	13.4	17.2	Well	
10-8.0	77	20	3	-	-	12.6	17.4	Moderate	
11-0 - 2.5	38	57	5	-	-	12.6, 13.3	19.1	Poor	
11-2.5- 4.5	-	67	1	32	6:1	13.2, 13.8	16.1	Well	
11-4.5- 6.0	-	65	1	34	6:1	13.6, 14.2	16.1	Well	
11-6.0- 9.0	-	49	1	50	9:1	13.8	16.4	Well	

\*Expanding Vermiculite

information of the exchange cations in the montmorillonite, the M/I angstrom ratio of the glycolated peak was compared to that on the pattern of the untreated sample. In most cases, the results suggested that the interlayered montmorillonite was of the Ca<sup>++</sup> or Mg<sup>++</sup> variety and very little, if any, Na<sup>+</sup> replacement had taken place.

The montmorillonite clays in the study area displayed (001) reflections ranging from 12-A to 14.4-A on untreated samples with the average occurrence being between 13.0 - 13.8-A. This indicated the presence of both one or two water layered montmorillonites. In many cases, two distinct phases of montmorillonite were present in the same sample.

Jones (1964) showed as a result of laboratory experimentation that the presence of ten percent or more Ca<sup>++</sup> or Mg<sup>++</sup> in a given solution will prevent clay dispersion. Ten percent or more of Ca<sup>++</sup> or Mg<sup>++</sup> prevents clay dispersion because the cation exchange properties of the clay minerals generally favor adsorption of divalent calcium and magnesium over sodium (Figure 6). The data gathered during this study indicate the presence of some Na<sup>+</sup> montmorillonite in zones which have more than ten percent of Ca<sup>++</sup> or Mg<sup>++</sup> cations (Table III). The presence of Na<sup>+</sup> montmorillonite in zones comprising more than ten percent of divalent cations suggests the possibility of small pockets of high Na<sup>+</sup> concentration clays in a zone which carries predominantly Ca<sup>++</sup> clays. These differences are probably because chemical analyses represent the composite soluble and leachable ionic population of the sampling interval; whereas X-ray diffraction patterns would detect migration paths of Na<sup>+</sup> containing brine solutions through the presence of Na<sup>+</sup> montmorillonite. When Ca<sup>++</sup> and Na<sup>+</sup> (two layers and one layer) montmorillonite clays were present as an interlayer mixture, one reflection would result in a proportionate position between the pure phases.

Sample 7 - 0-2.5 showed (001) montmorillonite reflections at 12.0-A, 12.4-A, 13.6-A, and 14.0-A indicating that this zone contains varying degrees of Na<sup>+</sup> adsorption. All phases are independent and thus reflect as separate peaks compared to one broad reflection when the montmorillonite types occurs as interlayered mixtures. The entire series of reflections on the treated sample shifted to 17.6-A negating the presence of traceable illite. Interpretation of this type of data is often speculative, but two possibilities arise: (1) The composite sample represented several small zones of Na<sup>+</sup> montmorillonite with the bulk of the clay being of the Ca<sup>++</sup> variety. Test hole 7 is in such a position to have received overflow from the pond during its active period. Undoubtedly sample 7 - 0-2.5 represents a former Na<sup>+</sup> saturated zone which is undergoing gradual Ca<sup>++</sup> replacement as the Na<sup>+</sup> is released and weathering progresses. Even with the aid of capillary action, replacement processes are probably slow since the zone is far above active seepage paths. (2) The laboratory method of separation caused dissociation of clay flakes from

EFFECT OF CALCIUM AND MAGNESIUM IONS ON  
PERCENT OF CATION EXCHANGE SITES FILLED  
BY CALCIUM OR MAGNESIUM IN THE PRESENCE  
OF SODIUM IONS

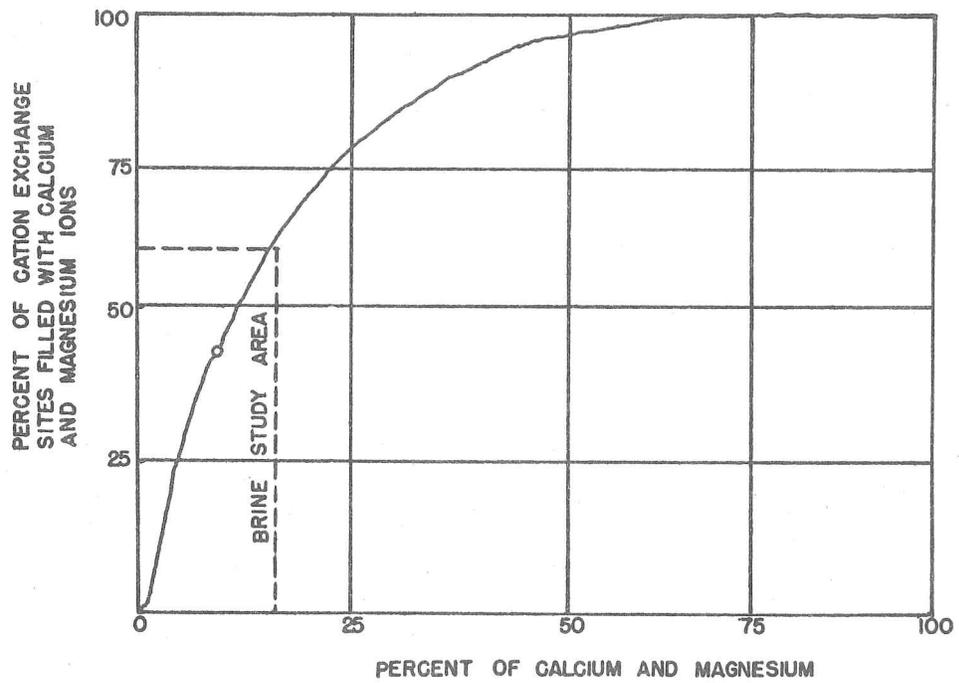


FIGURE 6

KANSAS STATE DEPT. OF HEALTH  
ENVIRONMENTAL HEALTH SERVICES  
OIL FIELD SECTION  
RESIDUAL SALT STUDY

DIA. BY JONES (1964)

