A NEW CLAY STABILIZER FOR USE IN COMPLETION FLUIDS

Joseph E. Thompson - Product Development Supervisor
Mike O. Smith - Senior Sales Engineer
Mike A. Smith - Area Engineer
G. E. Braun - Geologist
Titan Division, Dresser Industries, Inc.

INTRODUCTION

Formation protection, the prevention of damage to sensitive zones, is designed to prevent loss of permeability and porosity.[1] Clays that can produce significant damage can be classified into two general categories: the migrating clays, kaolinite and illite; and the swelling clays, such as smectite[2] and a variety of chlorites. Iron chlorite clays are acid sensitive and can produce precipitates in conjunction with acid treatments. The control of these chlorites will not be covered in this presentation.

Movement of fluids in the formation capillaries, ion balance of connate water, pH change, clay particle surface area in relation to mass (Table 1)[1], particle configuration, chemical elements (Table 2)[1], and the manner in which deposition has occurred must be considered. The potential for damage to the formation can be determined by the types of clay (Table 2) and the location of these clays within the formation matrix[3]. The capacity of clays to exchange cations is also a significant factor (Table 3).[4]

Analyses to identify and locate existing clay minerals were performed on several cores from various formations in different areas. The types of tests used were X-ray diffraction, thin section, and scanning electron microscope (SEM). The effect of fluids on these samples were evaluated via core flow analysis.

Controlling the swelling, sloughing, and migration of clays and fines by a chemical additive at low concentrations (1 to 10 gallons per thousand) has proven to be an effective and economical method of minimizing formation damage.

DEVELOPMENTAL RESEARCH

Review of Clay Stabilization Mechanisms

The oil industry customarily has utilized various clay control additives to prevent formation damage caused by the hydration (swelling) or migration of clays. These additives include inorganic metal cations[5,6,7], (e.g. Zr^{+4}, Al^{+3}, Ti^{+4}, et al.) synthetic polyacrylate polymer types, quaternary ammonium salts, and petroleum heavy ends.[8]

Clay stabilization using metal cations is accomplished by ion exchange with cations in the clay mineral lattice[5,9,10]. These types of clay control agents are limited in application due to their general incompatibility with most polymers used to viscosify completion fluids. This incompatibility is particularly apparent in crosslinked stimulation fluid systems because the metal cations interfere with the crosslinking mechanism of the fluid.

Quaternary ammonium salts are also used as clay control agents. They function in approximately the same manner as the metal cations. Synthetic polyacrylate polymers have been used as clay control agents in completion techniques. The polyacrylate function is two-fold. First, the polymer's cationic character under mildly acidic conditions exchanges with lower charged cations located on the clay mineral lattice. Secondly, because this polymer is a long chain molecule (due to molecular weight), it lines the pore wall which insulates the clays involved in the pore channels.

Clay damage control through physical isolation of formation clays has been achieved by using petroleum heavy ends[8,11] and other similar materials. This method of clay stabilization has shown a degree of effectiveness. A major problem in using this method is due to economics. A number of clay stabilizers have been reported to fuse migrating clays. These systems are used primarily in sand consolidation, hydraulic fracturing and acidizing applications.

TESTING

The basic tools used in the clay control additive research were core flow and column flow analyses. Recommended API procedures were followed in core handling, cleaning and testing. Petrographic studies of core by thin section analysis, SEM, and X-ray diffraction methods supplemented this testing. Thin section studies were used to examine the pore channels of the core to be tested. Utilization of SEM techniques identified the clays in the pore channels and characterized their orientation. X-ray diffraction methods described the type and concentration of crystalline compounds in each core. Figures 1 through 10 illustrate thin section petrographic analysis and SEM photographs of formation core as presented in this paper. The attached appendix has been provided to show a comprehensive review of our petrographic analysis on the formation cores under study. Table 4(4) presents results of the X-ray diffraction analysis of the samples.

Core flow evaluation followed a standard test procedure. The core flow analysis was conducted using a modified liquid permeameter. A schematic of the liquid permeameter system and the core test cell used in this analysis is presented in Figures 11 and 12.

The following procedure was used for clay stabilizer core flow analysis:

1. The core was saturated in standard brine (5% W/W [weight] NH_4Cl in deionized water).

2. The saturated core was weighed and the pore volume of the core was determined from the difference in the weight of saturated core and dry core.

3. The saturated core was placed in a Hassler cell in the permeameter, and suitable confining pressure (1500 psi) was applied outside the core sleeve to ensure linear flow through the core.

4. A 5% W/W NH_4Cl was pumped through the core at constant pressure to establish the initial permeability of the core sample. Once the initial permeability was established, or enough 5% NH_4Cl was injected, the test was routed to one of two different paths depending on whether a water damage test was planned or a clay stabilizer was being tested.

5. In a situation requiring a water damage test, once initial permeability was established, several pore volumes (>200 P.V.) of water were injected to see if water would damage (reduce the permeability of) the core.

6. Clay stabilizer was tested after initial permeability established a fixed volume (∿10 P.V.) of treatment fluid.

NOTE: Typical test core dimension was 0.5 cm thick X 2.54 cm long X 2.54 cm wide.

Initial core flow analysis, including a comparison of our clay control additive product vs. 2% W/W KCl, was conducted along with compatibility tests with the clay additive at 0.2% V/V (volume) in 2% W/W KCl solution. This research was done using Berea sandstone as the test media. Following the initial analysis, clay stability tests were run in a variety of actual formation core. The formations presented in this paper include:

1. Morrow formation
2. Burgess formation
3. Yates formation

An analysis of each of these formations' crystalline composition is shown in Table 4.

SUMMARY OF RESULTS

A summary of the core test in Berea sandstone is shown in Figures 13 through 16. The initial test in each formation evaluation was performed to determine if the core would damage. An initial permeability was established with a standard brine (5% W/W NH_4Cl). The standard brine was followed immediately (Figure 13) by the addition of deionized water. Data shown in Figure 13 indicate Berea core can be damaged by following this test sequence.

The second test (shown in Figure 14) was to evaluate 2% W/W KCl performance in Berea sandstone. Our test results show that 2% KCl can provide protection to the core, but subsequent flow of water will damage the core. The Dresser Titan clay control additive (CLA-BAN*) was tested to evaluate its performance in Berea sandstone. Our test results (shown in Figure 15) indicate that this additive protects Berea core equally as well as 2% W/W KCl. Furthermore, the new additive continues to protect the core while water is injected. Compatibility tests (Figure 16) indicate the Dresser Titan clay control additive is also effective when used in conjunction with KCl. Other laboratory studies have shown the clay additive to be compatible with most stimulation fluids including the crosslinked polymer systems.

Evaluation of the Morrow Formation sample (Figures 17 and 18) was challenging in that it was composed of varying permeability strata. Thin section analysis confirmed that the sample used for testing was interlayered with a more porous quartz section. Sampling of this formation was restricted to that portion of the core sample containing the majority of the clay components. The test conducted on that portion of the formation shows that a 22% damage (with fresh water) to the formation could be achieved. In some tests formation cores were saturated initially with 1.0% V/V clay control additive. A comparison of 5% W/W NH_4Cl vs. 1.0% V/V clay control additive indicated the core saturated in the Titan clay stabilizer had a more effective stability response (Figure 18). We found that, with the exception of the damage test shown in Figure 17, all other core samples (taken from the same core plug) saturated in NH_4Cl solution could not be pumped through within the pressure limitations of the core test equipment. This suggests that the standard brine concentration (5% W/W NH_4Cl) is not sufficient to protect this core from formation damage.

The Burgess Formation sample damage test (Figure 19) shows more than 40 percent damage by water flow. Data shown in Figure 20 indicate that after the initial permeability was established (∿400 P.V.), the treatment with the clay control additive maintained and apparently improved the permeability. Approximately 200-300 pore volumes of standard brine were required to stabilize flow to 5% W/W NH_4Cl in both the damage test and in the stability test. A minimum of five constant flow measurements were taken before the damaging fluid (H_2O) or treatment fluid (1.0% V/V CLA-BAN) was pumped through the core. Subsequent tests on samples from the same formation have shown essentially the same results. We suspect the large initial volume of NH_4Cl solution required to stabilize flow was due to insufficient saturation of this "tight" core sample.

Evaluation of the Yates Formation (Figures 21 and 22) showed the core sample contained mixed layers of chlorite-montmorillonite. The damage test indicated 30 percent damage by water. Considering the amount of this swellable clay present (∿19% W/W), we anticipated high damage. However, a review of the literature revealed that swelling clays often are not involved in the flow matrix and are occa-

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* Proprietary Product of Dresser Industries, Inc., Titan Division

sionally incapsulated by materials[4] composed in the rock. Core stability tests show no damage to water after treatment with the clay control additive.

APPLICATION

The clay controlling material referred to in this paper is being used in virtually all areas of Dresser Titan stimulation services. Use varies from load fluids for perforating to flush fluids. It is recommended 0.1 to 1.0 percent clay stabilizer be used in the load fluids. This additive has been recommended to prevent skin damage to the producing zones.

Satisfactory results have been produced from both weak and strong acid treatments containing the clay additive. The protection of clays as stated by Holcomb[3], is enhanced in low pH systems. The concentrations used in acid are as low as 0.2 percent by volume. The flush systems for both acid and fracturing treatments consist normally of 0.2 percent V/V clay control additive.