TABLE III

CHEMICAL AND X-RAY INTERPRETATIONS  
ON CALCIUM AND MAGNESIUM EXCHANGE SITE  
POPULATION IN THE PRESENCE OF SODIUM

SAMPLE NO.	PERCENTAGE OF Ca <sup>++</sup> AND Mg <sup>++</sup> OF TOTAL CATIONS	PREDICTED PERCENT-AGE OF CATION EX-CHANGE SITES FILLED WITH Ca <sup>++</sup> OR Mg <sup>++</sup> IONS	ESTIMATED Ca <sup>++</sup> + Mg <sup>++</sup> Na <sup>+</sup> (Chemical)	ESTIMATED Ca <sup>++</sup> + Mg <sup>++</sup> Na <sup>+</sup> (Montmori-llonite)	INDICATION OF CLAY DISPERSED ZONE
1- 0 - 4.0	77	98	1:0	0:1, 5:1	
1- 4.0- 6.0	43	92	9:1	3:1	
1- 6.0- 9.0	29	80	4:1	1:0	
1- 9.0-11.0	25	72	4:1	5:1	
2- 0 - 2.5	17	55	1:1	1:1, 1:0	
2- 2.5- 5.0	10	38	2:3	1:0, 7:1, 2:3	
2- 5.0- 7.5	6	28	3:7	3:1	Yes
2- 7.5- 9.0	5	25	1:3	1:0	Yes
3- 0 - 2.5	74	97	1:0	1:0	
3- 2.5- 4.0	18	64	3:2	9:1, 3:2	
3- 4.0- 6.0	6	28	3:7	1:0	Yes
3- 6.0- 9.0	11	40	2:3	5:3	
4- 0 - 2.5	12	43	2:3	3:7, 1:0	
4- 2.5- 5.0	14	50	1:1	3:7, 1:0	
4- 5.0- 6.0	21	64	3:2	4:1, 0:1	
4- 6.0	35	84	4:1	2:1, 1:3	
5- 0 - 2.5	15	51	1:1	1:1	
5- 2.5- 4.5	9	37	2:3	2:3, 0:1	Yes
5- 4.5- 5.0	5	25	1:3	2:3, 6:1	Yes
6- 0 - 2.5	11	40	2:3	1:6, 1:0, 0:1	
6- 2.5- 4.0	13	44	2:3	3:2	
6- 4.0- 6.0	10	38	2:3	4:1	
6- 6.0- 8.0	5	25	1:3	3:1	Yes
6- 8.0	22	66	7:3	1:0	
7- 0 - 2.5	71	97	1:0	1:0, 3:1, 1:9	
7- 2.5- 4.5	64	97	1:0	2:1	
7- 4.5- 6.5	14	50	1:1	5:4	
7- 6.5- 8.5	7	30	3:7	1:3	Yes
7- 8.5-10.5	4	24	1:3	7:3	Yes
7-10.5-12.5	7	30	3:7	1:0	Yes
7-12.5-13.5	15	51	1:1	9:1	
8- 0 - 2.5	80	98	1:0	4:1	
8- 2.5- 4.5	60	96	1:0	1:0, 9:1	
8- 4.5- 5.0	17	54	1:1	1:0	

SAMPLE NO.	PERCENTAGE OF Ca++ AND Mg++ OF TOTAL CATIONS	PREDICTED PERCENT-AGE OF CATION EX-CHANGE SITES FILLED WITH Ca++ OR Mg++ IONS	ESTIMATED Ca++ + Mg++ Na+ (Chemical)	ESTIMATED Ca++ + Mg++ Na+ (Montmori-llonite)	INDICATION OF CLAY DISPERSED ZONE
9- 0 - 2.5	45	92	9:1	1:5	
9- 2.5- 4.5	46	93	9:1	1:0, 1:5, 3:2	
9- 4.5- 7.0	34	84	4:1	5:1	
9- 7.0- 9.0	10	38	2:3	9:1	
9- 9.0-11.0	5	25	1:3	1:0	Yes
10- 0 - 2.5	87	99	1:0	1:0, 3:1	
10- 2.5- 4.0	68	97	1:0	7:3, 1:9	
10- 4.0- 6.0	40	89	9:1	3:1	
10- 6.0- 8.0	18	63	3:2	3:1	
10- 8.0	15	50	1:1	3:7	
11- 0 - 2.5	68	97	1:0	3:2, 1:3	
11- 2.5- 4.5	53	95	1:0	1:0, 3:1	
11- 4.5- 6.0	94	99	1:0	1:0, 9:1	
11- 6.0- 9.0	26	73	4:1	1:0	

their original arrangement to the extent that several phases of montmorillonite water layer arrangements appeared.

Reference to Figure 7 will show that the zones having calcium and magnesium cations totalling less than 10 percent generally possess illite or montmorillonite-illite mixed layer clay varieties. While these clay mineral arrangements have little influence over the existing cation population, they do appear to have a pronounced effect on the apparent lack of Na<sup>+</sup> cation exchange. Mixed layer illite-montmorillonite appears to form by alteration of montmorillonite under marine conditions (Weaver 1956). Weaver(1958) points out that this alteration is in the form of adsorption wherein the detrital clay lattices attempt to obtain equilibrium with their surrounding environment without basic alteration to the lattice structure. This brine seepage area would have undoubtedly imposed an environmental change, since the passage of brine solutions would cause changes in salinity of the soil or shale. If potassium was available, the clay layers with higher total and tetrahedral charge (mica-like basic lattice) would exchange their Ca<sup>++</sup> for K<sup>+</sup> and contract to a mica-like layer. The lower or octahedral charged layer (montmorillonite) would retain water and remain expanded. In the heavily polluted sections of the area, only small amounts of true montmorillonite are present. The chance of formation of sodium montmorillonite in the mixed-layer clay is extremely remote because the preference in cation exchange is K<sup>+</sup> Ca<sup>++</sup> Na<sup>+</sup>.

Zone 5 -4.5-5.0 has montmorillonite and montmorillonite-illite (5:1) mixed-layer clay with an indication of 60 percent replacement by Na<sup>+</sup>. In this example, the octahedral or lower charge condition probably prevails. Zone 7 - 10.5-12.5 has no free montmorillonite, only seven percent Ca<sup>++</sup> and Mg<sup>++</sup> cation availability, and about one-third of the clay fraction is 6:1 montmorillonite-illite mixed-layer which is highly crystalline. No evidence of Na<sup>+</sup> exchange exists.

Chemical analyses of potassium concentrations were not obtained, so the extent to which the clay mineral illite has lost K<sup>+</sup> by brine effects is not known.

Several significant items were noted from the clay mineral studies:

1. Assuming that the entire area to the east of the pond received brine solutions at some time or other, the highest degree of Na<sup>+</sup> adsorption coincided in the montmorillonite rich shale zones.
2. Indications are that Na<sup>+</sup> is slowly being replaced by Ca<sup>++</sup> as the exchange cation, and presumably due to flushing of Ca<sup>++</sup> from the immediate pond vicinity, there is a deficiency of Ca<sup>++</sup> cation

which further retards restoration of the area to pre-pollution conditions. A large influx of calcium would be needed to cause noticeable replacement.

3. The hydrolyzate material, typified by holes 2, 3, and the lower part of 7, have minerals that are saturated with sodium primarily because they have been exposed to highly saline waters. Calcium and magnesium already in solution and in contact with the clay mineral may replace the Na+, thus increasing the proportion of sodium in the water. Chemical analyses of water samples from holes 2, 3, and 5 show proportionately more sodium in solution than does the original brine. This would suggest that sodium adsorbed by clay minerals during the time of pond usage and maximum saturation is now being released. Zones above the passage of active water movement presently experience few leaching effects due to shale impermeability. These zones have montmorillonites which have more eagerly retained the sodium variety.

#### RESIDUAL SALT QUANTITIES IN STUDY AREA

One of the purposes of this study was to derive an estimate of the total amount of residual salt still remaining in the soil and shale under and adjacent to the pond site. All calculations and estimates are restricted to the residual salts in the Wellington shale since none of the test holes penetrated below the Wellington-Herington contact. The residual salts in this report include both soluble and leachable contaminants which are gradually being introduced into the groundwater by percolation along seepage routes.

For purposes of calculation, it was necessary to assume the following uniformities in the study area: (1) The leachable salts under the pond to a depth of nine feet (depth of hole 2 in the pond). (2) Leachable salts adjacent to the east side of the pond to a depth of nine feet and a distance of 200 feet. (3) The leachable salt quantities downslope from the brine pond to a depth of eight feet and a distance of 200 feet. (4) A bulk soil density of  $2.4 \text{ gms/cm}^3$  was assumed in all calculations. (The mass of soil for each zone was derived by the product of the volume of the material in cubic centimeters and a soil density constant of  $2.4 \text{ gm/cm}^3$ ). (5) The mass was subsequently divided by 40 to obtain the number of 40 gms samples contained in each section. A constant designation of grams of leachable salt in 40 gms of soil was used to determine the total quantity of dissolved solids in each section. (6) Because the concentration of leachable salts varied greatly throughout the area, a constant for each zone based on the average weight of leachable salts in a 40 gm sample was used.

The total dissolved solids was then converted into tons of leachable and soluble salts. The calculated amounts of residual salts for each zone are presented in Table IV.

The calculations indicate that a minimum of 434 tons of soluble and leachable salts remain in the immediate vicinity of the brine pond. The pond during its use as a brine disposal facility received over 32,000 tons of soluble salts which is over 98 percent more than the amount presently remaining in the top 9 feet of the Wellington shale in the pond area. Most of the salt originally placed in the pond probably escaped down drainage and penetrated below the Wellington-Herington contact. Therefore, the 434 tons of salt still remaining (about 1.4 percent of the original) in the upper few feet of the formation actually represents a considerable amount of original residual salts retained in the upper portion of the shale under the pond.

The fact the use of the surface pond for brine disposal has been discontinued for at least eight years demonstrates that leaching of soluble salts is a very slow process. At the present rate of leaching of salts in the Wellington shale under the brine pond, it was calculated that over 40 but less than 80 years would pass before the soil and shale would return to a normal soluble salt concentration level. This prediction is based on the following data and limitations: (1) The chemical composition of the water analyzed from test hole 2. (2) A water table increment of one foot in thickness and a leaching front of 200 feet. (3) A daily subsurface water volume of 472,300 cm<sup>3</sup> moving an average of one inch per day. (4) Brine composition of 22,800 mg/l. (5) This hypothetical determination assumes a normal rainfall cycle.

It is felt that subnormal seasonal precipitation retards the speed of leaching considerably and hence increases the number of years for the pollutants to dilute by at least one-half. Several test holes were dry, which lends support to the belief that the water encountered in the test holes is vadose and cannot be considered as part of a homogeneous zone of saturation below the water table. This would indicate the presence of an intermittent leaching front with low volume movement. Therefore, it is more likely that leaching is entirely dependent upon meteoric water as a flushing mechanism, and that under periods of deficient precipitation, seepage movement of leachates decreases.

#### EVALUATION OF LABORATORY TECHNIQUES USED IN THIS STUDY

Comparison of the chemical analyses and X-ray diffraction studies of clay minerals with respect to their coordinate value in future pollution investigations is extremely difficult to assess, particularly on the basis of one study.

TABLE IV QUANTITATIVE SUMMARY ON CALCULATED ESTIMATES  
 OF RESIDUAL DISSOLVED SOLIDS IN BRINE POND AREA  
 (All Data Values were Taken from Average Con-  
 centrations for Described Area)

AREA	CALCULATION DEPTH (Ft)	VOLUME OF CONTAMINATED MATERIAL (Cu Ft)	AVERAGE WEIGHT OF LEACHABLE SALT PER 40 GMS OF SAMPLE (Gms)	WEIGHT OF LEACHABLE TOTAL DISSOLVED SOLIDS (Gms)	WEIGHT OF LEACHABLE TOTAL DISSOLVED SOLIDS (Tons)
1. Under Source Ponds	9	248,400	0.80	336,714,000	370
2. Adjacent to the East Side of Pond (Dimension 200')	9	54,000	0.10	9,182,000	20
3. Downslope From Brine Pond (Dimension 200')	8	160,000	0.15	40,530,000	44
TOTALS		462,400		386,426,000	434

Chemical analyses measure occurrence of soluble and leachable ions and provide information of residual salt quantities and lanes of seepage movement. However, appraisalment of environmental factors which control brine seepage behavior patterns are often not found by chemical analyses.

This study shows that subtle variations in cation concentrations can be analyzed more accurately by use of X-ray diffraction techniques and subsequent studies on ion exchange. It is apparent from this investigation that cation adsorption activity by clay minerals depends not only upon the concentration of each cation, but also general clay mineral properties, such as ion exchange capacities, the natural adsorption cation, and the crystalline quality of the clay mineral lattice.

In this investigation, predicted cation exchange position occupancy held 50-60 percent agreement between chemical analyses and X-ray diffraction techniques. The authors believe that  $\text{Ca}^{++} + \text{Mg}^{++}/\text{Na}^{+}$  ratios of 4:1 and 5:1, or 1:3 and 3:7 can be considered in fairly reasonable agreement.

Since pollution patterns can change rapidly within a short distance, ten percent range of agreement between the two methods indicate that clay mineral studies provide a promising tool in tracing cation transportation rates, particularly those of sodium or calcium.

The basic limitation imposed on data interpretations in this study is the lack of pre-pollution information on natural water quality of the spring seeps and the normal  $\text{Na}^{+}$  montmorillonite population in the clay. It is important to know the pre-pollution environment so that the stage of contamination can be determined. The data in this report does not determine the location of the main pollution peak after eight years of surface pond dormancy. Indications are that the larger concentrations of leachable salts have progressed beyond hole 7. Also, much of the leachable salts have penetrated below the Wellington-Herington contact and are not considered in this study.

The following is an evaluation of the various laboratory techniques used in this project as to their applicability in future brine pollution work:

1. Chemical analyses are absolutely essential to quantitative study of oil field brine pollution and associated residual salt estimations. They should not be relied upon in tracing small pollution veins unless the sampling intervals are accordingly small.
2. Chloride analysis is the most useful single determinant in detecting the presence of oil field brine solutions. For a single brine pollution source, chlorides may be sufficient to pinpoint the location and extent of pollution. In mineralized water and multi-

source pollutants, chloride analyses may leave an incomplete picture unless the associated cation concentrations ( $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^{+}$ ) are also determined.

3. The application of cation adsorption studies appears to be extremely useful in brine affected soil and shale, but should not be used for quantitative studies. Clay mineral studies can give much information on the environmental characteristics of the pollution media. In this study cation exchange information helped explain some of the apparent differential transportation rates of ions in brine seepage solutions. The use of clay minerals in limestone or sand formations may be of little value due to the general deficiency of clay-sized particles.

In summation, a complete chemical analysis of samples of water and soils, including the physical characteristics of the bedrock medium, are necessary to determine the extent, effect, and composition of oil field brine contaminants. The methods all have limitations and the investigator must carefully select the techniques needed to solve a specific problem.

#### MECHANICS OF BRINE SEEPAGE MOVEMENT

Routes selected by brine constituents through shale during active seepage movement away from surface pond sources are primarily dependent upon differential permeability and fracture pattern characteristics of the underlying formations through which the solutions pass. These directional percolation paths of contaminants are also controlled by local bedrock structure and areal variations in formation lithology. Thus, seepage probably moves along the paths of least resistance in a shale medium.