Fracturing treatments have been performed in various formations using CLA-BAN as a clay control additive. These systems include:

1. Water based fracturing systems
    a. gelled fluids
    b. complexed fluids
    c. foamed fluids
    d. load and flush fluids
2. Acid based fracturing systems
    a. weak and strong acids
    b. gelled acid fluids
    c. foamed acid fluids
    d. load and flush fluids

Usage and Application In the West Texas - New Mexico Area

Dresser Titan Division has been active in the use of the new clay control additive in stimulation fluid systems in the West Texas-New Mexico area. These areas include:

1. Southeast New Mexico
2. Permian Basin
3. Delaware Basin
4. Abilene Area
5. Sonora Area
6. San Angelo Area
7. Snyder Area
8. Levelland Area

The Canadian, South Texas, Oklahoma, and Kansas areas are also involved in the use of this chemical. This clay control additive also has potential use in drilling fluids and tertiary recovery systems.

Formations in the West Texas-New Mexico area that have been treated with Dresser Titan's clay control additive are the:

MISSISSIPPIAN
CANYON
STRAWN
GARDNER SAND
GRAY SAND
PALO PINTO
QUEENS
SEVEN RIVERS
DEAN SAND
CLEARFORK
DRINKARD
CANYON REEF
LEONARD
WOLFCAMP
MORROW SAND
PENNSYLVANIAN LIMES
SAN ANDRES
GREYBURG
YATES
ELLENBURGER
SPRAYBERRY SANDS
DEVONIAN
EUMONT

CONCLUSIONS

1. Laboratory studies demonstrate this new additive's effectiveness as a clay control agent.

2. The effectiveness of this clay stabilizer will be influenced, to a degree, by the type and amounts of clay compounds present in a given formation. For this reason, flow tests should be conducted on those formations known to be sensitive to damage to determine the optimum concentration of the Titan additive required.

ACKNOWLEDGEMENT

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APPENDIX

PETROGRAPHIC ANALYSIS

Other tools used in this research included petrographic analysis of the core prior to the flow test to characterize the formation and the orientation of clays involved in the flow matrix. This analysis combined scanning electron microscope, (Figure 1) thin section, and X-ray diffraction techniques.

BEREA SANDSTONE DESCRIPTION

Generally speaking, Berea sandstone (Figures 2 and 3) is a light tan, thinly bedded (∿2 - 5 mm), medium indurated quartz arenite. The mineralogy of Berea core was elucidated by three different techniques. These were: thin section micrographs, scanning electron microscopy and X-ray diffraction spectrometry.

The Berea sandstone is a fine grained, well sorted quartz containing minor feldspar (plagiodoze and K-feldspar), rock fragments, chert, kaolinite and a trace of detrial muscovite. The quartz is angular to subrounded, ranges in size from 0.05 to 2 mm and commonly contains minor inclusions (rarely large zircon inclusions are present). The quartz grains are generally single crystalline but not uncommonly polycrystalline. The feldspars are commonly altered to clay (kaolinite), subangular to rounded and range in size from 0.05 to 1.5 mm. Rock fragments and chert are subangular to subrounded and range in size from 0.03 to 2 mm. The primary cement appears to be clay (Figures 2 and 3) with minor carbonate (Figure 4). The rock has a very open framework with primary and secondary pores, the latter possibly due to carbonate dissolution. The rock shows evidence of deformation including bent detrial muscovite, fractured grains and common extinction exhibited by quartz.

MORROW FORMATION DESCRIPTION

The Morrow formation sample (Figures 5 and 6) is a fine-coarse grained, well sorted (within laminae) quartz arenite cemented with carbonate, quartz and clay. The quartz is medium-coarse grained, generally has overgrowths, contains inclusions and ranges in size up to 0.5 mm. The rock is thinly laminated with secondary pores formed from carbonate dissolution. Secondary pores are commonly partially clay filled.

Organized spherical carbonate structures are common and are frequently associated with clay fragments in secondary pores. Rock fragments are present and accumulate in the finer laminae.

The primary cements are calcite (usually poikiloptically encloses framework grains), quartz and clay. The pores are generally plugged with calcite, clay or quartz overgrowths, but some large (secondary) pores remain open.

Mineral Type	Visual Estimate Volume %
Quartz	75
Carbonate	10
Clay	10
Pores	5

BURGESS FORMATION

Burgess formation rock (Figures 7 and 8) is a medium grained, medium-well rounded, medium-well sorted argillaceous quartz arenite with fossil and rock fragments. The quartz grains are "floating" in a clay-carbonate cement. The quartz grains range in size up to 0.5 mm, are commonly included with opaque material (pyrite), and infrequently are zircon. Rock fragments range in size up to ∿ 3 mm, consist of clay ± chert , and are commonly squeezed between quartz grains. Minor detrial chlorite containing pyrite inclusion is also present. Pyrite is also common in the clay-carbonate cement.

The pores are essentially clogged with clay-carbonate with no visible voids. Relatively large areas of clay-carbonate suggest clogging of secondary pores. Secondary pores are probably the result of carbonate dissolution.

Mineral Types	Visual Estimate Volume %
Quartz	65
Carbonate	15
Clay	15

YATES FORMATION

Yates Formation rock (Figures 9 and 10) is a fine grained, well-sorted, argillaceous-feldspathic quartz arenite cemented with clay-carbonate. Both the quartz and feldspar grains are "floating" within the fine grained carbonate ± clay with grain to grain contact relatively uncommon. The quartz is subangular to subrounded, ranges in size up to ∿ .2 mm and may contain inclusions. The feldspar (microcline and plagioclase) is angular to subangular, ranges up to .2 mm in size and is commonly altered to clay. Detrial muscovite is present in minor amounts and is commonly bent indicating post depositional compaction. The pores are generally plugged with clay-carbonate, but rarely unclogged, isolated pores are present.

Mineral Type		Visual Estimate Volume %	
Quartz		55	
Feldspar		10	
	Carbonate		25
Matrix		35	
	Clay		10
Pores		Tr.	
Muscovite		< 1	
Zircon		Tr.	
Tourmaline		Tr.	

TABLE 1—SURFACE AREAS*

QUARTZ	0.15 cm^2/gm
KAOLINITE	22 m^2/gm
SMECTITE	82 m^2/gm
ILLITE	113 m^2/gm

* Values Determined by Nitrogen Adsorption Analysis.

TABLE 2—MAJOR CLAY MINERAL FAMILIES AND THEIR IMPORTANT CHEMICAL ELEMENTS

CLAY MINERAL	IMPORTANT ELEMENTS
KAOLINITE	Al Si O H
SMECTITE (Montmorillonite)	Na Mg Ca Al Si O H (± Fe)
ILLITE	K Al Si O H
CHLORITE	Mg Fe Al Si O H

TABLE 3—CATION EXCHANGE CAPACITY OF SELECTED CLAYS AND SAND

Clay	Range of Cation Exchange Capacity
Montmorillonite	80 to 150
Illite	10 to 40
Kailonite	3 to 15
Chlorite	10 to 40
Sand (2 to 62 microns)	0.6

TABLE 4—X-RAY DIFFRACTION ANALYSIS

Mineral Type	Berea Sandstone (Out Crop) Amherst, Ohio	Morrow Formation 6912 - 6913' Harper Co., Oklahoma	Burgess Formation 1068 - 1069' Rogers Co.,Oklahoma	Yates Formation 2689 - 2694' Ward Co., Texas
Quartz	75-80	90	45-50	46
K-Feldspar	2- 5	-	Tr	4
Plagioclase	-	-	-	5
Siderite	1- 2	-	-	-
Calcite	-	5	10-15	<1
Dolomite	2- 5	-	-	15
Halite	-	-	-	<1
Kaolinite	2- 5	Tr	2- 5	
Chlorite-Montmorillonite * (Tosudite)	-	-	-	19
Illite - Mica	2- 5	-	2- 5	10
Chlorite	-	5	5-10	-
Montmorillonite	-	-	2- 5	-
Pyrite	-	-	1- 2	-

* Regularly interstratified chlorite-montmorillonite. The relative abundance of each component is not known.

Analyst: Dr. G. E. Braun

FIGURE 1—A SCANNING ELECTRON MICROGRAPH OF BEREA SANDSTONE SHOWING VERMICULAR KAOLINITE OCCUPYING PORE SPACE BETWEEN FRAME-LEFT AND CARBONATE ON QUARTZ AT FAR UPPER LEFT CORNER.

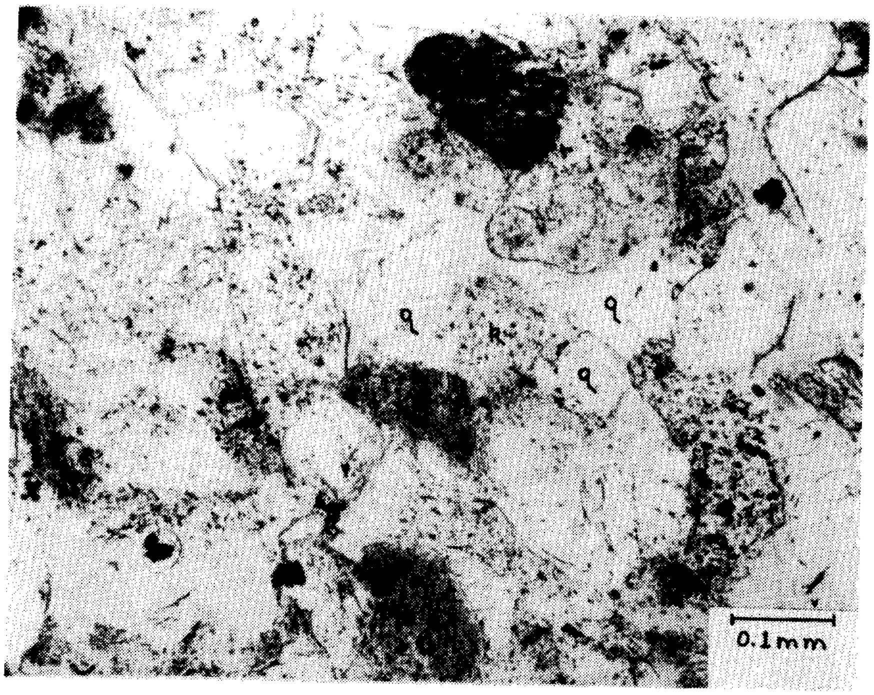


FIGURE 2—PHOTOMICROGRAPH OF THIN SECTION OF BEREA SANDSTONE SHOWING FRAMEWORK GRAINS WITH A THIN COATING OF CLAY. MOST QUARTS GRAINS CONTAIN INCLUSION. DARK GRAIN AT TOP CENTER IS A ROCK FRAGMENT. A KAOLINITE PARTICLE IS PRESENT AT CENTER. Q = QUARTZ, K = KAOLINITE. PLANE POLARIZED LIGHT.