In the study area, lateral and diagonal seepage movement is substantial although vertical percolation allowed much brine to escape through fractures in the Herington limestone below the Wellington-Herington contact. The Wellington formation in this area possesses two shale zones which differ lithologically and to some extent structurally. The presence of a dispersed clay zone along the approximate contact between the two shales was indicated by the chemical analyses. This dispersion zone represents the path of maximum contamination in that  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  comprise less than ten percent of the total cation concentration. Dispersion extends to the depth of present seepage movement in holes 2, 5, 6, and 7 but is not quite as deeply developed in hole 3. The dispersed zone is shown in Figure 8 and cross sections depicting the apparent  $\text{Ca}^{++} + \text{Mg}^{++}/\text{Na}^{+}$  ratios are presented in Figures 9 and 10.

The chemical water analyses indicate a predominantly southeast seepage direction along a line connecting holes 2 and 7. The highest chloride concen-

POSITION OF CLAY DISPERSION ZONE BASED  
ON PERCENTAGE OF CALCIUM AND MAGNESIUM  
CATIONS

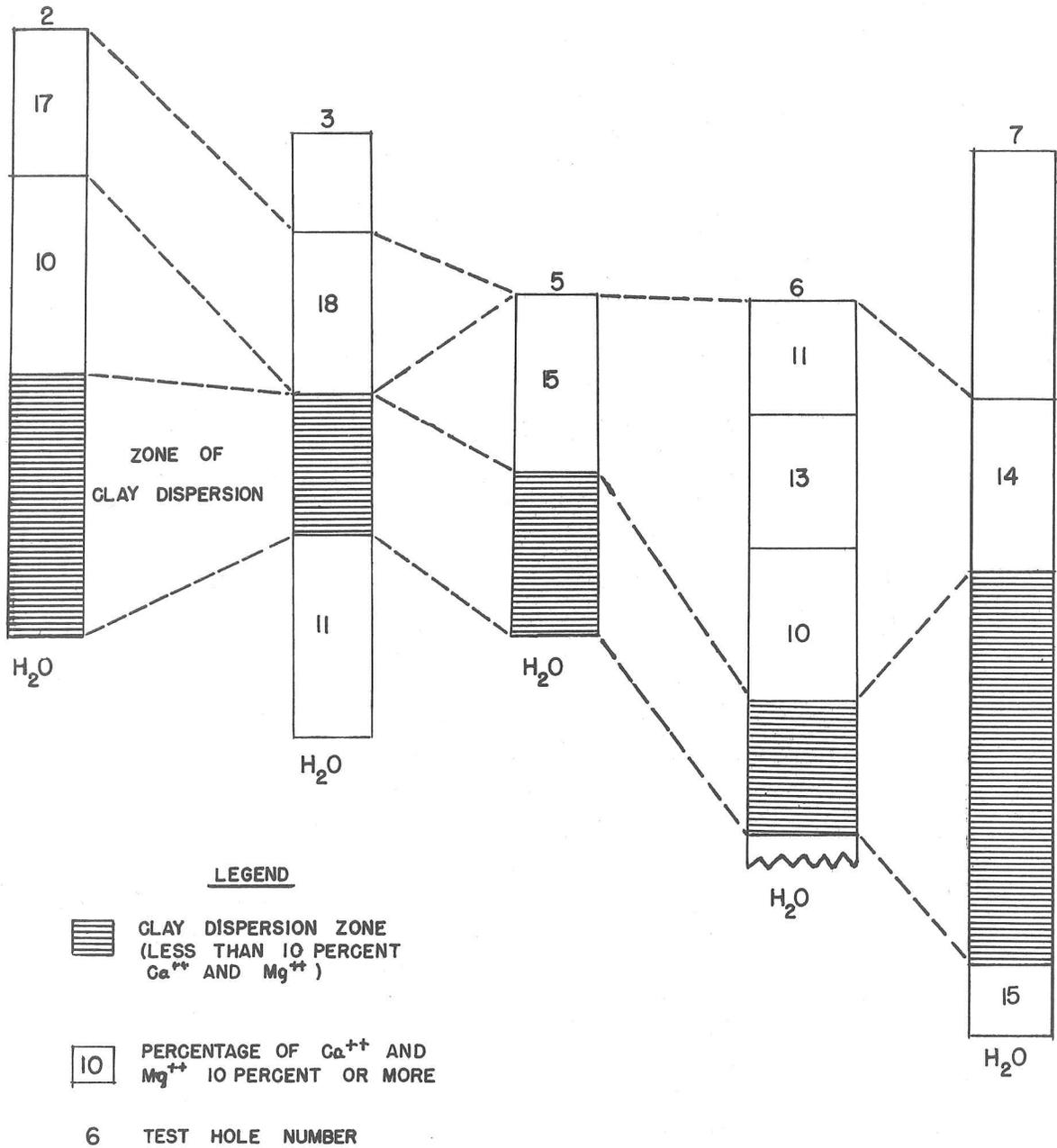
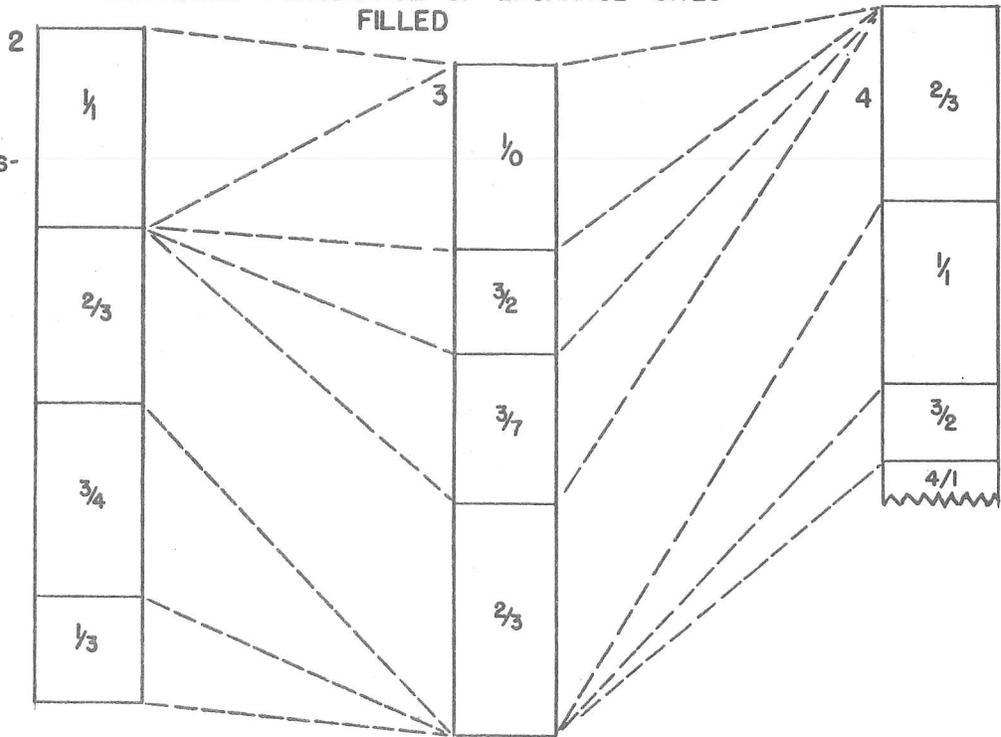


FIGURE 8

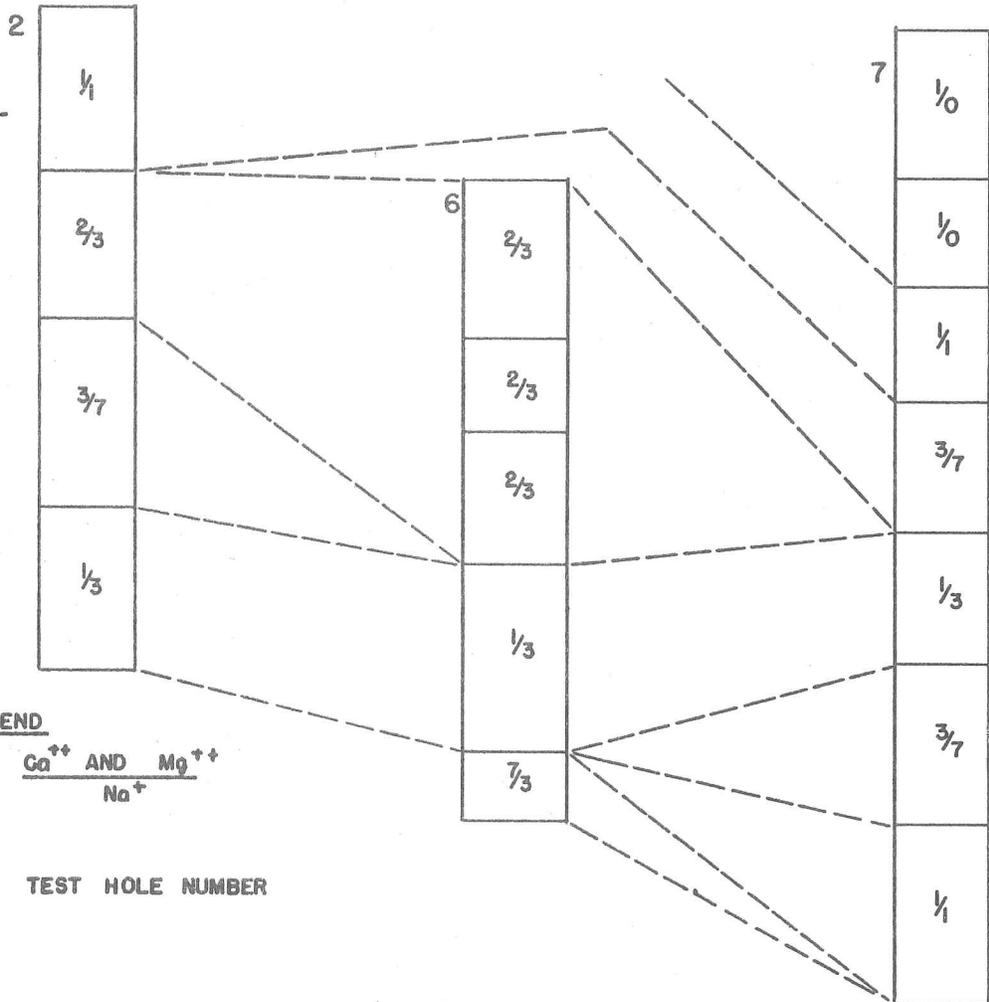
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ENVIRONMENTAL HEALTH SERVICES  
OIL FIELD SECTION  
RESIDUAL SALT STUDY

RATIO OF CALCIUM AND MAGNESIUM TO SODIUM WITH RESPECT TO THE ESTIMATED PERCENTAGE OF EXCHANGE SITES FILLED

A) WEST TO EAST CROSS SECTION



B) NORTHWEST-SOUTHEAST CROSS SECTION



LEGEND

$\frac{1}{3}$

$\frac{Ca^{++} \text{ AND } Mg^{++}}{Na^{+}}$

4

TEST HOLE NUMBER

FIGURE 9

RATIO OF CALCIUM AND MAGNESIUM TO SODIUM WITH RESPECT  
TO ESTIMATED PERCENTAGES OF EXCHANGE SITES  
FILLED

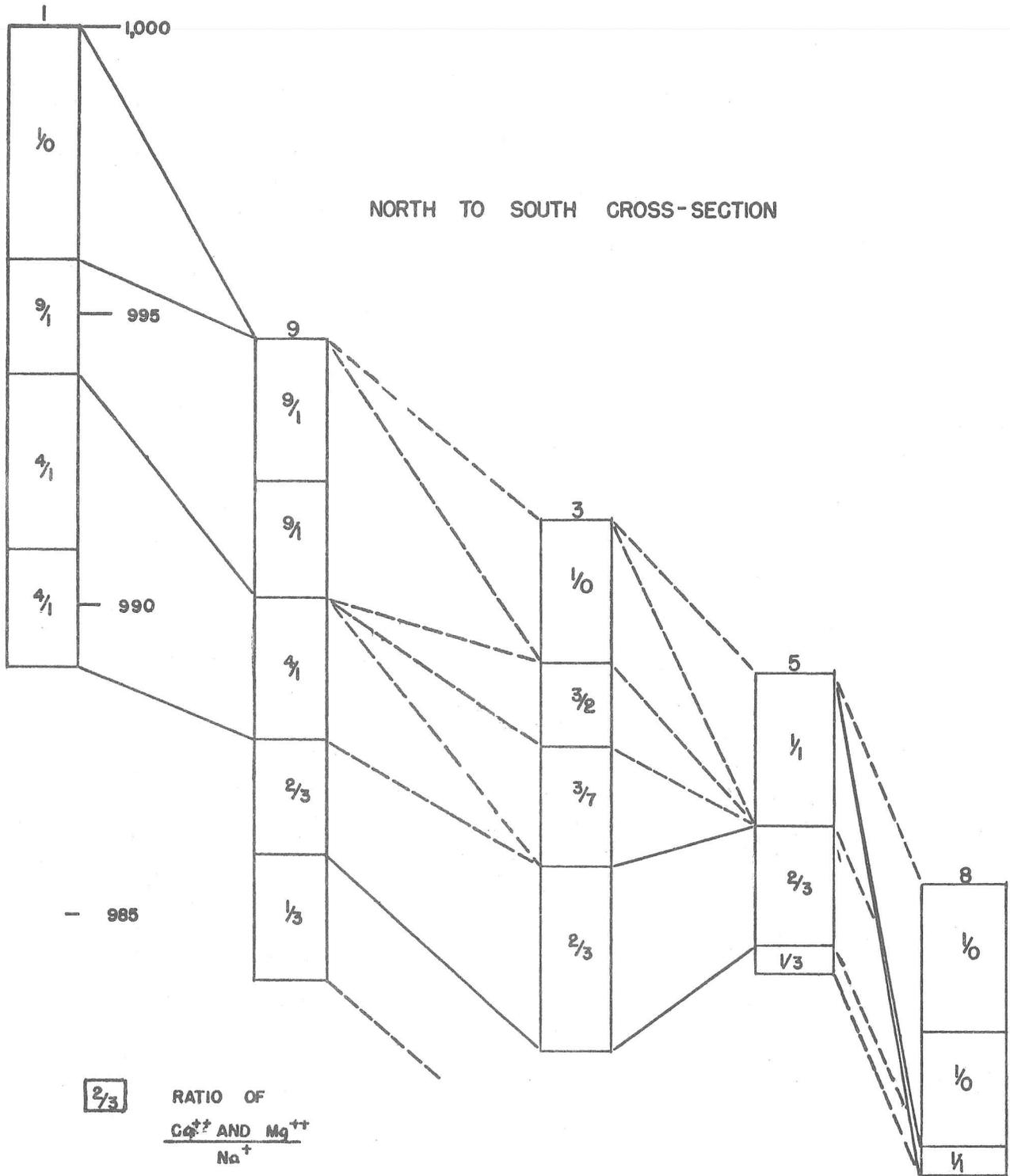


FIGURE 10

tration of 24,500 mg/l was found in the water sample collected from hole 7. Holes 4, 5, and 6 are positioned near this line and had highly contaminated water, indicating that pollutants from the pond have formed a seepage fan which encompasses much of the southeast quadrant downslope from the pond. Seepage, leaving the pond during its active use, had evidently formed a lateral front which roughly conformed to the north-south pond dimension. This resulted in more extensive lateral coverage at or near the surface by contaminants than would have been probable in a vertical seepage environment of unconsolidated sediments where the bottom of the pond would serve as a point seepage source.