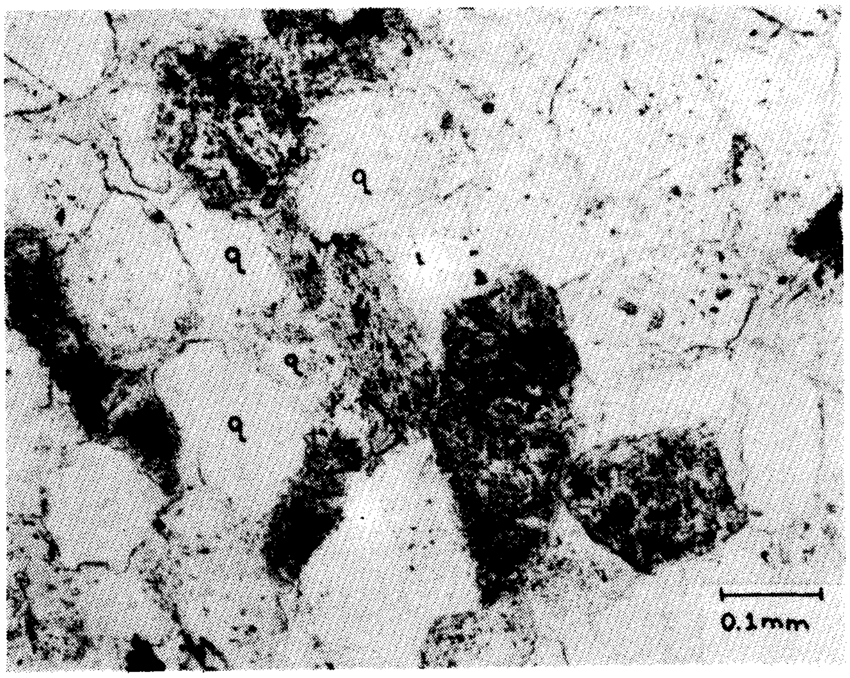


FIGURE 3—PHOTOMICROGRAPH OF THIN SECTION OF BEREA SANDSTONE SHOWING FRAMEWORK QUARTZ AND KAOLINITE. MOST QUARTZ GRAINS HAVE A THIN COATING OF CLAY. A KAOLINITE PARTICLE IS PRESENT AT CENTER LEFT. Q = QUARTZ, K = KAOLINITE. PLANE POLARIZED LIGHT.

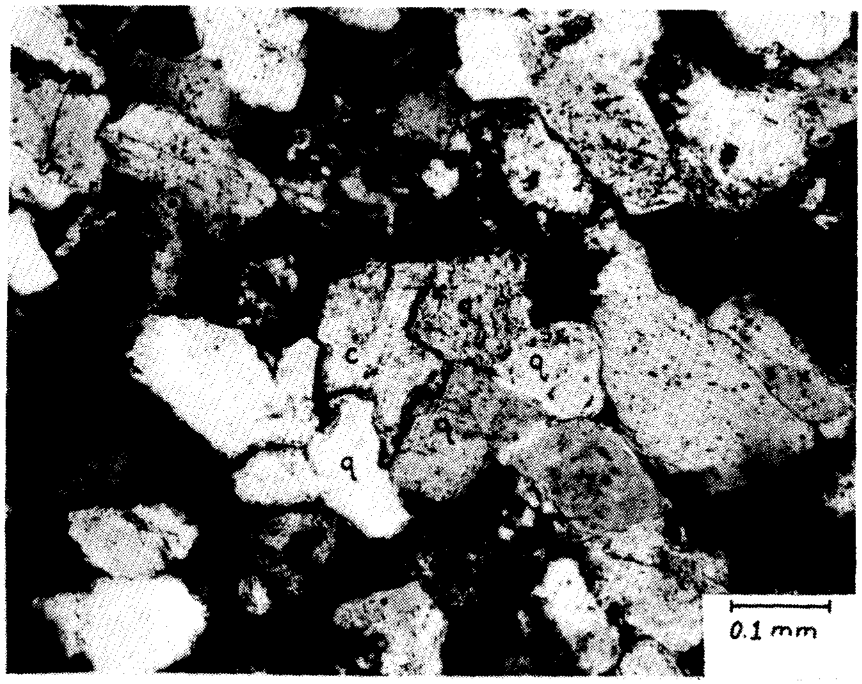


FIGURE 4—PHOTOMICROGRAPH OF THIN SECTION OF BEREA SANDSTONE SHOWING FRAMEWORK QUARTZ CEMENTED BY CARBONATE. Q = QUARTZ, C = CARBONATE. CROSS POLARIZED LIGHT.

FIGURE 5—SCANNING ELECTRON MICROGRAPH OF MORROW FORMATION (6913′) SHOWING AUTHIGENIC CHLORITE.

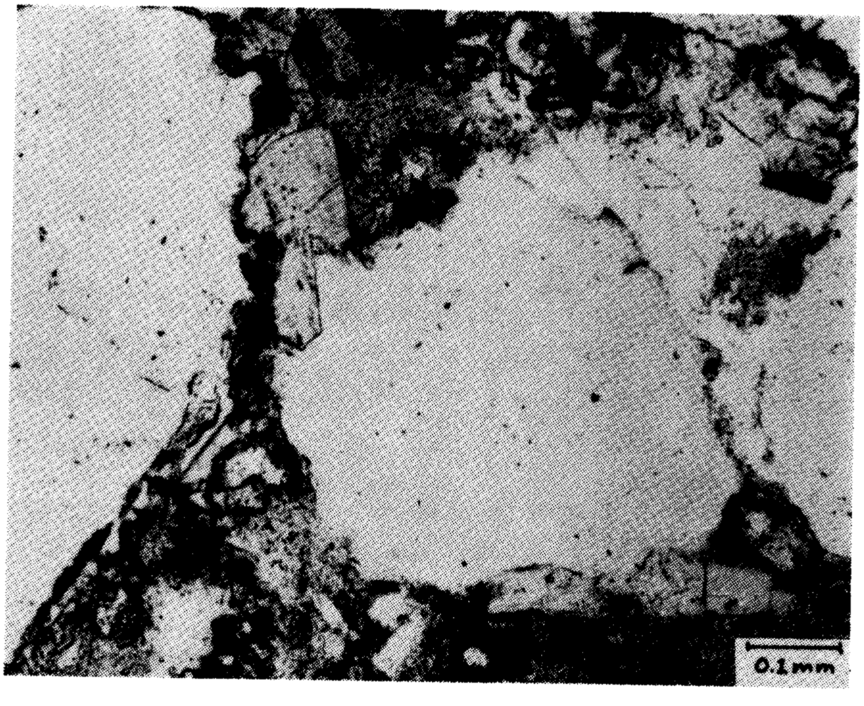


FIGURE 6—THIN SECTION OF MORROW FORMATION (6912′ - 6913) SHOWING LARGE POSES SURROUNDED BY CALCITE AND CLAY. PLANE POLARIZED LIGHT.

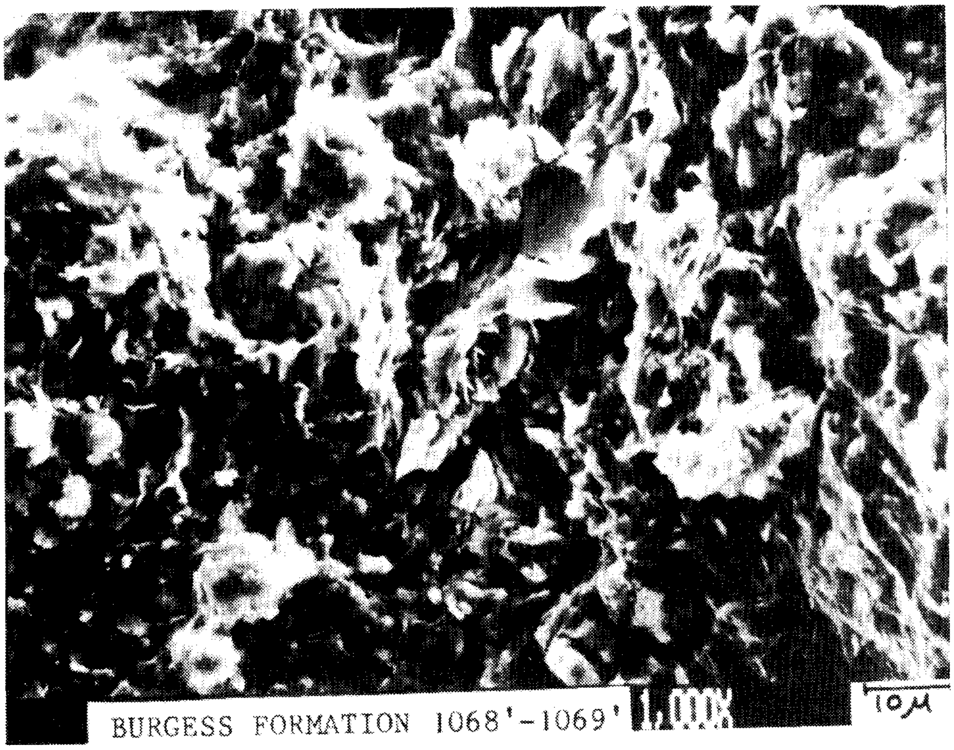


FIGURE 7—SCANNING ELECTRON MICROGRAPH OF BURGESS FORMATION (1068' - 1069') SHOWING DENSITY PACKED CHLORITE.