Seepage from dike leaks and pond overflow conditions have probably contributed some pollution to the surface soil zone area in holes 3, 4, 5, and 8. In the case of holes 5 and 8, the upper two feet of each hole contained the greatest concentration of mineralization.

The preceding description of seepage movement is probably restricted to shale sections and is not believed to be applicable to other types of sediments. There is evidence that the seepage in this area has formed a system of small semi-isolated pockets of contaminants which are temporarily restricted from further movement. The chemical constituent strength of each pocket is dependent upon the accessibility to diluting water. If the fresh water source is constant, the concentration of contaminants will be weaker than in occluded areas where water movement is restricted to saturated seepage. Most of the shale sample analyses are examples of saturated seepage conditions. This comparison seems reasonable after a decade of leaching where no active brine source is present.

The cross sections of the polluted shale (Figures 9 & 10) show the apparent selectivity of brine seepage. Hole to hole correlation of  $Ca^{++} + Mg^{++}/Na^{+}$  ratios could not be made which demonstrates the lack of homogeneity of the seepage front. The northwest-southeast line is undoubtedly the most descriptive of the seepage movement. Seepage from the pond at a time when the source was active probably did not diminish in strength appreciably within the boundaries of the study area. Natural water volumes from springs and seeps are not sufficient to permit much dilution. Recent observations indicate that this volume has decreased from the time when the pond was in active use. At that time, the area reportedly had several active springs which are now dry. There is no known record of the chemical quality of the spring water prior to surface pond brine disposal.

Observations of brine pollutants indicate that seepage should lose its contaminating potencies according to a transcendental function of distance and time away from the source (Figures 11 and 12). As time passes, the amplitude of maximum concentration will shift from the pond source to progressively distant points in the direction of optimum seepage movement. Indications are that hole 7 represents one of the higher potency levels, and