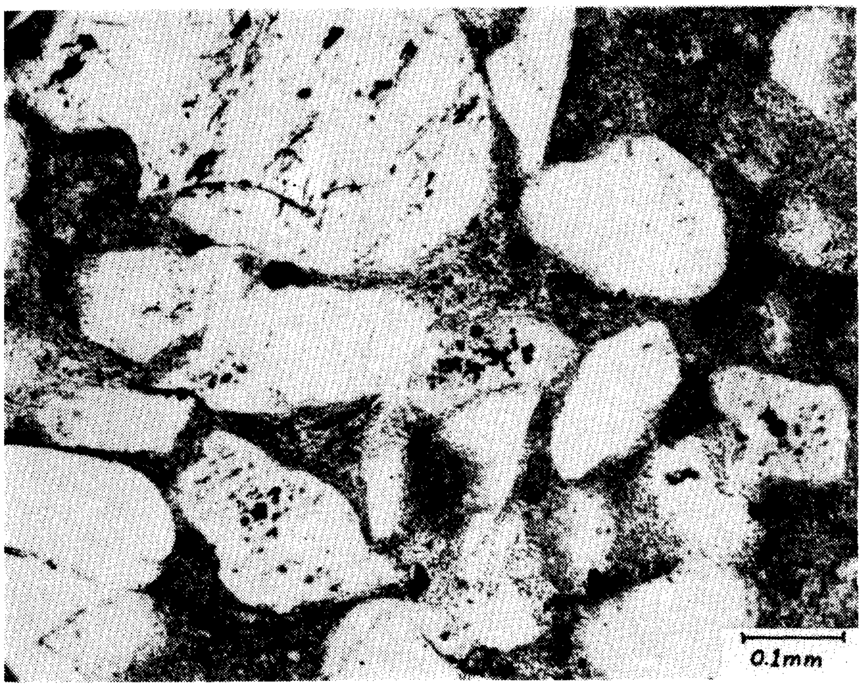


FIGURE 8—THIN SECTION OF BURGESS FORMATION (1068' - 1069') SHOWING QUARTZ AND DETRIAL CHLORITE "FLOATING" IN CLAY-CARBONATE CEMENT. PLANE POLARIZED LIGHT.

FIGURE 9—SCANNING ELECTRON MICROGRAPH OF YATES FORMATION (2689′ - 2694′, 0, #4) SHOWING AUTHIGENIC QUARTZ PARTIALLY COATED WITH CHLORITE-MONTMORILLONITE.

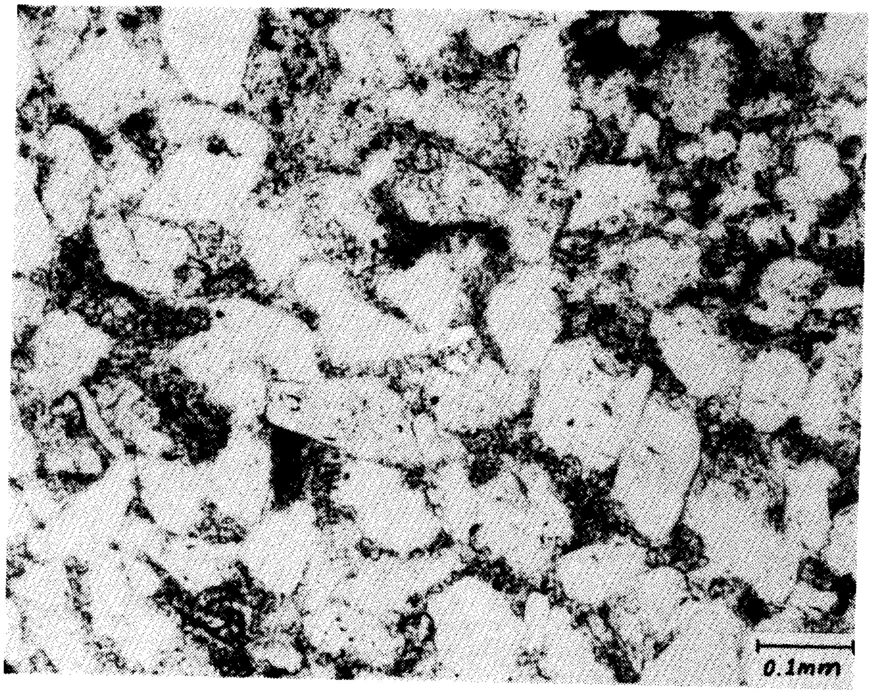
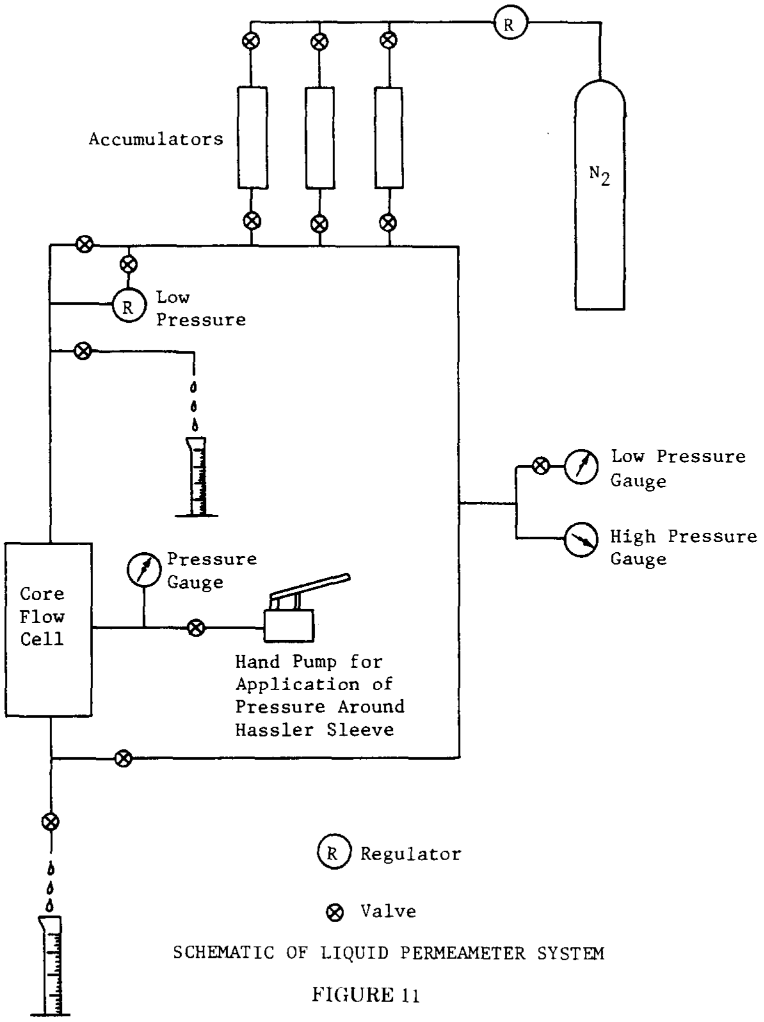


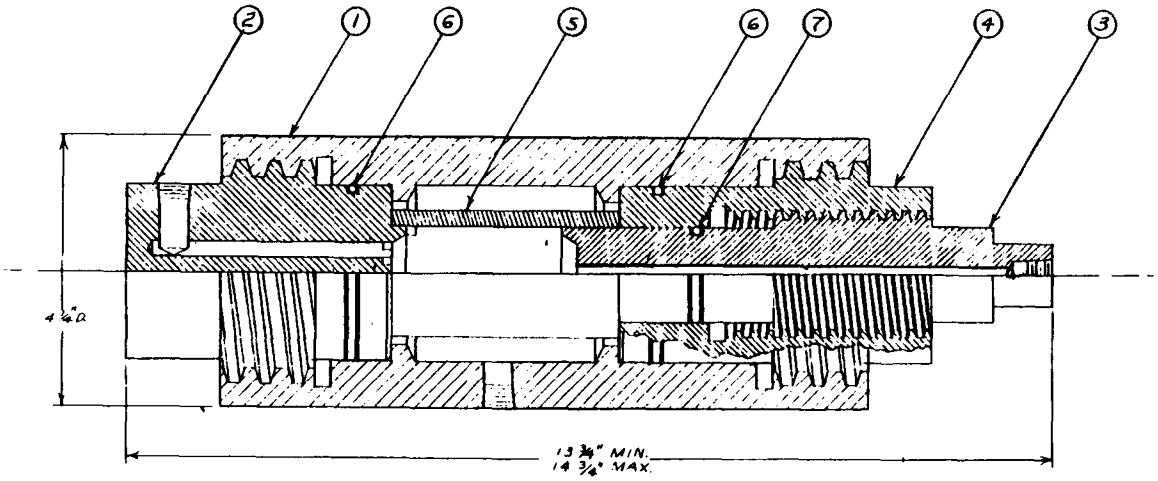
FIGURE 10—THIN SECTION OF YATES FORMATION (2689′ - 2694′, 0 #4) SHOWING QUARTZ GRAINS “FLOATING” IN CLAY + CARBONATE CEMENT. PLAN POLARIZED LIGHT.



SCHEMATIC OF LIQUID PERMEAMETER SYSTEM

FIGURE 11

CORE TEST CELL



PARTS LIST			
1	BODY	5	SLEEVE
2	STATIONARY PLUG	6	O-RING
3	ADJUSTABLE PLUG	7	O-RING
4	BUSHING		

FIGURE 12

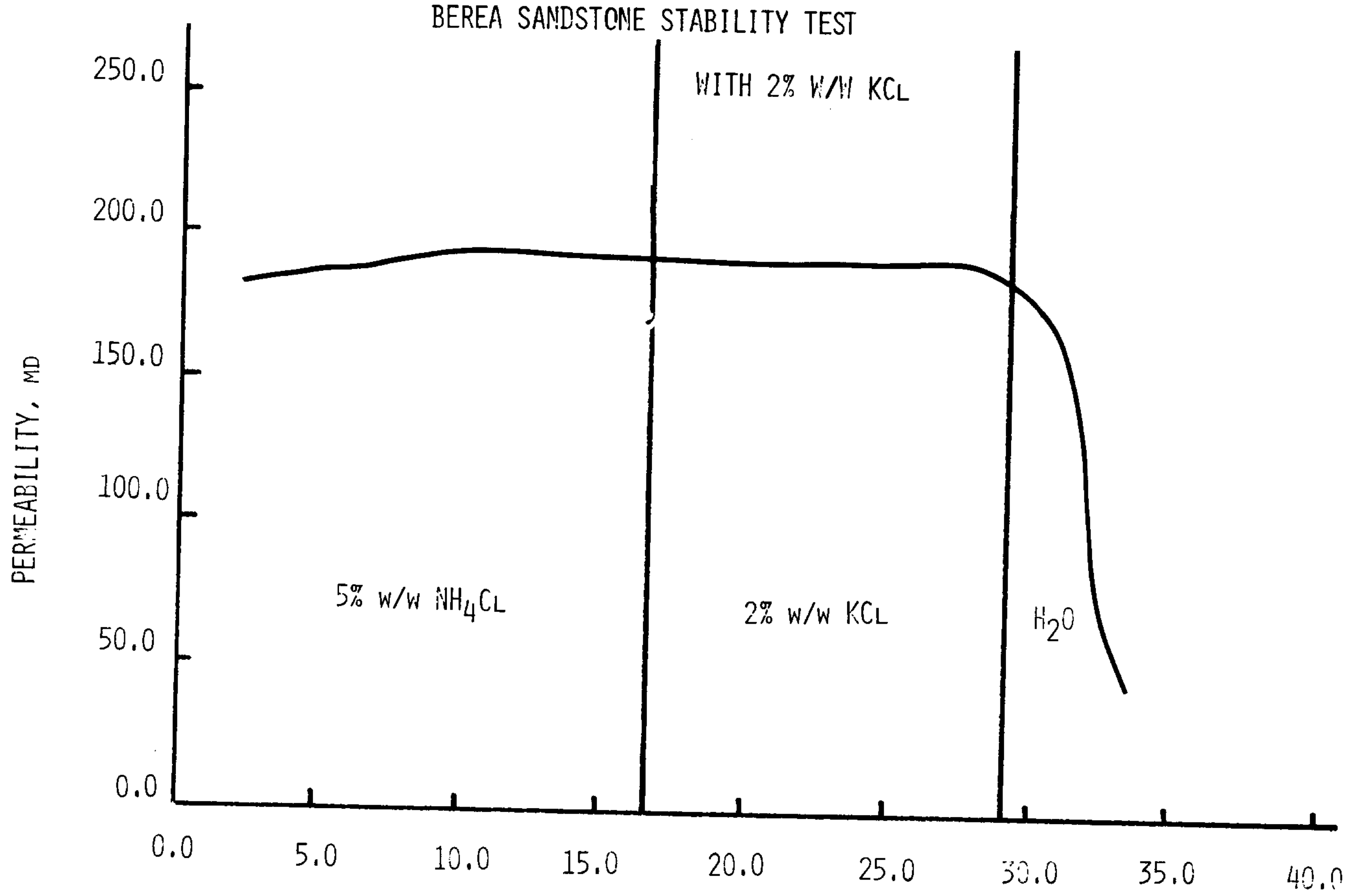