THEORIZED STRENGTH OF CHLORIDE CONCENTRATION  
WITH DISTANCE FROM BRINE SOURCE

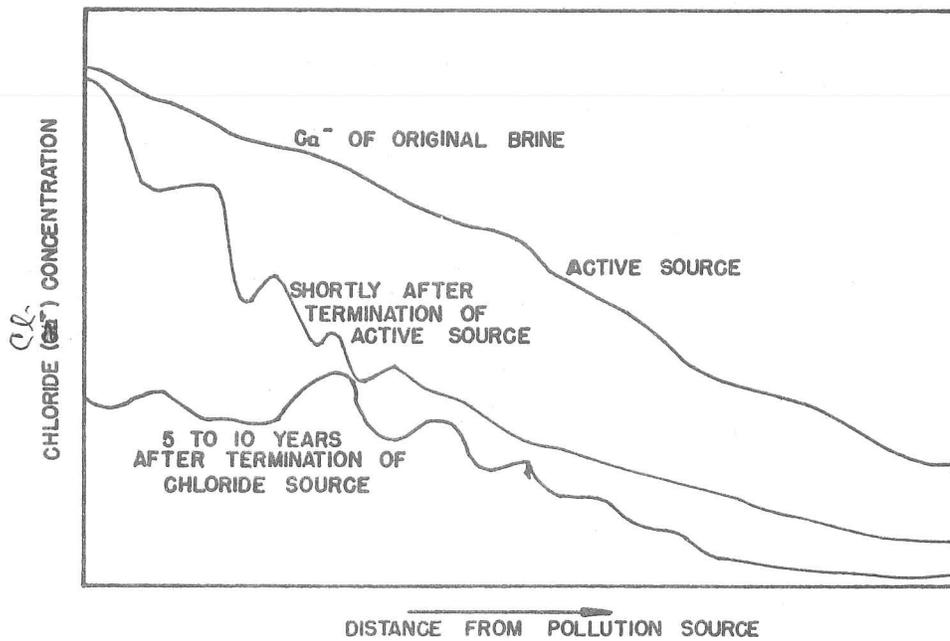


FIGURE 11

STRENGTH OF CHLORIDE CONCENTRATION IN WATER  
SAMPLES AWAY FROM HOLE 2

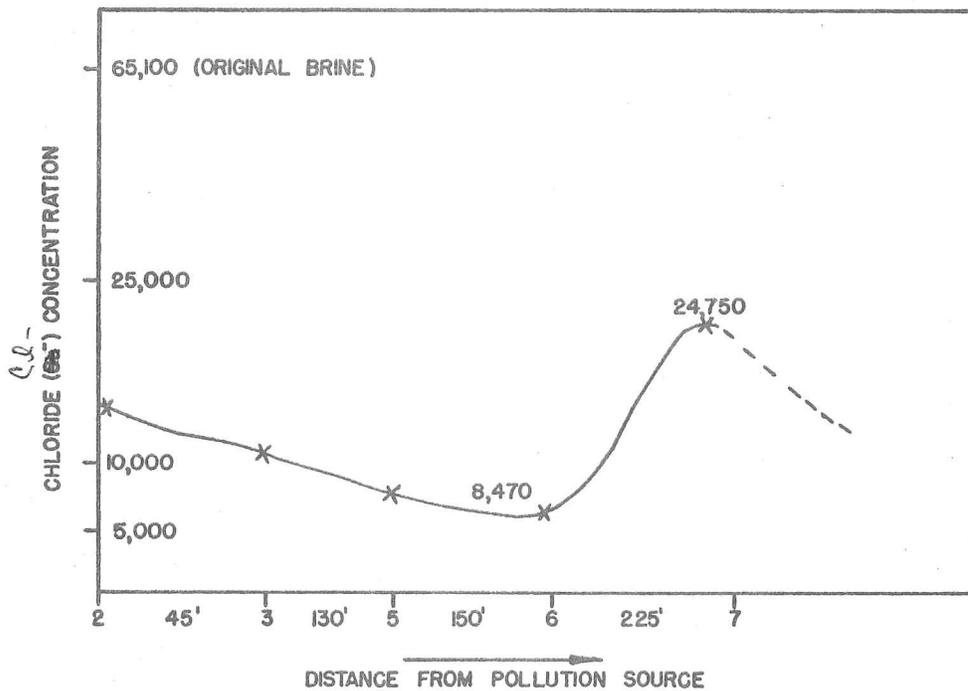


FIGURE 12

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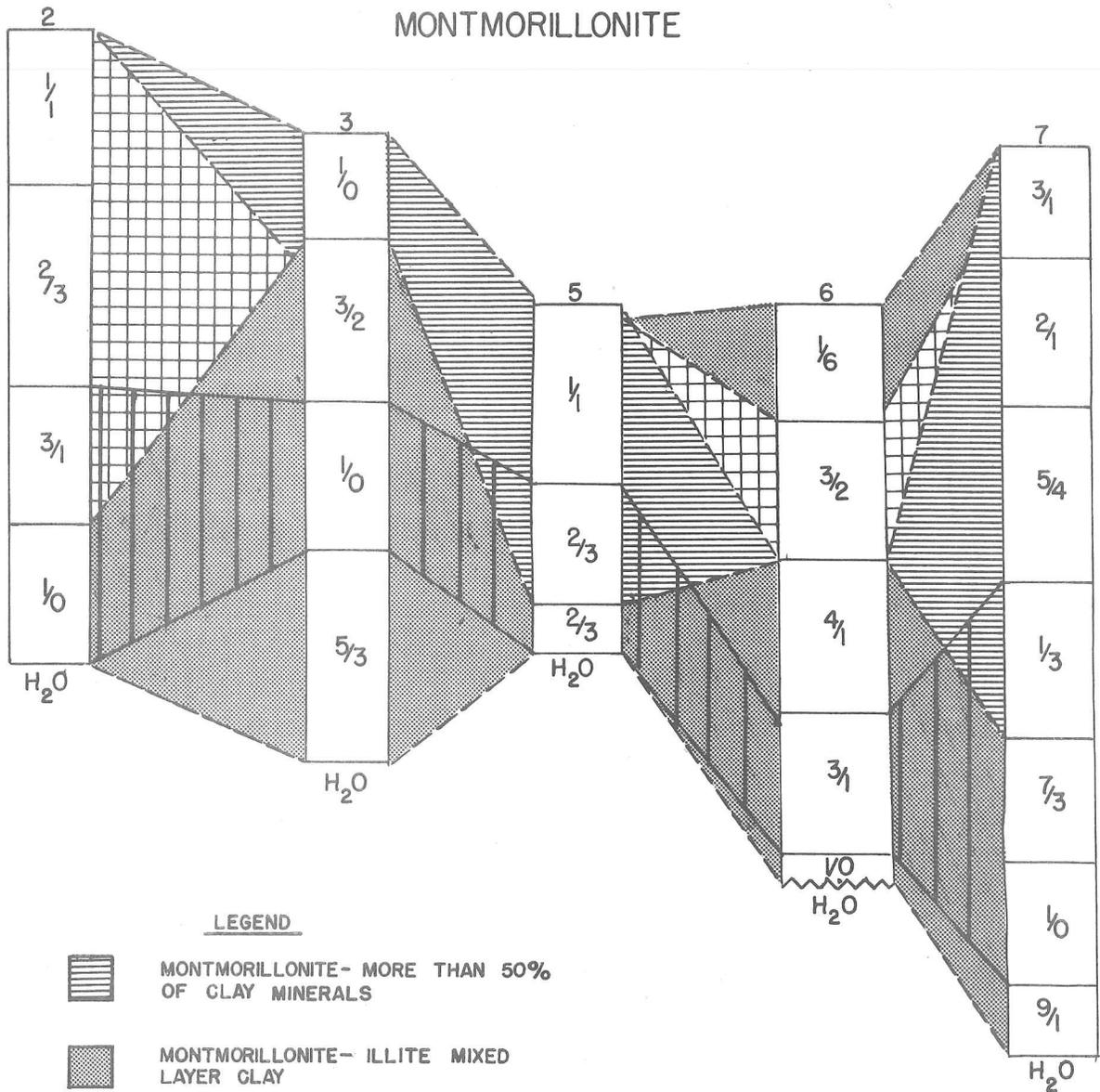
probably the major one for the study area. Seepage from the pond probably created a series of potency maxima in the direction of the pollution spread. The weaker routes of seepage will probably become non-existent or at least static with respect to distance away from the pond because they are an expression of fringe movement. The lower zones of test hole 1 are possibly an example of this. Areas adjacent to the maximum seepage line (hole 2 through hole 7) are probably controlled by the same drainage system and will demonstrate the same general relationship of pollutants with distance.

## EFFECT OF ENVIRONMENT ON DILUTION

Attenuation of the brine pond contaminants evidently occurs very gradually by a complex intervention of several factors:

1. Dilution appears to be the prime mechanism of weakening concentrations of brine contaminants with distance during and after discontinuing usage of a surface pond for salt water disposal. Dilution effectiveness is dependent upon the original concentration of the brine and the amount of subsurface water available for transportation away from the source. In this study area the amount of vadose water available is a dilution factor since the subsurface water flow is from low volume springs. Dilution in the study area is also closely related to the number and size of fractures available for seepage movement. There is little question that fractures in the Herington limestone have served as paths for vertical drainage for much of the total seepage. The lower shale of the Wellington in test holes 2, 5, and 8 is calcareous, which is indicative of the gradual change to the underlying limestone.
2. The role of sorption by clays is of lesser importance than dilution in alteration of brine pond contaminants. The amount of  $\text{Na}^+$  involved in cation exchange reactions by montmorillonite or other clay minerals possessing water layer ion exchange properties is limited by clays' inherent preference for  $\text{Ca}^{++}$  as an exchange cation. The deficiency of montmorillonite in the lower shale in comparison to the less adsorbic clay minerals also limits adsorption of sodium. Most of the  $\text{Na}^+$  is retained in a leachable and readily soluble form with localized participation as an inter-layer cation in exchange position. Evidence indicates that  $\text{Na}^+$  replacement takes place in isolated environments where impervious strata blocks further seepage movement. If the  $\text{Na}^+$  cation concentration is greater than 90 percent and there is at least 60 percent of exchange sites available, sodium can be exchanged for the normal

CROSS-SECTION OF POLLUTED ZONES WITH CLAY DISPERSION  
 ZONES SUPERIMPOSED ON ESTIMATED RATIOS OF CALCIUM  
 AND MAGNESIUM TO SODIUM AS ADSORBED CATIONS IN  
 MONTMORILLONITE



LEGEND

 MONTMORILLONITE- MORE THAN 50% OF CLAY MINERALS

 MONTMORILLONITE- ILLITE MIXED LAYER CLAY

 ILLITE- MORE THAN 50% WITH LITTLE MIXED-LAYER CLAY

 ZONE OF < 10%  $Ca^{++}$  AND  $Mg^{++}$  CATION POPULATION (CLAY DISPERSION ZONE)

$\frac{2}{3}$  ESTIMATED  $\frac{Ca^{++} \text{ AND } Mg^{++}}{Na^{+}}$  ADSORPTION BY MONTMORILLONITE

6 TEST HOLE NUMBER

FIGURE 7

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 RESIDUAL SALT STUDY

divalent cation, usually  $\text{Ca}^{++}$  or  $\text{Mg}^{++}$ . Because the samples used are composites of one to four feet of hole, small pockets of high  $\text{Na}^+$  concentrations are probably masked by a chemical analysis of soluble cations. The X-ray diffraction patterns of clay samples taken from the effected strata tend to show that one such interval might contain several localized  $\text{Na}^+$  phases.

## CONCLUSIONS

An attempt has been made during this study to relate new applications of established analytical techniques to brine pollution problems. While the authors are cognizant of the limited area studied, the data compiled does indicate that most cause and effect relationships in brine pollution mechanics are complex. Reasonable explanations of the source, directional alteration, and dilution of such contaminants cannot always be determined by dependence upon the chloride concentration of the groundwater and soil samples.

Several observations of conclusive importance were noted during the course of the investigation.