FIGURE 14—PORE VOLUME

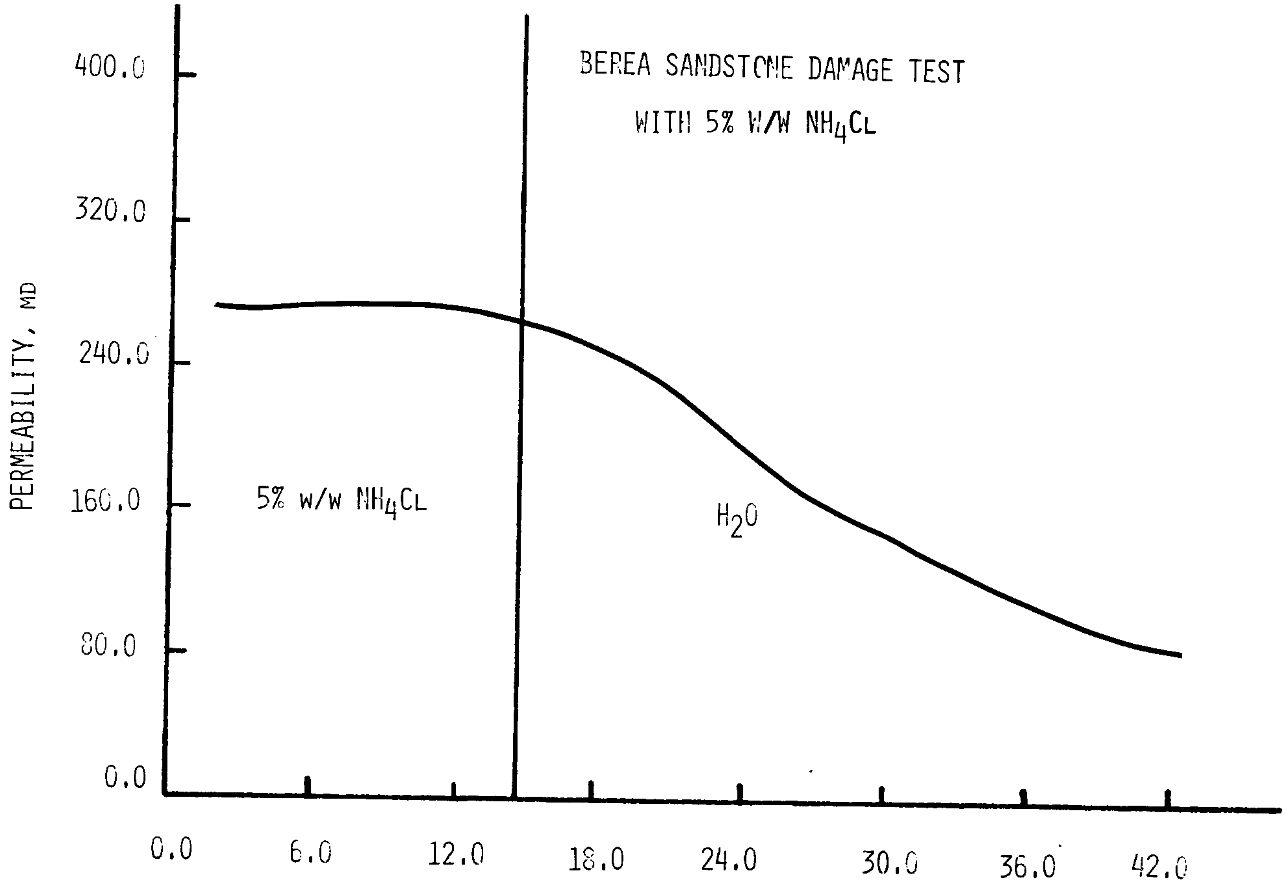


FIGURE 13—PORE VOLUME

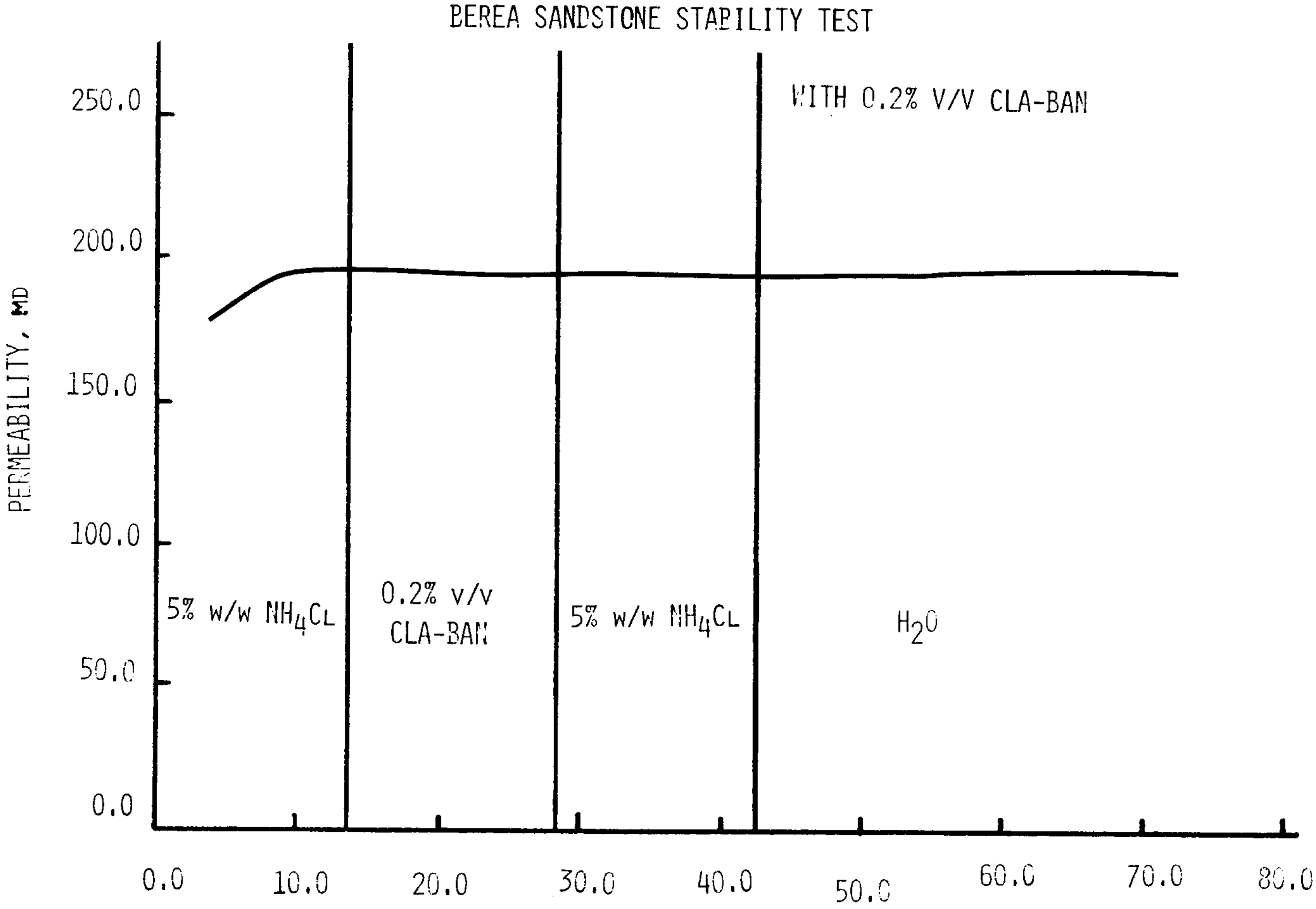


FIGURE 15—PORE VOLUME

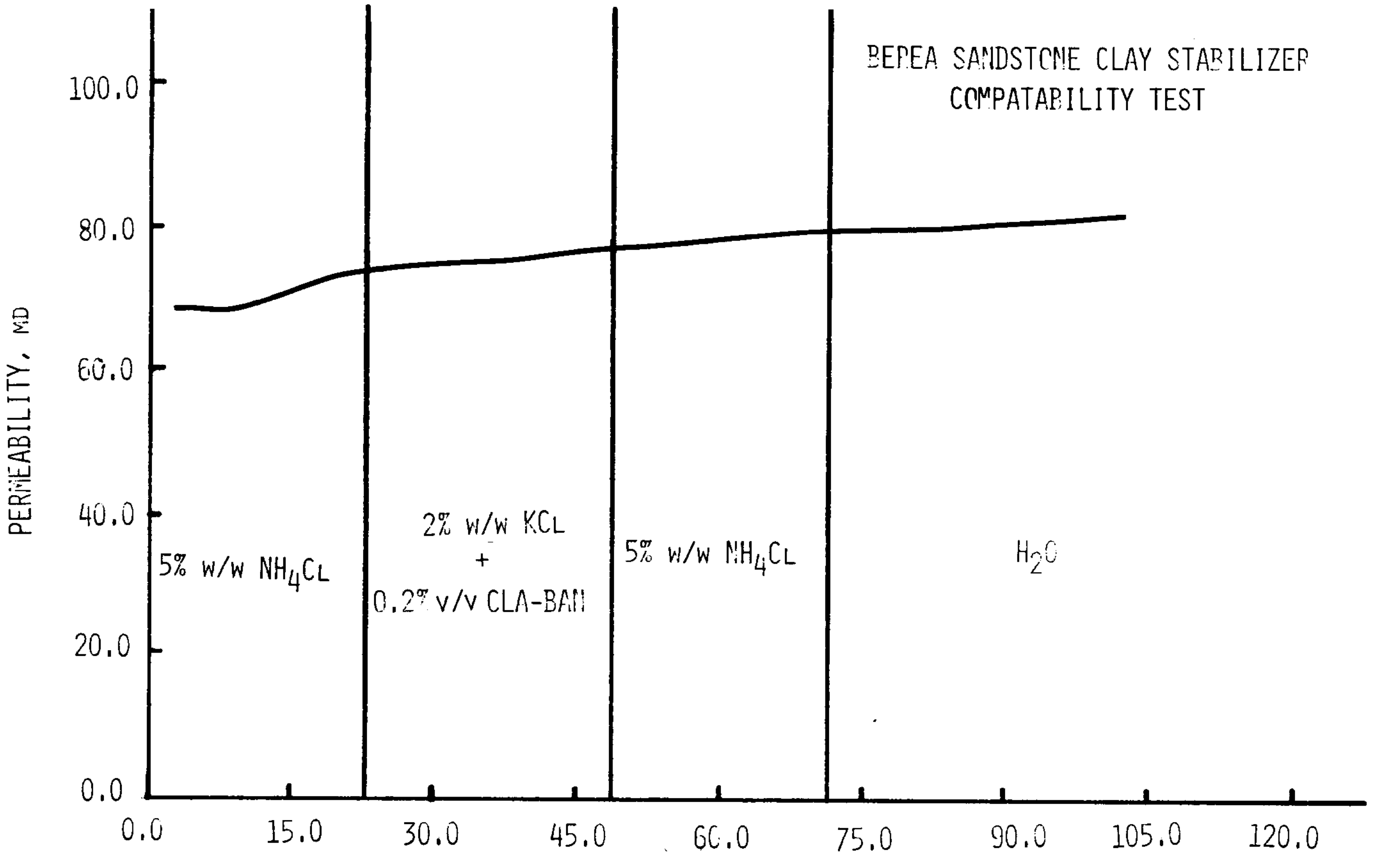


FIGURE 16—PORE VOLUME

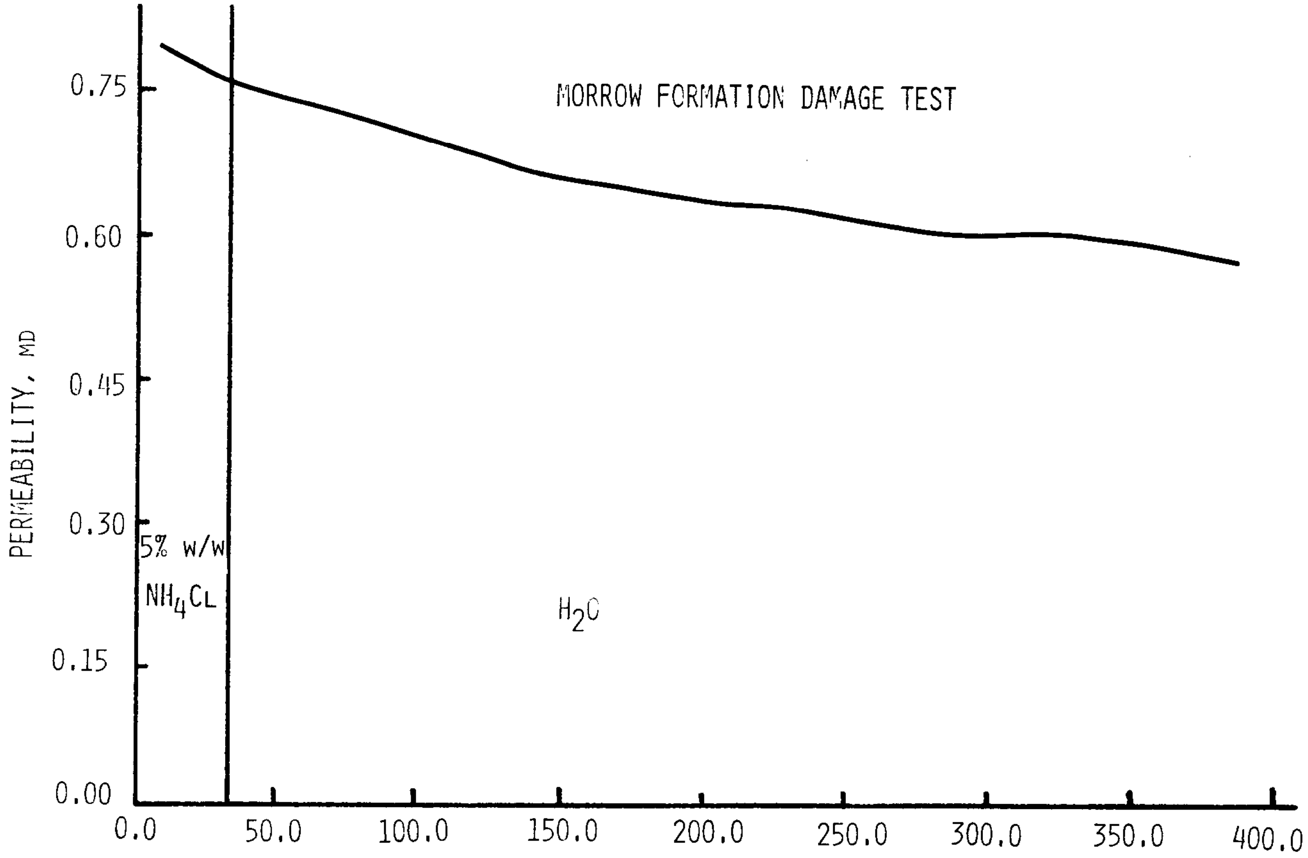


FIGURE 17—PORE VOLUME

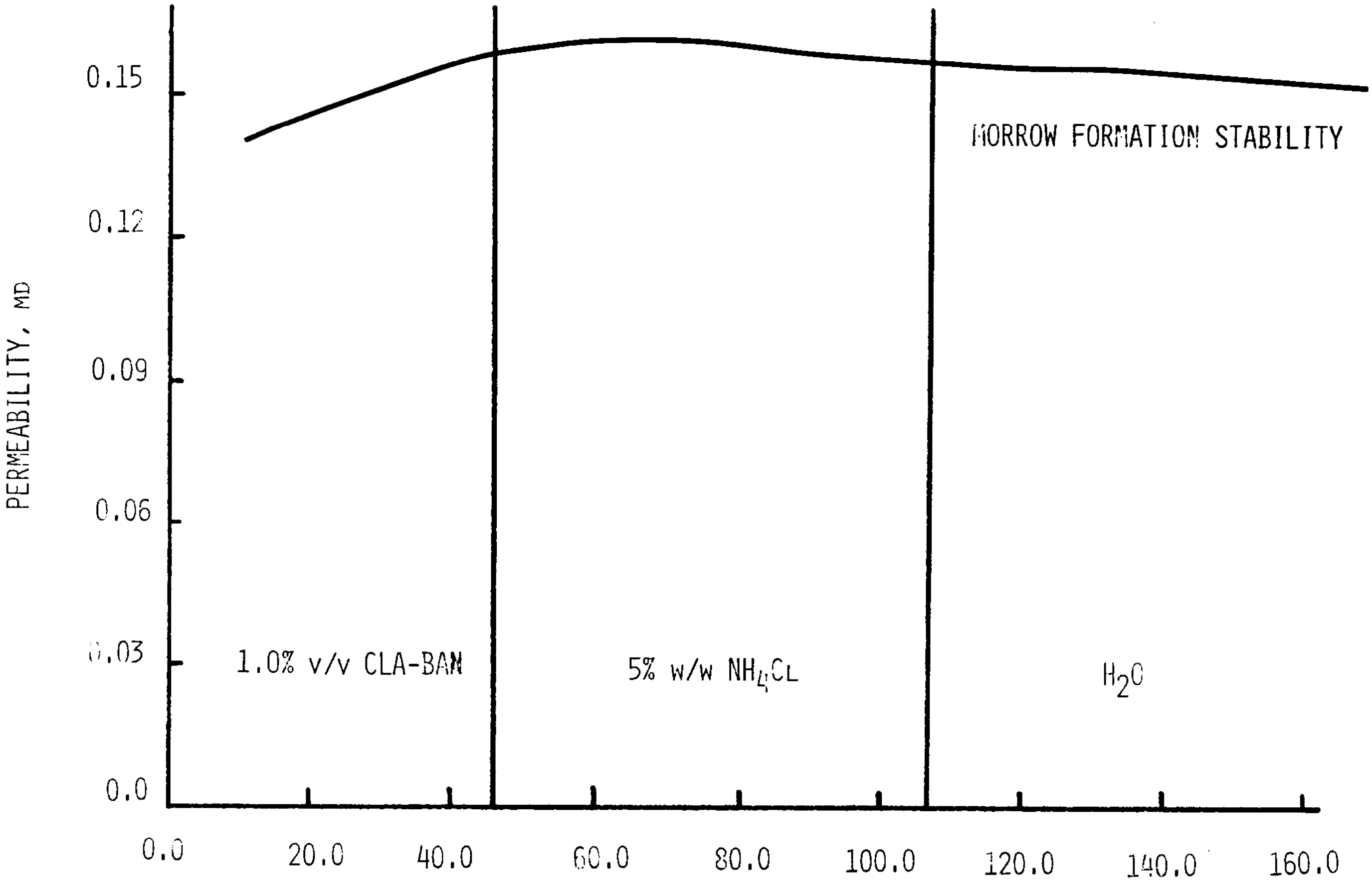


FIGURE 18—PORE VOLUME

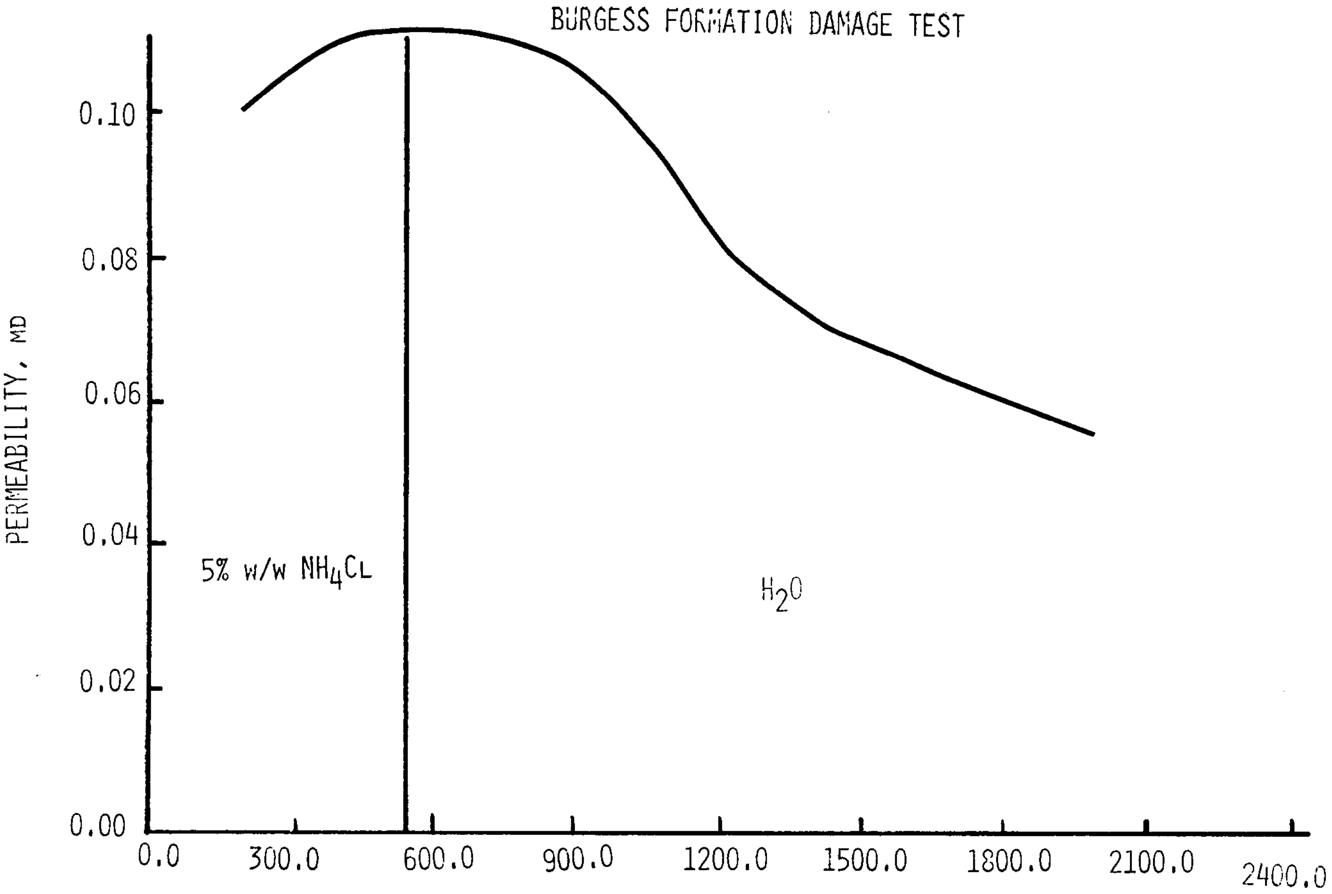