1. While brines generally have predominant concentrations of sodium and chloride ions in solution, they also carry other ions which contribute heavily to the total dissolved solids transported by seepage to groundwater-bearing formations.
2. The calculated quantities of soluble and leachable salts remaining in the area of the disposal pond show that the return of the subsurface water and soil to a natural or pre-pollution level of mineralization is a very slow process and may encompass several decades. The above statement holds particular credence for areas with intermittent or limited groundwater and seepage flow, especially where the formation is of low permeability.
3. Seepage from the brine pond follows routes of sufficient permeability and apparently does not form a homogeneous pollution front. Data from this study indicate that polluted groundwater is often separated from the source by areas left untouched by polluting solutions, thus creating a network of pollution zones which may intersect where formation fracture conjugates occur.
4. Dissolved salts carried by the soil water usually follow the general laws governing standard hydrology. However, because of physical and chemical phenomena and dispersion, the movement of soluble pollutants is slow in relation to the water flow rate. The resulting displacement causes the contaminated zone to grow.

5. It was observed that adsorption of ions by clay minerals evidently occurs, but has very little effect on brine seepage volume or chemical characteristics during times of source activity. Adsorption may occur to the extent that retardation of Na<sup>+</sup> leaching occurs after the brine source has been discontinued. This possibly explains the finding that Na<sup>+</sup> concentrations proportionately lags the Cl<sup>-</sup> concentration. There also are indications that brine seepage causes the crystallinity of clay minerals to alter, thus affecting their ion exchange capacities. However, the overall role of clay minerals and organic compounds in brine seepage alteration and movement was not determined by this study.
6. The chemical analyses of all major ion concentrations is invaluable in determining the quantities of pollutants in water and soil material and in ascertaining the defined or approximate routes from the pollution source.

At present, most governmental agency investigations into the sources of oil field pollution ceases when the apparent source is indicated by comparison of chloride analyses. Therefore, much valuable information is not obtained for application in situations where the source or mechanism is not so easily located or explained. Although chloride analyses are invaluable for a single pollution source, they are not by themselves a terminal analytical tool when more than one source exists in the same area and needs to be identified. This is particularly true where the aqueous components involved are mixed with groundwater and the polluted water represents only a percentage of the mixture.

By compiling case histories of brine pollution under different environmental conditions, patterns can be established which will aid in complex pollution investigations, particularly those from suspected subsurface sources.

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APPENDIX  
LITHOLOGIC DESCRIPTION OF SAMPLES

TEST HOLE NUMBER	DEPTH OF ZONE (Feet)	TYPE OF FORMATION MATERIAL	COLOR	NATURE OF MATERIAL LARGER THAN SILT SIZE
1.	0.1- 4.0	Soil and Shale	Buff	Sand, Medium to Fine
	4.0- 6.0	Shale	Brown - Buff	Fine Sand
	6.0- 9.0	Shale	White	Fine Sand, a few Chert Fragments
	9.0-11.0	Shale	White - Light Tan	Sugary Fine Sand
2.	0 - 2.5	Shale	Tan	Sand - Medium to Fine, a few Chert Fragments
	2.5- 5.0	Shale	Tan - Grey Tan	Sand - Fine to Medium, Pieces of Limestone
	5.0- 7.5	Shale	Light Tan - Grey	Fine Sand, Angular Pieces of Chert
	7.5- 9.0	(Calcareous) Shale	Light Grey	Fine Sand, Large Pieces of Rounded Limestone
3.	0 - 2.5	Soil and Shale	Buff	Fine Sand
	2.5- 4.0	Shale	Grey - Tan	Fine Sand
	4.0- 6.0	Shale	Grey - White	Fine to Medium Sand
	6.0- 9.0	Shale	Grey Tan - Ochre	Fine Sand, Large Rounded Pieces of Limestone
4.	0 - 2.5	Soil	Grey Buff	Fine Sand
	2.5- 5.0	Shale	Buff	Fine Sand, Few Pieces Angular Limestone
	5.0- 6.0	Shale	Tan Grey - Brown	Fine Sand, Abundant Rounded and Angular Fragments of Limestone
	6.0	Shale	Ochre - Tan	Fine Sand, Larger Rounded Limestone Fragments
5.	0 - 2.5	Soil and Shale	Buff	Fine Sand
	2.5- 4.5	Shale	Light Brown - Tan	Fine Sand, Angular Chert Fragments
	4.5- 5.0	Shale	Light Grey	Fine Sand, Rounded Chert Fragments
6.	0 - 2.5	Soil	Chocolate - Buff	Fine Sand, Small Limestone Pebbles
	2.5- 4.0	Shale	Light Tan - White	Fine Sugary Sand Angular Chert Pieces
	4.0- 6.0	Shale	Tan - Brown	Fine to Medium Sand
	6.0- 8.0	Shale	Buff - White	Fine Sugary Sand
	8.0-	Shale	Ochre - Tan	Fine Sand, Larger Rounded Limestone Fragments

APPENDIX  
LITHOLOGIC DESCRIPTION OF SAMPLES

TEST HOLE NUMBER	DEPTH OF ZONE (Feet)	TYPE OF FORMATION MATERIAL	COLOR	NATURE OF MATERIAL LARGER THAN SILT SIZE
7.	0 - 2.5	Soil	Chocolate - Buff	Fine Sand, Small Pebbles
	2.5- 4.5	Shale	Buff - Brown	Fine Sand
	4.5- 6.5	Shale	Grey Tan - Buff	Fine Sand, Larger Rounded Limestone Fragments
	6.5- 8.0	Shale	Tan - Ochre	Fine Sand, Abundant Angular Pieces of Limestone
	8.5-10.5	Shale	Tan	Rounded Limestone Fragments, Fine Sand
	10.5-12.5	Shale	Tan	Fine Sand, Chert Fragments
	12.5-13.5	Shale	Tan	Fine Sand
8.	0 - 2.5	Soil and Shale	Tan - White	Medium Sized Sand Few larger pieces
	2.5- 4.5	Shale	Tan	Fine Sand with Rounded Chert and Limestone Fragments
	4.5- 5.0	Shale	Tan	Sugary Fine Sand
9.	0 - 2.5	Soil	Buff	Very Fine Sand
	2.5- 4.5	Shale	Tan - Buff	Fine Sand
	4.5- 7.0	Shale	White - Light Buff	Fine Sugary Sand
	7.0- 9.0	Shale	Tan - Ochre	Fine Sand, Large Pieces of Chert and Limestone
	9.0-11.0	(Calcareous) Shale	Grey to Grey White	Mostly Larger Pieces of Limestone
10.	0 - 2.5	Soil and Shale	Buff	Fine to Medium Fine Sand
	2.5- 4.0	Shale	Buff	Fine to Medium Fine Sand
	4.0- 6.0	Shale	Tan - Brown	Fine Sand, Larger Limestone Pebbles
	6.0- 8.0	Shale	White	Fine Sand, Angular Limestone Fragments
	8.0	Shale	White - Light Tan	Fine Sugary Sand, Angular Fragments of Chert
11.	0 - 2.5	Soil	Grey - Buff	Very Fine Sand
	2.5- 4.5	Shale	Tan - Brown	Mostly Angular Pieces of Limestone
	4.5- 6.0	(Calcareous) Shale	White - Light Tan	Mostly Angular Pieces of Limestone
	6.0- 9.0	(Calcareous) Shale	Tan - Grey Tan	Crystalline Grey Limestone Fragments