FIGURE 19—PORE VOLUME

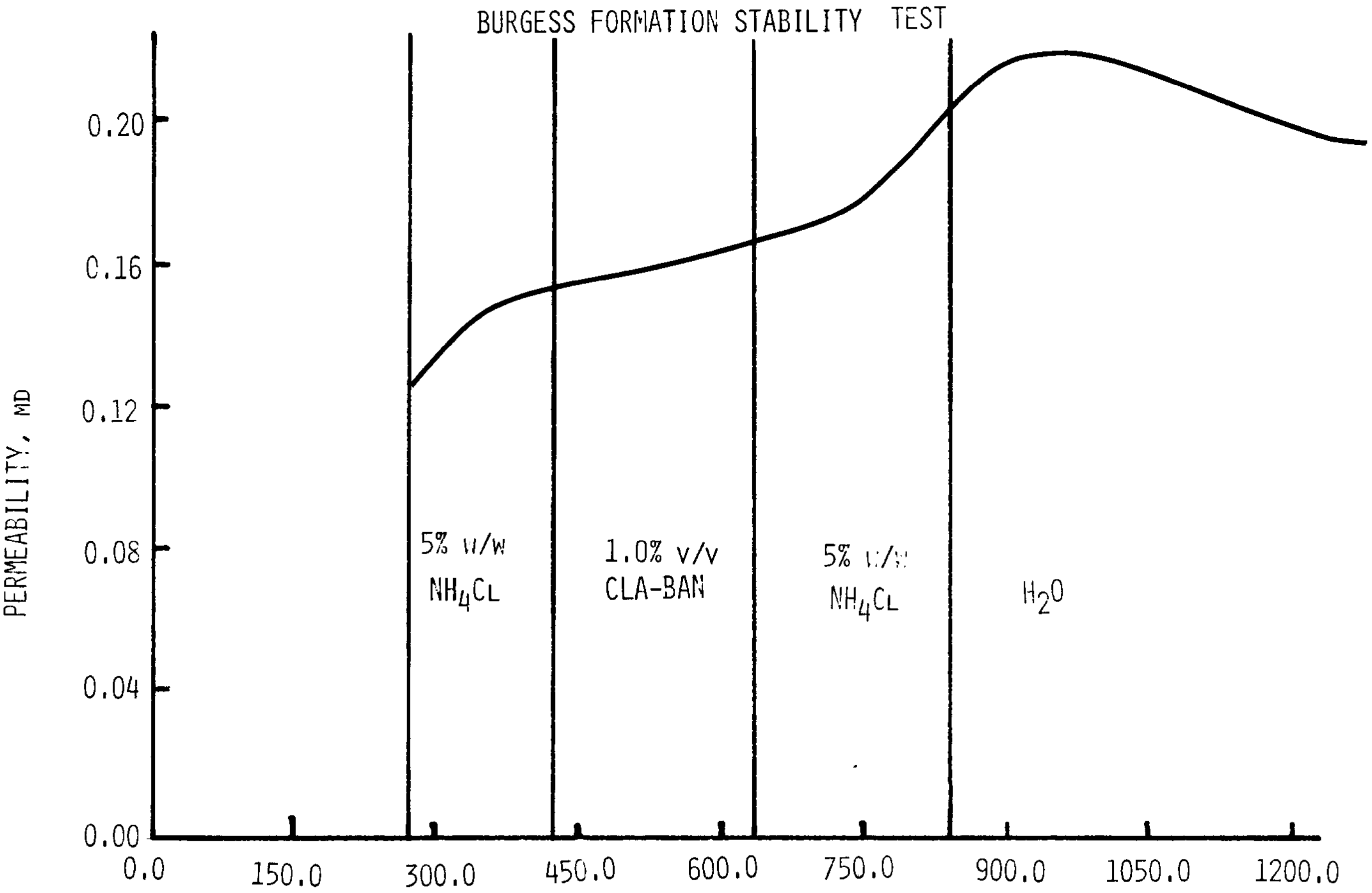


FIGURE 20—PORE VOLUME

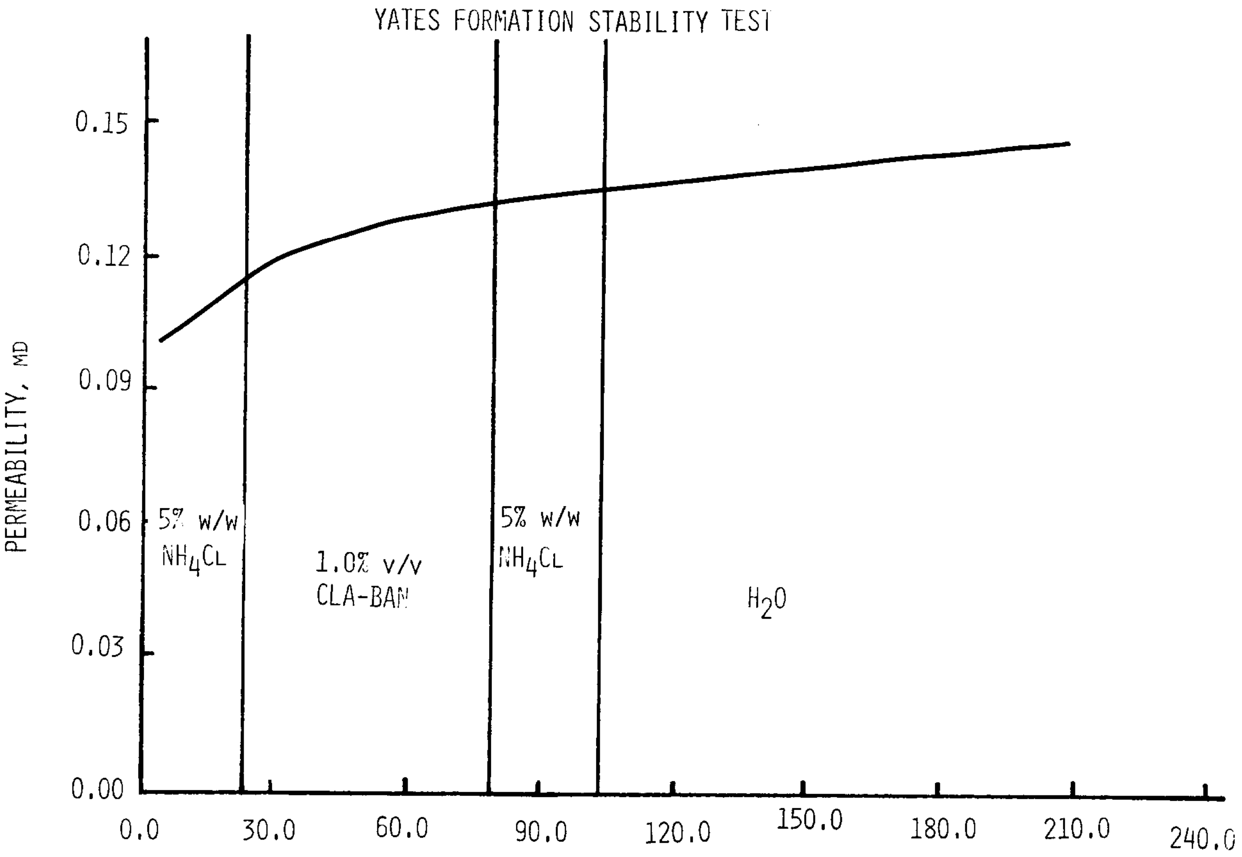


FIGURE 21—PORE VOLUME

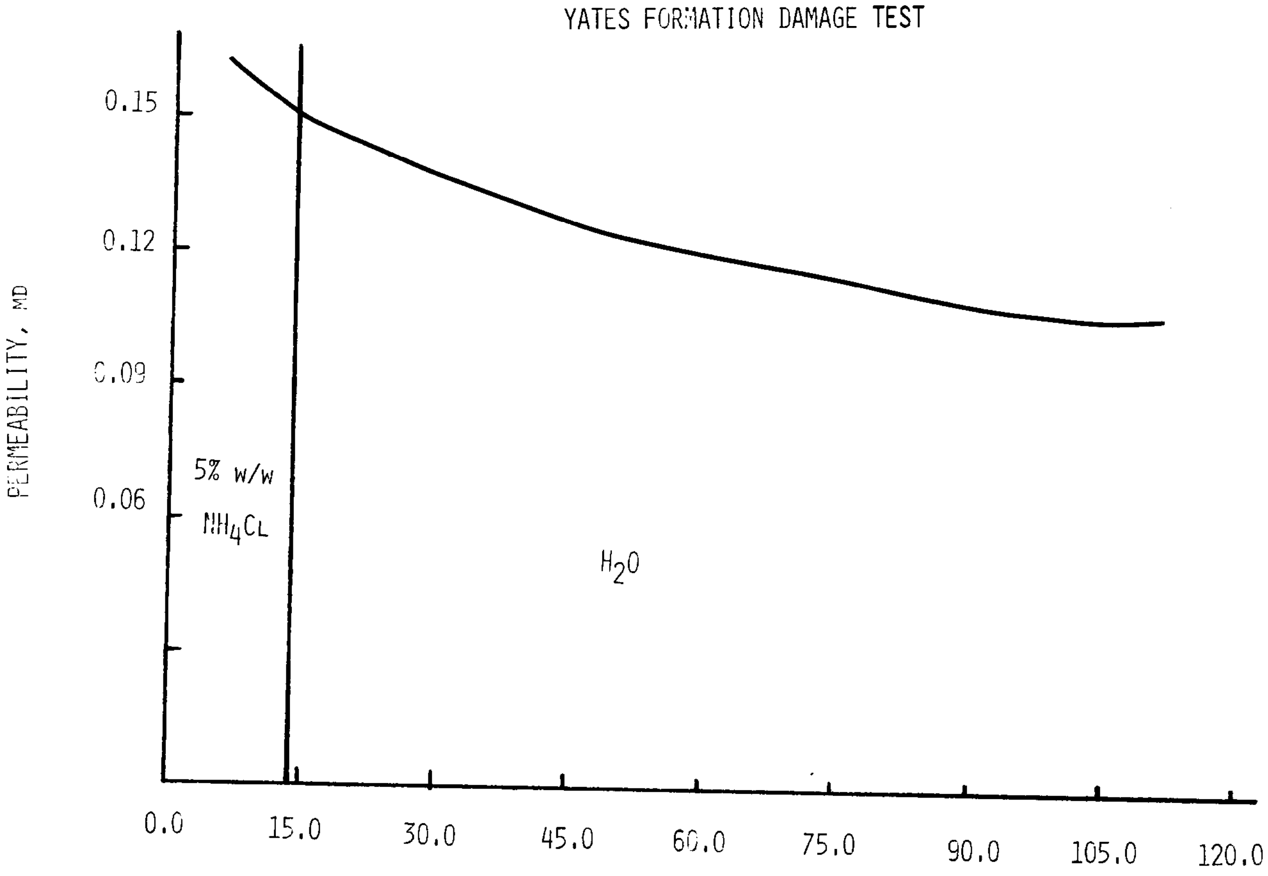


FIGURE 22—PORE VOLUME